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Hot-atom Chemistry of Cobalt-60 Atoms in Neutron Irradiated Organic Solutions of Tris(acetylacetonato)cobalt(III)

Takeshi Tominaga, Takuhiko Sakai, and Kitao Fujiwara
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

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Thermal neutron irradiation has been carried out on the solutions of tris(acetylacetonato)cobalt(III) in benzene, ethanol, acetone and acetic acid containing various additives such as metallic salts and mineral acids. The ^{60}Co retention in the irradiated solutions has been found to decrease sharply with the increase in the concentration of various metallic salts. This indicates that the thermal diffusive reactions which contribute greatly to the apparent retention in the irradiated solutions can be suppressed by the addition of adequate metallic salts as scavengers. Salts of the metals which can form more stable complexes with acetylacetone (*i.e.*, Fe(III), Cu(II), Al(III), *etc.*) work as more effective scavengers in these systems. The upper limit for the primary retention of tris(acetylacetonato)cobalt(III) in the benzene solutions has been estimated as 0.00±0.02%. The use of adequate scavengers appears to be a useful technique to determine the primary retention in the irradiated solution systems. The ^{60}Co retention of the solid complex irradiated at dry ice temperature was 1.4—1.5% irrespective of the organic solvents used for dissolution if they contain ferric chloride, while it increased to 2.0% in the absence of the scavenger.

While a lot of detailed works have been made on the recoil and subsequent reactions of metal complexes in solid state, only a few studies have been reported for such reactions in solutions of these compounds.[1-5]

In 1970 we initiated a systematic study to irradiate the organic solutions of metal complexes with thermal neutrons in order to elucidate the mechanism of hot-atom reactions in these systems.[6] Our results on the irradiated benzene solutions of tris(acetylacetonato) cobalt(III)[7] indicated that the thermal diffusive reactions in the irradiated solutions could be suppressed effectively by the addition of ferric chloride as scavenger for free acetylacetone. Since the addition of scavengers appears to be a useful technique for investigating the hot-atom chemistry of complexes in solutions, we have studied the influence of various scavengers and solvents in more detail. This paper deals with our recent data on the ^{60}Co hot-atom reactions and the scavenger effect in the neutron irradiated solutions of tris(acetylacetonato)cobalt(III) in organic solvents.

Experimental

Reagents. Tris(acetylacetonato)cobalt(III), Co(acac)$_3$, was prepared as described in literature.[8] This was further purified by repeating recrystallization from acetone. Found: C, 50.6%; H, 5.71%. Calcd for Co(C$_5$H$_7$O$_2$)$_3$: C, 50.6%; H, 5.94%.

All the solvents and scavengers (metallic salts, acids, *etc.*) used in the experiments were purchased from Wako Pure Chemical Industries Ltd. as of G.R. grade.

Preparation of Co(acac)$_3$ Organic Solutions with Scavengers. Various Co(acac)$_3$ solutions containing scavengers were prepared for neutron irradiation.

Benzene Solutions: Co(acac)$_3$ benzene solutions containing anhydrous FeCl$_3$ were prepared by simply adding various amounts of FeCl$_3$ to Co(acac)$_3$ benzene solutions. To prepare Co(acac)$_3$ benzene solutions containing other metallic salts or inorganic acids as scavengers, various amounts of the scavengers were dissolved first in ethanol and then they were added to Co(acac)$_3$ benzene solutions so that the resulting solutions contained 10% by volume of ethanol.[9] To investigate the influence of the other organic solvents as additives, they were directly added to Co(acac)$_3$ benzene solutions.

Ethanol, Acetone and Acetic Acid Solutions: Ferric chloride, FeCl$_3$·6H$_2$O, was added directly to the solutions of Co(acac)$_3$ in ethanol, acetone or acetic acid.

Neutron Irradiation. About 1 m*l* each of the Co(acac)$_3$ organic solutions was placed in a quartz tube with a Teflon stopper and 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 was 5×10^{11} n/cm^2·sec. The accompanying γ dose was 7×10^4R. The solutions were frozen 15—20 min after the completion of the irradiation and stored in dry ice for 2—3 hr before chemical separation.

For making a comparison with the solution systems, solid Co(acac)$_3$ samples were irradiated for 5 min at dry ice or room temperature. After the irradiation they were stored in dry ice until chemical separation.

