Chemical Behavior of Recoil Species in Benzene Solutions of Neutron-irradiated Tris(acetylacetonato)cobalt(III) and Tris(acetylacetonato)chromium(III)

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Neutron-irradiated $\text{Co}(\text{acac})_3$ or $\text{Cr}(\text{acac})_3$ was dissolved in benzene containing various metal acetylacetonates as additives and the change in the apparent ^{60}Co - or ^{51}Cr -retention with the time after the dissolution was investigated at various temperatures. Unstable metal acetylacetonates such as $\text{Mg}(\text{acac})_2$ were found to enhance thermal reactions (or the apparent retention) in the solutions. The behavior of the recoil species was very similar in both the irradiated benzene solutions and benzene solutions of the irradiated solids of these complexes. The reactions of the recoil species in solutions of the irradiated $\text{Co}(\text{acac})_3$ or $\text{Cr}(\text{acac})_3$ and the effects of various additives in such systems (especially the correlation between the apparent scavenging power of metal salts and the stability constant of their acetylacetonates) were explained in terms of recombination, scavenging and ligand transfer reactions.

Introduction

We reported previously that thermal recombination reactions in the neutron-irradiated benzene solutions of $\text{Co}(\text{acac})_3$ or $\text{Cr}(\text{acac})_3$ were effectively suppressed by the addition of certain metal salts as scavengers prior to the neutron irradiation^{1)–3)}. Furthermore, thermal reactions taking place in benzene solutions of the irradiated solid $\text{Co}(\text{acac})_3$ or $\text{Cr}(\text{acac})_3$ were similarly suppressed by the presence of such metal salts in solvents^{2), 3)}. Contrary to the metal salts, unstable metal acetylacetonates as additives were found to enhance thermal reactions in the irradiated benzene solutions of $\text{Co}(\text{acac})_3$ or $\text{Cr}(\text{acac})_3$ and in solutions of the irradiated solid $\text{Co}(\text{acac})_3$ or $\text{Cr}(\text{acac})_3$ ^{4), 5)}.

In the present article are reported our recent results on the change in the ^{60}Co - or ^{51}Cr -retention with the time after the dissolution of the irradiated solid $\text{Co}(\text{acac})_3$ or $\text{Cr}(\text{acac})_3$ in benzene containing various metal acetylacetonates and at various temperatures so as to describe the outline of the reactions of the recoil species in benzene

containing various additives.

Experimental

The 0.2 M $\text{Co}(\text{acac})_3$ benzene solutions containing 3×10^{-3} M metal acetylacetonates ($\text{Fe}(\text{acac})_3$, $\text{Al}(\text{acac})_3$, $\text{Cu}(\text{acac})_2$, $\text{Ni}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$, $\text{Co}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mg}(\text{acac})_2$) were prepared by mixing one part ethanol solutions of the metal acetylacetonates and 9 parts $\text{Co}(\text{acac})_3$ benzene solution. One ml of the solutions was irradiated with thermal neutrons (flux: $5 \times 10^{11} \text{ n/cm}^2 \cdot \text{sec}$; γ -dose for 5 min: $7 \times 10^4 \text{ R}$) for 5 min at room temperature in the rotary specimen rack of a TRI-GA Mark II reactor at Rikkyo University. The irradiated solutions were kept standing for a desired length of time at room temperature. Then they were diluted with benzene to 5 ml and extracted with three 5-ml portions of a 3% EDTA–0.8% sodium potassium tartrate aqueous solution containing 10 mg of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ as carrier. At least one week after the irradiation radioactivities of the benzene and aqueous fractions were measured with a well-type NaI scintillation counter. The ^{60}Co retention,

or the radiochemical yield of the parent chemical form, $^{60}\text{Co}(\text{acac})_3$, was determined as the percentage of the total ^{60}Co activity retained in the benzene phase.

Solid $\text{Co}(\text{acac})_3$ samples were irradiated with thermal neutrons for 5 min at dry ice temperature in the rotary specimen rack of the TRIGA Mark II reactor. The irradiated solid samples were dissolved in benzene containing metal acetylacetonates to give 0.2 M $\text{Co}(\text{acac})_3$ solutions. The solutions were kept standing for a desired length of time at 30, 40, 50, or 60°C in a constant-temperature bath. The procedures of chemical separation were similar to those described above for the irradiated solutions.

