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Thermal Annealing Behavior of the Recoil ^{57}Co Formed by the Decay of ^{57}Ni-Labeled Hexamminenickel(II) Complexes

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Thermal annealing reactions of ^{57}Co formed by the EC and β^+-decay of the ^{57}Ni-labeled hexamminenickel(II) halide complexes were investigated in detail by means of ion-exchange techniques. When the annealing is carried out at high temperatures, the chemical behavior of ^{57}Co is remarkably affected by the thermal decomposition of the parent and daughter complexes. In the intrinsic annealing, however, the annealing curves have characteristic shapes and the plateau yields of $^{57}Co(NH_3)_6^{3+}$ ion are independent of the temperature, depending on the nature of the outer-sphere anion. The unusual oxidation reaction of the recoil ^{57}Co(II) species is explained by the action of the crystal defects in the near-neighborhood of the recoil site.

Since Collins and Harbottle[1] found that the annealing reaction can take place in the hexabromoethane even if the γ-dose is negligibly small, there have appeared several studies of the intrinsic annealing of the recoil atom in the decay-atom system. For instance, Andersen *et al.*[2,3] have reported that, in the β^--decay process of $K_2{}^{125}SnCl_6$, the distribution of ^{125}Sb is strongly affected by the inherent crystal defects in the crystal, while in the IT process of $^{127m}Te(OH)_6$, the influence of crystal defects introduced prior to the decay event on the initial distribution of ^{127}Te and on the thermal annealing reaction can be ignored. In the IT process of $K^{80m}BrO_3$, it has also been found that the thermal annealing might be promoted by the inherent crystal defects.[4]

Studies of the intrinsic annealing process, therefore, would seem to provide very important information on the recombination mechanism in the solid phase. In a previous paper,[5] the chemical behavior of the ^{57}Co produced by the EC and β^+-decay of the ^{57}Ni-labeled hexamminenickel(II) complex was reported. The results showed that a fairly large amount of the ^{57}Co(III) species is produced, depending on the nature of the outer-sphere anion. Moreover, the heating of the sample at 60°C generally increases the yield of the cobalt(III) species. The present study has been carried out in order to clarify the thermal-annealing behavior of ^{57}Co in the hexamminenickel(II) halide complexes.

Experimental

All the reagents used were of a guaranteed-reagent grade.

Nickel-57 was produced by a (γ, n) reaction using an electron linear accelerator of Tohoku University. Nickel oxide which had been irradiated by bremsstrahlung with a maximum energy of 40 MeV was dissolved in concentrated hydrochloric acid, and then the solution was passed through an anion-exchange resin in order to separate the ^{57}Co produced by the EC and β^+-decay of ^{57}Ni and that produced by the (γ, p) reaction.[6] The ^{57}Ni-labeled hexamminenickel(II) halides were synthesized by ordinary methods[7] and were then stored in the dark at the temperature of dry ice. After the complete decay of the ^{57}Ni, the ^{57}Co-labeled species were separated by means of a cation-exchange resin method, with reference to the procedure previously reported by Ikeda *et al.*[8]

The thermal-annealing procedure was carried out in a constant boiling bath or in an electric oven. Crystals were placed in brown glass tubes in air unless otherwise stated. The macroscopic thermal decomposition of the hexamminenickel(II) complexes was studied under the same conditions as was the thermal annealing.

The radioactivity of ^{57}Co was measured with a 100-channel pulse-height analyzer equipped with an NaI(Tl) well crystal.

Results and Discussion

In the present investigation, the following ^{57}Co recoil species were separated by means of a cation-exchange resin method: $^{57}Co^{2+}$, $^{57}CoX(NH_3)_5{}^{2+}$, and $^{57}Co(NH_3)_6{}^{3+}$, where X denotes Cl, Br, or I. The experimental results for the initial distribution of ^{57}Co-labeled species in the hexamminenickel(II) complexes are summarized in Table 1. The yields shown are average values of at least five determinations.