Chemical Separation. The solvent extraction method was mainly employed in chemical separation of the irradiated complex in order to determine the ^{60}Co retention.[10]

Solutions: One milliliter of the irradiated organic solutions

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[1] G. Kayas and P. Süe, *J. Chim. Phys.*, **45**, 188 (1948); *Bull. Soc. Chim. France*, **17**, 1145 (1950).

[2] A. W. Adamson and J. M. Grunland, *J. Amer. Chem. Soc.*, **73**, 5508 (1951).

[3] A. Zuber, USAEC Document NYO-6142 BNL (1954).

[4] N. Saito, H. Sano, and T. Tominaga, This Bulletin, **33**, 20 (1960).

[5] S. Kaufman, *J. Amer. Chem. Soc.*, **82**, 2963 (1960).

[6] The study of hot-atom reactions in the irradiated organic solutions of metal complexes had not been reported before our previous work,[7] although several works have been made on the solutions of organometallic compounds (U. Zahn, *Radiochim. Acta*, **7**, 170 (1967); I. C. Yang and D. R. Wiles, *Can. J. Chem.*, **45**, 1357 (1967).

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

[8] T. Moeller, "Inorganic Syntheses," Vol. 5, McGraw-Hill Book Co., Inc., New York (1957), p. 188.

[9] The scanvenger-free Co(acac)$_3$ solutions also contained 10% of ethanol. It was confirmed that the scavenger effect of metallic salts and acids was not affected by the presence of about 10% of ethanol in the benzene solutions.

[10] The retention obtained corresponds to the percentage of the ^{60}Co activity retained in the form of Co(acac)$_3$.

was diluted to 5 m*l* with benzene and extracted with three 5-m*l* portions of 3% EDTA aqueous solution containing 0.8% sodium potassium tartrate and 10 mg of $CoSO_4 \cdot 7H_2O$ as carrier. On mixing with Co^{2+} carrier and EDTA aqueous solution, all the ^{60}Co-labeled species other than $^{60}Co(acac)_3$ are extracted into the aqueous phase, whereas only $^{60}Co(acac)_3$ remains in the organic phase.[11] For the irradiated solutions of $Co(acac)_3$ in ethanol, acetone, or acetic acid, the ion exchange method was also used for the purpose of comparison: after being mixed with water containing Co^{2+} carrier, the irradiated solution was passed through a cation exchange column. The effluent contains only the neutral ^{60}Co-labeled species which does not exchange with Co^{2+} (*i.e.*, $^{60}Co(acac)_3$). Since the radiochemical yield of the neutral fraction by the ion exchange separation was in good agreement with that of the organic phase by the solvent extraction, it is evident that the retention as $^{60}Co(acac)_3$ can be determined by either method for the solutions in these solvents.

Solid Samples: The irradiated solid samples (30—50 mg) were dissolved in 5 m*l* of benzene (containing 10% of ethanol) ethanol, chloroform, carbon tetrachloride, or acetic acid, all with or without ferric chloride additive, and analyzed by means of solvent extraction or ion exchange.

Radioactivity Measurement. The radioactivity of each fraction was counted with a well-type NaI scintillation counter at least one week after neutron irradiation. All the solvents and scavengers (metallic salts and acids) used in the experiments were irradiated separately and the radioactivity of the organic phase after solvent extraction was measured to check the upper limit of induced radioactivity other than ^{60}Co. It was confirmed that the possible contribution to organic phase activities (*i.e.*, retention) from induced activities other than ^{60}Co did not exceed 0.03% when measurements were carried out at least one week after irradiation. Since this contribution was generally smaller than the statistical errors in counting, no correction was necessary.

Results and Discussion

Recoil Species Formed in the Irradiated Co(acac)$_3$ Systems. Various metastable recoil species can be formed as a result of hot-atom reactions in the irradiated solid $Co(acac)_3$ systems. As an example, existence of ligand deficient species such as [bis(acetylacetonato)cobalt (III)]$^+$ has been suggested in the irradiated and unannealed solid $Co(acac)_3$ systems.[11,12] However, all the chemical procedures of separation involving aqueous media (*i.e.*, ion exchange, solvent extraction and paper electrophoresis) have revealed only two ^{60}Co-labeled species which are identified as $Co(acac)_3$ and Co^{2+}.[7,11,12] This indicates that the metastable recoil species are converted into more stable entities on dissolution in an organic solvent and mixing with an aqueous medium.