In case of $\text{Cr}(\text{acac})_3$, the 0.5 M benzene solutions containing 3×10^{-3} M metal acetylacetonates were irradiated similarly with thermal neutrons. Chemical separation of the ^{51}Cr species was performed by solvent extraction with 0.3 M oxalic acid containing 0.01 M Cr^{3+} carrier. When solid $\text{Cr}(\text{acac})_3$ were irradiated, they were dissolved in benzene containing metal acetylacetonates to give 0.5 M $\text{Cr}(\text{acac})_3$ solutions. The ^{51}Cr retention, or the radiochemical yield of the parent chemical form, $^{51}\text{Cr}(\text{acac})_3$, was obtained as the percentage of the total ^{51}Cr activity retained in the benzene phase.

Results and Discussion

Previous works in this series^{(1),(2)} have shown that thermal reactions in the neutron-irradiated benzene solutions of $\text{Co}(\text{acac})_3$ can be suppressed effectively by the presence of metal salts as scavengers. As seen in Fig. 1, the apparent scavenging power of the metal salts (expressed as the percentage of thermal reactions scavenged by an equal molar concentration of the salt) appears to correlate well with the thermodynamic stability constants of their acetylacetonates in aqueous media. It is obvious that the metal salts which form more stable acetylacetonates (i.e., $\text{Fe}(\text{III})$, Al , Cu , etc.) can scavenge thermal reactions effectively while the metal salts which form unstable acetylacetonates (Mg , etc.) are only ineffective

Fig. 1 Correlation of apparent scavenging powers of various metal salts (2×10^{-3} M) in irradiated 0.2 M $\text{Co}(\text{acac})_3$ benzene solutions with the thermodynamic stability constants of their acetylacetonates.
—○—: Separated within a few hours after irradiation;
--■--: Separated after 7 days.

scavengers. In an earlier paper⁽²⁾, we suggested that the mechanism of the scavenger effect of metal salts on the thermal reactions in the irradiated solutions could be explained tentatively in terms of the competition between ligand-deficient ^{60}Co recoil species and metal salt to capture free acetylacetonate ions. However, this mechanism was so simplified that there remained some points still to be clarified: why the apparent scavenging power decreased with the time after the irradiation for the metal salts which form less stable acetylacetonates, and why the thermodynamic stability and not the kinetic one was related to the scavenging power. These questions can be answered by postulating ligand transfer reactions in addition, on the basis of our recent results on the effect of metal acetylacetonates as additives in the benzene solutions of the irradiated complexes.

Effects of Metal Acetylacetonates as Additives in Benzene Solutions of the Irradiated $\text{Co}(\text{acac})_3$ and $\text{Cr}(\text{acac})_3$. Fig. 2 indicates the change in the apparent ^{60}Co retention with the time after the irradiation of benzene solutions of $\text{Co}(\text{acac})_3$ containing metal acetylacetonates. Fig. 3 reveals the change in the apparent ^{60}Co retention with the time after the dissolution of irradiated $\text{Co}(\text{acac})_3$

in benzene containing metal acetylacetonates (at 30°C). In both Figs. 2 and 3, the retention curves are all essentially alike in shape: rapid increase at an early stage followed by a slowly increasing pseudoplateau or a plateau*. Moreover, in both Figs. 2 and 3, a common trend is observed: unstable

Fig. 2 The change in the ^{60}Co retention with the time after the irradiation of 0.2 M solutions of $\text{Co}(\text{acac})_3$ in benzene containing 10% of ethanol and various additives.

In Figs. 2, 3, 4, 5, and 7,

- : No additive
- ◇---: $3 \times 10^{-3} M$ $\text{Fe}(\text{acac})_3$
- : $3 \times 10^{-3} M$ $\text{Ni}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$
- △---: $3 \times 10^{-3} M$ $\text{Mg}(\text{acac})_2$
- : $3 \times 10^{-3} M$ acetylacetone.

Fig. 3 The change in the ^{60}Co retention with the time after the dissolution of irradiated solid $\text{Co}(\text{acac})_3$ in benzene containing 10% of ethanol and various additives (at 30°C).

Keys to symbols are given in the caption of Fig. 2.

metal acetylacetonates such as $\text{Mg}(\text{acac})_2$ or $\text{Ni}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ enhanced the increase in the ^{60}Co retention (i.e., thermal reactions) with the time, as compared with the retention curve in the absence of any additive, whereas the addition of a stable metal acetylacetonate, $\text{Fe}(\text{acac})_3$, had practically no effect on the retention curve. The transfer of ligand acetylacetonate ion from the unstable metal acetylacetonates to the ligand-deficient ^{60}Co recoil species (possibly via dissociation of the former complexes) may mainly contribute to the increase in the ^{60}Co retention in the presence of these acetylacetonates as additives. The similarity of the behavior of the ^{60}Co recoil species in both Figs. 2 and 3 implies that very similar reactions may take place in both the irradiated solutions and solutions of the irradiated solids. Accordingly, the behavior of the ^{60}Co recoil species in solution phase can be studied by using either the irradiated solutions or solutions of the irradiated solids.