TABLE 1. INITIAL YIELD OF ^{57}CO-LABELED SPECIES IN HEXAMMINENICKEL(II) HALIDES

Compound	Yield of ^{57}Co-labeled species (%)		
	Co^{2+}	$CoX(NH_3)_5{}^{2+}$	$Co(NH_3)_6{}^{3+}$
$[^{57}Ni(NH_3)_6]Cl_2$	72.6 ± 1.5	2.3 ± 0.5	24.7 ± 0.8
$[^{57}Ni(NH_3)_6]Br_2$	72.8 ± 1.7	1.6 ± 0.4	25.7 ± 1.6
$[^{57}Ni(NH_3)_6]I_2$	70.3 ± 2.0	2.7 ± 0.6	26.9 ± 1.5

Although the initial yields of the radioactive ^{57}Co species in the hexamminenickel(II) halides are nearly all equal, there appears a remarkable difference among the isothermal annealing curves, as is shown in Figs.

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[1] K. E. Collins and G. Harbottle, *Radiochim. Acta*, **3**, 21 (1964).

[2] T. Andersen, F. Christensen, and K. Olesen, *Trans. Faraday Soc.*, **62**, 248 (1966).

[3] T. Andersen, L. Johansen, and K. Olesen, *ibid.*, **63**, 1730 (1967).

[4] T. Shiokawa, T. Sasaki, and S. Takahashi, *Radiochem. Radioanal. Lett.*, **1**, 31 (1969); T. Shiokawa and T. Sasaki, This Bulletin, **43**, 2835 (1970).

[5] T. Omori, S. C. Wu, and T. Shiokawa, *Radiochem. Radioanal. Lett.*, **3**, 405 (1970).

[6] G. E. Moore and K. A. Kraus, *J. Amer. Chem. Soc.*, **74**, 843 (1952).

[7] H. Ito, "Jikken Kagaku Koza," Vol. 11, Maruzen, Tokyo (1956), p. 74.

[8] N. Ikeda, K. Yoshihara, and S. Yamagishi, *Radiochim. Acta*, **3**, 13 (1964).

1—3. In all cases, an increase in the ^{57}Co(NH$_3$)$_6^{3+}$ yields corresponds substantially to a decrease in the ^{57}Co^{2+} yield, and the yield of the ^{57}Co-labeled halopentamminecobalt(III) fraction is almost independent of the heating time and the temperature. Thus changes in the ^{57}CoX(NH$_3$)$_5^{2+}$ yield are not plotted in the figures.

Figure 1 shows the annealing curves for the chloride complex. For temperatures below 80°C, the annealing isotherms exhibit normal kinetic patterns. At 119°C, the yield of the ^{57}Co(NH$_3$)$_6^{3+}$ fraction increases at first, then reaches a maximum after 2 hrs' heating and subsequently decreases. This kind of annealing pattern is presumably due to the thermal decomposition of the reformed complex.

In the bromide complex, the annealing isotherms at various temperatures are shown in Fig. 2. Up to 100°C, the annealing curves possess characteristic shapes; that is, they show the inflection near the point of origin. However, the curve at 119°C shows a normal kinetic pattern.

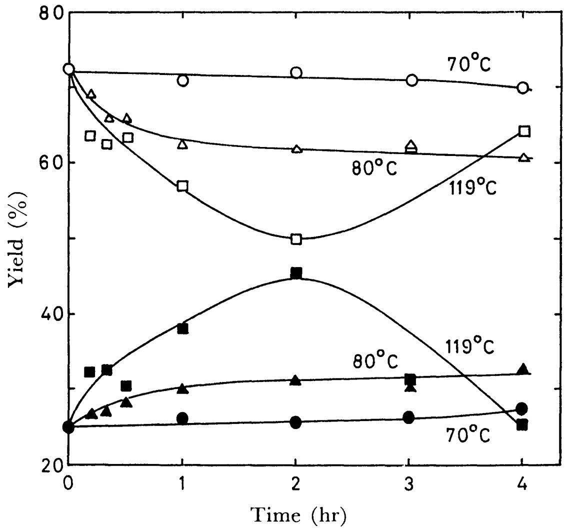

Fig. 1. Isothermal annealing curves of ^{57}Co in [^{57}Ni(NH$_3$)$_6$]Cl$_2$.
○, △, □: ^{57}Co^{2+}; ●, ▲, ■: ^{57}Co(NH$_3$)$_6^{3+}$