Although similar metastable recoil species might be produced through hot-atom reactions in the irradiated solutions of $Co(acac)_3$ in organic solvents, only two ^{60}Co-labeled species (*i.e.*, $Co(acac)_3$ and Co^{2+}) were found after chemical separation by means of solvent extraction or ion exchange, both of which involved aqueous media. It is presumed that all the metastable recoil species are finally converted into the stable species in aqueous solutions (*i.e.*, Co^{2+}). Accordingly, the ^{60}Co recoil reactions and scavenger effect in the $Co(acac)_3$ systems have been studied in terms of the ^{60}Co retention which is not perturbed by the procedures of chemical separation.

Retention and Scavenger Effect in the Irradiated Solutions of Co(acac)$_3$ in Benzene Containing 10% of Ethanol. In the absence of scavengers, the apparent ^{60}Co retention in the irradiated 0.2M solutions of $Co(acac)_3$ in benzene (containing 10% of ethanol) was found to be about 7 ± 1% which was higher than the retentions in the irradiated solid samples. No appreciable concentration dependence was observed for 0.01—0.25M solutions of $Co(acac)_3$ in benzene. The apparent retention increases gradually when the irradiated solutions are kept at room temperature[7] whereas it remains nearly unchanged at dry ice temperature. When acetylacetone was added to the solutions before irradiation, the apparent retention was found to increase with acetylacetone concentration. Thus the ^{60}Co retention in the irradiated benzene solutions containing 50% by volume of acetylacetone was about 25%. A retention value of 90% was observed in the irradiated solution of $Co(acac)_3$ in pure acetylacetone after being kept standing for three days at room temperature. Thus it can be concluded that thermal diffusive reactions taking place during and after the irradiation contribute greatly to the apparent retention in the irradiated solutions without scavengers. The higher apparent retention in solutions than in solid can be explained by assuming that the thermal diffusive reactions proceed more rapidly in irradiated solutions than in irradiated solid.

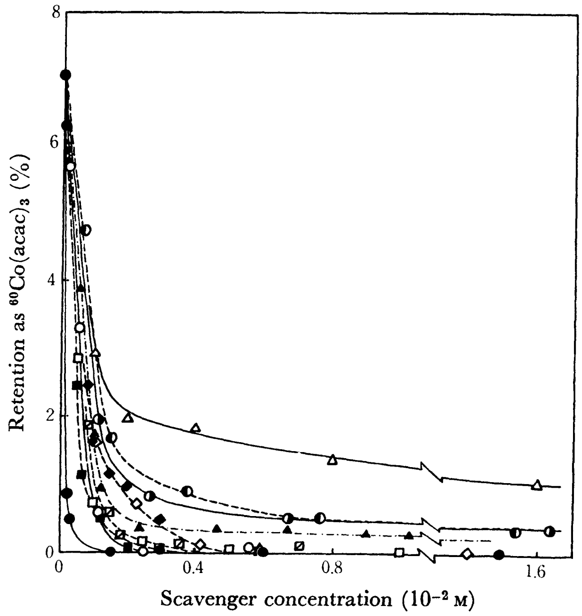

Fig. 1. Scavenger effect of various metallic salts and mineral acids on ^{60}Co retention in the irradiated 0.2M solutions of $Co(acac)_3$ in benzene containing 10% of ethanol.

-●- $FeCl_3 6H_2O$; -○- $FeCl_3$; --▨-- $AlCl_3$; --■-- $CuCl_2 \cdot 2H_2O$; --□-- $Cu(CH_3CO_2)_2 \cdot H_2O$; --▲-- $NiCl_2 \cdot 6H_2O$; -◑-$CoCl_2 \cdot 6H_2O$; --◐-- $CoCl_2$; -△- $MgCl_2 \cdot 6H_2O$; --◆-- HCl; --◇-- HNO_3.

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[11] J. Shankar, K. Venkateswarlu, and A. Nath, "Chem. Effects Nucl. Transform., Proc. Symp. Prague," Vol. 1, 309 (1961).

[12] J. Shankar, K. S. Venkateswarlu, and M. Lal, *Radiochim. Acta*, **4**, 52 (1965).

In order to study the hot-atom reactions in these systems, the thermal diffusive reactions should be suppressed so that the true primary retention can be determined. Although the scavenger technique has been used successfully to suppress thermal diffusive reactions in organic systems, it has seldom been applied to the hot-atom reactions in inorganic systems. We found that ferric salts could be used as good scavengers to minimize the thermal reactions in the irradiated $Co(acac)_3$ solutions.[7] In the present work we have studied the effect of the addition of various metallic salts on the ^{60}Co retention in the irradiated 0.2M solutions of $Co(acac)_3$ in benzene containing 10% of ethanol (Fig. 1).