Figs. 4 and 5 indicate the ^{60}Co retention curves obtained at 40° and 60°C, respectively.

Fig. 4 The change in the ^{60}Co retention with the time after the dissolution of irradiated solid $\text{Co}(\text{acac})_3$ in benzene containing 10% of ethanol and various additives (at 40°C).

Keys to symbols are given in the caption of Fig. 2.

* More detailed kinetic analysis of these retention curves is necessary for the complete understanding of the mechanism of the overall reactions.

Fig. 5 The change in the ^{60}Co retention with the time after the dissolution of irradiated solid $\text{Co}(\text{acac})_3$ in benzene containing 10% of ethanol and various additives (at 60°C).

Keys to symbols are given in the caption of Fig. 2.

The observed trend is similar to that at 30°C : unstable metal acetylacetonates enhance the increase in the ^{60}Co retention with the time. The magnitude of the effect as additive is in the order: $\text{Fe}(\text{acac})_3 < \text{Ni}(\text{acac})_2 \cdot 2\text{H}_2\text{O} < \text{Mg}(\text{acac})_2$. Hence, the effect of metal acetylacetonates appears to correlate with their stability constants. At 60°C , $\text{Fe}(\text{acac})_3$ behaves somewhat anomalously, probably because free acetylacetonate ions produced by thermal decomposition of $\text{Fe}(\text{acac})_3$ at higher temperatures accelerate thermal recombination of the recoil species and thus enhance remarkably the increase in the ^{60}Co retention. Fig. 6 indicates the temperature dependence of the pseudoplateau value of the ^{60}Co retention curve in the presence of $\text{Mg}(\text{acac})_2$ as an additive. Irrespective of additives, the pseudoplateau value increased generally as the temperature was elevated.

The effects of metal acetylacetonates as additives in benzene solutions of the irradiated $\text{Cr}(\text{acac})_3$ were found to be very similar to those observed in benzene solutions of the irradiated $\text{Co}(\text{acac})_3$. Fig. 7 represents the change in the ^{51}Cr retention with the time after the dissolution of the irradiated $\text{Cr}(\text{acac})_3$ in benzene containing

Fig. 6 The temperature dependence of the ^{60}Co retention curve in $0.2M$ solutions of irradiated solid $\text{Co}(\text{acac})_3$ in benzene containing 10% of ethanol and $3 \times 10^{-3}M$ $\text{Mg}(\text{acac})_2$.

In Fig. 6, —○—: 30°C , —●—: 40°C , —△—: 50°C , —▲—: 60°C .

Fig. 7 The change in the ^{51}Cr retention with the time after the dissolution of irradiated solid $\text{Cr}(\text{acac})_3$ in benzene containing 10% of ethanol and various additives (at 40°C).

Keys to symbols are given in the caption of Fig. 2.

metal acetylacetonates as additives (at 40°C). As in the case of the $\text{Co}(\text{acac})_3$ —benzene systems, unstable metal acetylacetonates such as $\text{Mg}(\text{acac})_2$ accelerated remarkably the increase in the ^{51}Cr retention with the time. The pseudoplateau value of the ^{51}Cr retention curve generally increases with the increase in temperature. The apparent similarity between the behaviors of the ^{60}Co - and ^{51}Cr -recoil species in benzene solutions may reflect the essential similarity between the mechanisms of reactions of such species.

Effects of Various Additives on the Reactions of the Recoil Species in Benzene Solutions of the Irradiated $\text{Co}(\text{acac})_3$ and $\text{Cr}(\text{acac})_3$. In view of the present results, the overall phenomenon (i.e., the effects of metal salts and acetylacetonates on the reactions of the recoil species in benzene solutions) may be explained generally by presuming the combination of the following types of reactions:

- (1) Recombination reactions.

- (2) Scavenging reaction.

- (3) Ligand transfer reactions.

where $[\text{M}^*(\text{acac})_{3-x}]$ denotes the ligand-deficient ^{60}Co - or ^{51}Cr -recoil species ($x=1, 2$, or 3)[†]; $\text{M}'\text{X}_n$, the scavenger salt of metal M' ; and $\text{M}'(\text{acac})_n$, its acetylacetonate. The formula $[\text{M}^*(\text{acac})_{3-x}]$ may not necessarily represent the actual chemical form of the ligand-deficient recoil species. Since all reactions take place in a slightly polar medium (benzene-ethanol mixture), such species may not be dissociated as in polar media, but possibly form ion pairs. Probably such species might be solvated with ethanol or benzene molecules. Although the oxidation states of the ligand-deficient recoil species are not fully known, we have recently found that the atmospheric oxygen affects greatly the change in the ^{60}Co retention with the time and that at least 50% of the ligand-deficient ^{60}Co recoil species should have been initially $^{60}\text{Co}(\text{II})$ species whereas the rest, probably $^{60}\text{Co}(\text{III})$ species⁶.