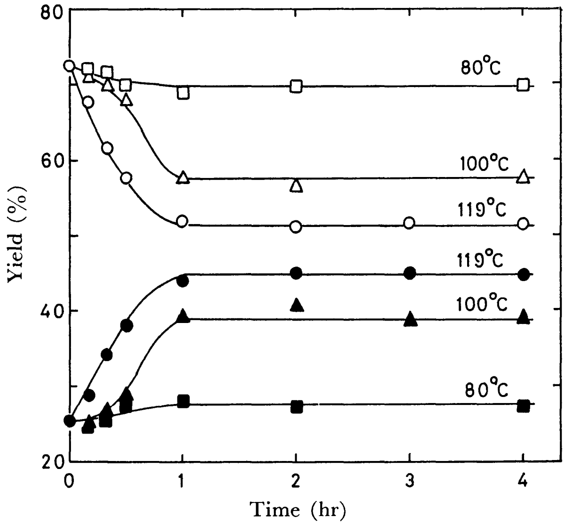

Fig. 2. Isothermal annealing curves of ^{57}Co in [^{57}Ni(NH$_3$)$_6$]Br$_2$.
○, △, □: ^{57}Co^{2+}; ●, ▲, ■: ^{57}Co(NH$_3$)$_6^{3+}$

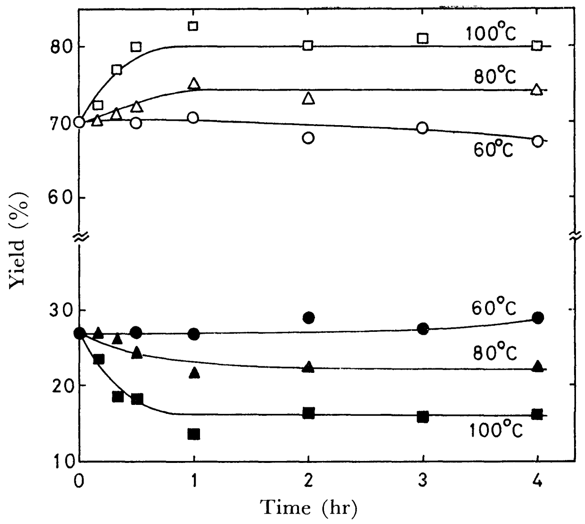

Fig. 3. Isothermal annealing curves of ^{57}Co in [^{57}Ni(NH$_3$)$_6$]I$_2$.
○, △, □: ^{57}Co^{2+}; ●, ▲, ■: ^{57}Co(NH$_3$)$_6^{3+}$

In the iodide complex, the annealing isotherms differ appreciably from those of the chloride and bromide complexes, as is shown in Fig. 3. The ^{57}Co(NH$_3$)$_6^{3+}$ yield decreases gradually at 80°C, though it increases slightly at 60°C after 4 hrs' heating.

These experimental results suggest that the chemical behavior of the recoil ^{57}Co atoms in the nickel(II) complexes is influenced by the thermal decomposition of the daughter cobalt complexes. It is necessary to study also the effect of the thermal decomposition of the parent complexes, because the hexamminenickel(II) chloride decomposes at a lower temperature than does the hexamminecobalt(III) chloride.[9]

The macroscopic thermal decomposition of the hexamminenickel(II) chloride was noticeable after heating for 4 hr at 80°C, where it amounted to 6.2 per cent, while at 70°C no appreciable decomposition was observed after 20 hrs' heating. In the bromide and iodide complexes, no macroscopic decomposition of the crystal took place after 4 hrs' heating at 80°C, but the decomposition began at 100°C.