We see that the ^{60}Co retention in the irradiated solutions decreases sharply on addition of most metallic salts as scavengers although no decomposition of the parent complex is detected spectrophotometrically. Ferric chloride appears to be the most effective scavenger while magnesium chloride is the least effective. The hydrate might be slightly more effective as scavenger than the anhydride of the corresponding salt. However, the ^{60}Co retention was not influenced by the presence of water up to 0.5% (about 0.25M) in the irradiated benzene solutions. For the convenience of comparison, the scavenging power may be expressed in terms of the percentage of the thermal diffusive reactions scavenged by the addition of an equal molar concentration of the salt. The scavenger curves in Fig. 1 reveal that the scavenging power of the metallic salts generally increases in the order:

$$\mathrm{Mg(II)} < \mathrm{Co(II)} < \mathrm{Ni(II)} < \mathrm{Cu(II)} \sim \mathrm{Al(III)} < \mathrm{Fe(III)}$$

Although the stability constants of the acetylacetonates of these metals in benzene or benzene-ethanol solutions are not known, it has been reported that the stability constants in aqueous media (and in 50% or 75% dioxane) increase in the order:

$$\mathrm{Mg(II)} < \mathrm{Co(II)} < \mathrm{Ni(II)} < \mathrm{Cu(II)} < \mathrm{Al(III)} < \mathrm{Fe(III)}^{13-18)}$$

Thus the scavenging power of the salts of these metals are correlated well with the stability constants of their acetylacetonates in aqueous media,[19] that is, salts of the metals which can form more stable complexes with free acetylacetone work as more effective scavengers. Thus a probable mechanism of the metal scavenger effect in the irradiated solutions of $Co(acac)_3$ in benzene-ethanol is as follows. The metallic salt competes with the ^{60}Co recoil species (ligand deficient species, *etc.*) in thermal diffusive reactions to combine with free acetylacetone in solutions, thus minimizing the apparent ^{60}Co retention effectively.

Since the ^{60}Co retention in the well-scavenged solutions shows a minimum value of 0.00±0.02%, this can be considered as an upper limit for the primary retention in the irradiated $Co(acac)_3$ benzene solutions. In other words, the probability of the rupture of at least one ligand of this complex is nearly 100% in the solution systems.

Mineral acids such as HCl and HNO_3 are also good scavengers to reduce the apparent retention (Fig. 1). Acetic acid appears to be less effective in the concentration range below 0.1M, yet it can be used as a good scavenger if its concentration exceeds about 0.2M (Fig. 2).

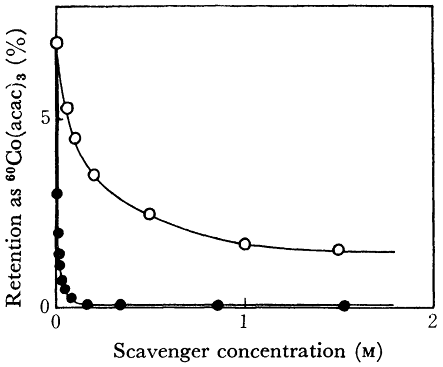

Fig. 2. Scavenger effect of acetic acid and carbon tetrachloride on ^{60}Co retention in the irradiated 0.2M solutions of $Co(acac)_3$ in benzene.

-●- CH_3CO_2H; -○- CCl_4.

We see that the addition of carbon tetrachloride (well-known electron scavenger) gradually decreases the apparent retention. However, the effect is slight as compared with the scavenger effect of metallic salts: the retention cannot be reduced to below 1% even if 1.6M (several hundred times as concentrated as the metallic scavengers) of carbon tetrachloride is present in the irradiated solutions. The results suggest that a different mechanism may be proposed to account for the effect of carbon tetrachloride on the ^{60}Co retention.

The ^{60}Co retention was not influenced significantly by the addition of ethanol (up to 15% by volume) or acetone (up to 100%).

Retention in the Irradiated Solutions of Co(acac)₃ in Ethanol, Acetone and Acetic Acid. The effect of ferric chloride on the ^{60}Co retention in the irradiated solutions of $Co(acac)_3$ in ethanol (0.017M) or acetone (0.03M) was similar to the effect observed in the benzene solutions. The apparent retention decreases sharply with the increase in the ferric chloride concentration and reaches nearly 0% if more than 3×10^{-4}M of ferric chloride is present in the solutions.