If an unstable metal acetylacetonate is present as additive, we should presume that reactions (1) and (3) take place and the apparent ^{60}Co - or ^{51}Cr -retention is increased as compared with the systems without any additive, corresponding to the contribution from ligand transfer reactions (3). In Fig. 8(a), such increment of the apparent ^{60}Co retention at equilibrium is plotted against the thermodynamic stability constant of the

Fig. 8 (a) The increment in the ^{60}Co retention (at equilibrium) due to ligand transfer reactions vs. the thermodynamic stability constants of metal acetylacetonates used as additives, and (b) analysis of the correlation between the apparent scavenging power of metal salts in benzene solutions of irradiated solid $\text{Co}(\text{acac})_3$ and the thermodynamic stability constants of their acetylacetonates (see text).

metal acetylacetonate used as additive, and the extent of ligand transfer reactions (3) correlates well with the stability of the metal acetylacetonate. Similar correlation was observed between the increment of the apparent ^{51}Cr retention at equilibrium and the thermodynamic stability constants of metal acetylacetonates in the $\text{Cr}(\text{acac})_3$ -benzene systems.

In the systems which contain metal salts as scavengers, the mechanism of the overall phenomenon can be explained in terms of the combination of reactions (1), (2) and (3).

[†] Electric charge depends on the oxidation state of the recoil species: $x+$ and $(x-1)+$ for $\text{M}^*(\text{III})$ and $\text{M}^*(\text{II})$, respectively.

Immediately after the dissolution of the irradiated solid, the competition between reactions (1) and (2) is important, while reactions (3) may still be relatively unimportant. Such competition kinetically favors the scavenging reaction (2), and the correlation curve of the scavenging power with the stability constant may approach closely to 100%, or the broken horizontal line (1+2) in Fig. 8(b), only if the storage period in solution becomes as short as possible. As ligand transfer reactions (3) between $[\text{}^{60}\text{Co}(\text{acac})_{3-x}]$ (or $[\text{M}^*(\text{acac})_{3-x}]$) and $\text{M}'(\text{acac})_n$ resulting from the scavenging reaction proceed gradually in the solution, the apparent ^{60}Co retention increases and the apparent scavenging power decreases on prolonged standing in the solution. Accordingly, the corresponding point on the correlation curve may be lowered from the broken horizontal line (1+2) by a magnitude equivalent to the contribution of ligand transfer reactions (3) (i.e., arrow 3 in Fig. 8(b)). As indicated for the $\text{Co}(\text{acac})_3$ -benzene systems in Fig. 8(a), the extent of reactions (3) reached at equilibrium after standing for a sufficiently long time depends on the stability of the metal acetylacetonate relative to that of the parent complex, $\text{Co}(\text{acac})_3$. Similar observations were obtained with the $\text{Cr}(\text{acac})_3$ -benzene systems. Hence, the scavenging

effect of the metal salts which can form stable acetylacetonates is ascribed mainly to the competition between recombination reactions (1) and scavenging reaction (2) to combine with free acetylacetonate ions. For the metal salts which form acetylacetonates of low stability, however, ligand transfer reactions (3) may proceed appreciably on standing and apparently diminish the overall scavenging effect.

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要 旨

中性子照射したトリシアセチルアセトナトコバルトおよび クロムのベンゼン溶液中における反跳化学種の挙動

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中性子照射した $\text{Co}(\text{acac})_3$ または $\text{Cr}(\text{acac})_3$ を種々な金属アセチルアセトネートを含むベンゼンに溶解し, 見かけの ^{60}Co または ^{51}Cr のリテンションの変化を種々の温度で研究した。 $\text{Mg}(\text{acac})_2$ などの不安定な金属アセチルアセトネートの添加は溶液中のサーマル反応(見かけのリテンション)を増大させる。溶液を照射した場合も照射固体を溶液とした場合も反跳化学種は液相で同様な挙動を示す。照射した固体錯体の溶液中における反跳化学種の挙動や添加物効果(とくに金属塩のスカベンジャー効果の大きさとそのアセチルアセトネートの安定度との相関関係)は, 再結合, スカベンジ, 配位子移動などの反応を組み合わせで説明できる。