On the basis of the data for the thermal decomposition of the parent nickel(II) complexes, the chemical behavior of the recoil ^{57}Co atoms can be explained as follows: when the parent complex is thermally stable, the annealing reaction does not proceed essentially after 4 hrs' heating. On the contrary, when the parent complex, [Ni(NH$_3$)$_6$]Cl$_2$, begins to decompose, the ^{57}Co(NH$_3$)$_6^{3+}$ yield increases remarkably. This suggests that freely-available ammonia molecules will participate in the formation reaction of the hexamminecobalt(III) complex. In the iodide, however, the decrease in the ^{57}Co(NH$_3$)$_6^{3+}$ yield at 80°C is possibly to be ascribed to low thermal stability of hexamminecobalt(III) iodide, since the thermal

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[9] W. W. Wendlandt and J. P. Smith, "Thermal Properties of Transition-Metal Ammine Complexes," Elsevier, Amsterdam (1967).

decomposition of the hexamminenickel(II) iodide can be ignored.

In the (n, γ) process of the hexamminecobalt(III) complexes, Yasukawa and Saito[10,11] have also found that the thermal annealing reaction of ^{60}Co to reform the parent is promoted by the atmosphere of ammonia gas. This effect was interpreted in terms of the diffusion of ammonia, penetrating into the interior of the crystal and reacting with fragments to reform the parent.

Extensive kinetic studies of the thermal decomposition of the hexamminecobalt(III) complexes have been carried out by Tanaka and Nagase.[12] They proposed that the decomposition of $[Co(NH_3)_6]Cl_3$ *in vacuo* proceeds as follows:

$$[Co(NH_3)_6]Cl_3 \rightarrow [Co(NH_3)_6]Cl_2 + Cl \rightarrow CoCl_2 + 6NH_3 + (1/2)Cl_2 \qquad (1)$$

The first step, which is rate-determining, is the electron-transfer process from the outer-sphere chloride ion to the central cobalt(III) ion. The reaction of the second step is very fast, because hexamminecobalt(II) chloride is thermally unstable. On the other hand, when the samples were treated in a sealed system or in air, the reaction was complicated:

$$\begin{aligned} &[Co(NH_3)_6]Cl_3 \overset{A}{\rightleftharpoons} [Co(NH_3)_6]Cl_2 + (1/2)Cl_2 \rightleftharpoons R \\ &\quad \xrightarrow{B} [CoCl(NH_3)_5]Cl_2 + NH_3 \overset{A'}{\rightleftharpoons} \\ &\qquad [Co(NH_3)_5]Cl_2 + (1/2)Cl_2 \\ &\qquad\qquad + NH_3 \rightleftharpoons R \qquad (2) \end{aligned}$$

where R represents the mixture of the decomposition products. The B process takes place when the electron-transfer reaction is strongly interfered with. It should be noticed that the A process of Eq. (2) is a reversible electron-transfer reaction, in which oxygen in the air can oxidize the cobalt(II) to cobalt(III) complexes instead of halogen molecules. In both systems, the order of the increase in the rate of the electron-transfer reaction is expressed as follows: $[Co(NH_3)_6]Cl_3 < [Co(NH_3)_6]Br_3 < [Co(NH_3)_6]I_3$.

In the present system, the apparent annealing reaction is the oxidation of the cobalt(II) ion to the cobalt(III) ion. Since the yield of the halopentamminecobalt(III) ion does not vary during the annealing reaction, the oxidation reaction seems to proceed as the reverse of the reaction expressed in the A process of Eq. (2). Furthermore, the fact that, when the ammonia molecules produced by the thermal decomposition of the parent complex are available, the formation of the hexamminecobalt(III) ion proceeds rapidly and extensively, suggests that the reformation of $^{57}Co(NH_3)_6{}^{2+}$ is also a rate-determining step in the thermal annealing.

In order to study further the effect of the ammonia molecules, a thermal annealing reaction in air was compared with that in a vacuum-sealed tube. After heating for 12 hr at 80°C, the $^{57}Co(NH_3)_6{}^{3+}$ yield increases to 24.9 per cent in the sealed system, but only to 15.1 per cent in air. In the sealed system, the ammonia molecules formed by the decomposition of the hexamminenickel(II) ion cannot escape from the system and participate in the reformation reaction.