A different behavior was observed with the irradiated 0.1M $Co(acac)_3$ solutions in acetic acid. The ^{60}Co retention remains at 0%, independent of the ferric chloride concentration since acetic acid can work as both scavenger and solvent.

Retention in the Irradiated Solid Co(acac)₃ Samples. Table 1 summarizes the ^{60}Co retentions in the irradi-

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13) L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Amer. Chem. Soc.*, **75**, 457, 2736 (1953).

14) B. E. Bryant, *J. Phys. Chem.*, **58**, 573 (1954).

15) R. M. Izatt, C. G. Haas, Jr., B. P. Block, and W. C. Fernelius, *ibid.*, **58**, 1133 (1954).

16) R. M. Izatt, W. C. Fernelius, and B. P. Block, *ibid.*, **59**, 80 (1955).

17) R. M. Izatt, W. C. Fernelius, C. G. Haas, Jr., and B. P. Block, *ibid.*, **59**, 170 (1955).

18) H. A. Droll, B. P. Block, and W. C. Fernelius, *ibid.*, **61**, 1000 (1957).

19) We have recently obtained a similar correlation for the irradiated solutions of tris(nitrosonaphtholato)cobalt(III) in benzene. The results will be published shortly.

Table 1. ^{60}Co retentions in irradiated solid Co(acac)$_3$

Temp. of irradiation	Solvent[a]	Method of separation[b]	^{60}Co retention (%)	
			Immediately after dissoln.	After standing in solution
Dry ice	C_6H_6+Fe(III)	S.E.	1.4±0.1	1.4±0.1[c]
Dry ice	C_6H_6	S.E.	2.0±0.1	2.6±0.1[c]
Dry ice	0.4 M acetylacetone in C_6H_6	S.E.		7.8±0.1[d]
Dry ice	$CHCl_3$+Fe(III)	S.E.	1.7±0.1	1.5±0.1[c]
Dry ice	$CHCl_3$	S.E.		2.5±0.1[c]
Dry ice	C_2H_5OH+Fe(III)	I.E.	1.4±0.1	1.4±0.1[c]
Dry ice	C_2H_5OH	I.E.	2.0±0.1	2.3±0.1[c]
Dry ice	CH_3COOH+Fe(III)	I.E.	1.5±0.1	
Room	C_6H_6+Fe(III)	S.E.	2.4±0.1	
Room	C_6H_6+CH_3COOH	S.E.	2.3±0.1	
Room	C_6H_6	S.E.		10.0±0.1[e]
Room	CCl_4	S.E.		6.8±0.1[e]

a) C_6H_6: Benzene containing 10% of ethanol.
b) S.E. : Solvent extraction; I.E.: ion exchange.
c) Standing for 3 days in solutions.
d) Standing for 2 days in solutions.
e) Standing for 6 days in solutions.

ated solid Co (acac)$_3$ samples. Retentions of the samples irradiated at dry ice temperature generally fall within the range 1.4—1.5% irrespective of solvents used for dissolution, if they contain 3—5$\times 10^{-3}$M ferric chloride. The ^{60}Co retention remains unchanged even after standing the solutions of the irradiated solid complex for three days if they contain ferric chloride. In the absence of ferric chloride, however, the ^{60}Co retention is 2.0±0.1% for irradiations at dry ice temperature and increases further after the solutions of the irradiated solid samples were kept standing for three days.[20] The increment of the retention is accelerated considerably when the irradiated complex is dissolved in a benzene-acetylacetone mixture. The results indicate that the thermal reactions after the dissolution of the irradiated solid complex contribute appreciably to the apparent retention. Therefore, the retention obtained in the presence of an adequate scavenger can be considered to be a true retention of the irradiated solid systems.

It is concluded that the thermal reactions taking place in the irradiated organic solutions of the complex or after the dissolution of the irradiated solid complex are effectively suppressed by using adequate scavengers such as metallic salts which can form more stable complexes with the free ligand molecules, ions or radicals. We believe that this technique will be useful for determining the primary retention in solution systems or the initial retention in solid systems.

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20) A similar increase of retention after dissolution has been observed in the methanol and benzene solutions of irradiated solid tris(acetylacetonato)chromium(III) (I. Găinar and A. Ponta, *Rev. Roum. Chem.*, **13**, 401 (1968); T. Omori and T. Shiokawa, *Radiochem. Radioanal. Lett.*, **3**, 39 (1970)).