In Mössbauer studies, the formation of ^{57}Fe(III) species is often observed in the EC process of the ^{57}Co(II) compound.[13] In the hot-atom chemistry of the solid state, however, few examples have been reported of the oxidative reaction in the recoil process.[14] In other words, the recoil species other than the parent are, as a general rule, found, partly or entirely, in an oxidation state lower than their original condition. On annealing, the parent compound is reformed, even if the recoil species is found in a higher oxidation state than is the parent. These trends suggest that the chemical behavior of the recoil species is influenced mostly by the crystal matrix of the parent compound and secondarily by the chemical nature of the recoil species.

The present results contrast strongly with the general trends and indicate that the chemical property of the daughter species plays an important role in determining the chemical fate of the recoil atom in the foreign matrix. As an extension of this discussion, further study of the chemical behavior of the recoil ^{57}Co was designed in the temperature region where the effect of the thermal decomposition could be ignored. The experimental results are summarized in Fig. 4.

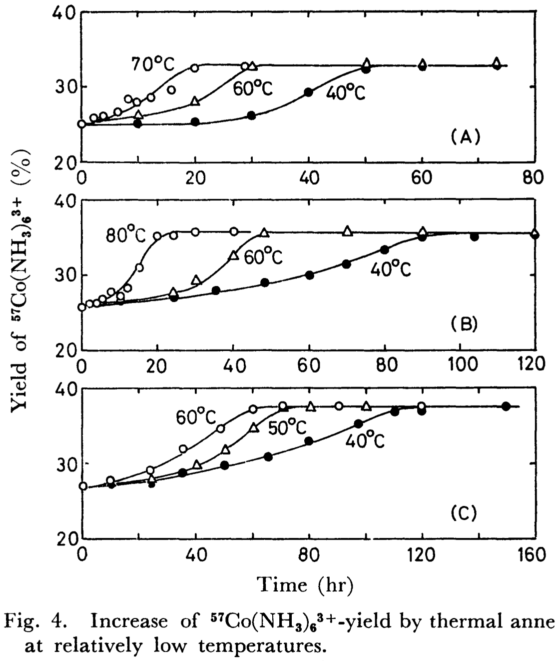

Fig. 4. Increase of $^{57}Co(NH_3)_6{}^{3+}$-yield by thermal annealing at relatively low temperatures.
(A): $[^{57}Ni(NH_3)_6]Cl_2$; (B): $[^{57}Ni(NH_3)_6]Br_2$; (C): $[^{57}Ni(NH_3)_6]I_2$

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[10] T. Yasukawa and N. Saito, *J. Inorg. Nucl. Chem.*, **27**, 1433 (1965).

[11] T. Yasukawa, *ibid.*, **28**, 17 (1966).

[12] N. Tanaka and K. Nagase, This Bulletin, **40**, 546 (1967).

[13] For example, R. Ingalls and G. Depasquali, *Phys. Lett.*, **6**, 169 (1966); A. Nath, M. P. Klein, W. Kundig, and D. Lichtenstein, *Radiation Effects*, **2**, 211 (1969); J. M. Friedt, A. Creset, L. Asch, and J. P. Adloff, *Radiochem. Radioanal. Lett.*, **3**, 81 (1970).

[14] J. S. Butterworth and G. Harbottle, *Radiochim. Acta*, **6**, 169 (1966); A. H. W. Aten, Jr., and J. C. Kapteyn, *ibid.*, **9**, 223, 224 (1968).

Table 2. Thermal annealing of ^{57}Co-doped hexamminenickel(II) complexes

Compound	Thermal treatment	Yield of ^{57}Co-labeled species (%)		
		Co^{2+}	$CoX(NH_3)_5^{2+}$	$Co(NH_3)_6^{3+}$
$[Ni(NH_3)_6]Cl_2$	None	51.8	0.1	48.2
	100°C, 4 hr	50.6	0.5	48.9
$[Ni(NH_3)_6]Br_2$	None	57.5	0.1	42.4
	100°C, 4 hr	57.3	0.2	42.5

The shape of these annealing curves is similar to that in the bromide complex at 100°C. However, some interesting features can be found: the characteristic plateau values are dependent on the nature of the outer-sphere anions, but independent of the temperature, and the order of the increase in the rate of the annealing reaction is expressed as follows: chloride> bromide>iodide.

Mathematical analyses showed that a composite annealing curve for the present data is incompatible with a single first- or second-order rate process, nor does it fit error-function kinetics. However, some qualitative explanation would be possible on the supposition that, in this temperature region, the annealing reaction could be considered to be stoichiometrically the same as that taking place at higher temperatures.

About 53 per cent of the decay events of ^{57}Ni is the EC process, and the remainder is the β^+-decay.[15] The recoil energy (max. 34 eV) is too low for the ^{57}Co atoms to allow displacement into the interstitial site.[16] However, the electronic excitation following the decay will affect the chemical behavior of the daughter species.

The emission of a positron from the nucleus of a constituent atom should produce a negatively-charged species. Accordingly, the immediate effect of the decay of the ^{57}Ni(II) complex would be the formation of the univalent cobalt complex, and this cobalt complex would be found in the cobalt(II) species upon dissolution. On the other hand, the decrease in nuclear charge by electron capture is balanced by the decrease in the number of electrons. However, the vacancy created in the K shell is followed by the Auger cascade, which results in a multiply charged daughter species.[17] The neutralization of the charged ion causes the decomposition of the compound and creates the crystal defects surrounding the recoil atom. In this case, the recoil species will be found in the oxidation states of Co(II) and Co(III).[13]

The electron-transfer reaction is also affected by the oxidative power of the outer-sphere anion.[5] In the halide complexes, the driving force for the oxidation seems to be electron trapping by positive holes produced during the neutralization of multiply-charged recoil species. In fact, the annealing rates increase with an increase in the electron affinity of the halogen atom. A thermal ionization mechanism for the thermal annealing of ^{60}Co in the hexamminecobalt(III) bromide has been proposed by Yoshihara and Harbottle.[18] This explanation was further confirmed by the ^{57}Co-doping experiment. The ^{57}Co-doped hexamminenickel(II) complexes which were synthesized from a solution of the nickel(II) ion containing carrier-free ^{57}Co were subjected to thermal treatment. In this case, all the ^{57}Co may exist in the form of the hexammine complex. The experimental results are listed in Table 2. The fairly large $^{57}Co(NH_3)_6^{3+}$ yield is due to the air-oxidation of the cobalt(II) ion during synthesis. No appreciable change in the $^{57}Co(NH_3)_6^{3+}$ yield is observed at 100°C, where the annealing behavior of the recoil ^{57}Co is noticeable, as may be seen in Fig. 1. This fact indicates that, when the crystal defects are absent in the near-neighborhood of the ^{57}Co atom, the oxidation reaction of the cobalt(II) species does not take place.

The temperature-independent plateau value of the $^{57}Co(NH_3)_6^{3+}$ yield suggests that the intrinsic annealing takes place in a small region affected by the recoil. If the damage to the crystal lattice is extensive, synthetic reaction such as the formation of the pentamminecobalt(III) complex will occur simultaneously, as has been pointed out by Yoshihara.[19]

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15) C. M. Lederer, J. M. Hollander, and I. Perlman, "Table of Isotopes" (Sixth edition), John Wiley & Sons, New York (1967).

16) K. Yoshihara, M. H. Yang, and T. Shiokawa, *Radiochem. Radioanal. Lett.*, **4**, 143 (1970); K. Yoshihara and H. Kudo, *J. Chem. Phys.*, **52**, 2950 (1970).

17) S. Wexler, "Actions Chemiques et Biologiques des Radiations" (ed. M. Haissinsky), Masson, Paris (1965), Vol. 8, pp. 180—193.

18) K. Yoshihara and G. Harbottle, *Radiochim. Acta*, **1**, 68 (1963).

19) K. Yoshihara, *Nature*, **204**, 1296 (1964).