Studies of the Yields of ^{57}Fe(II)-species Produced after the EC-decay and of ^{60}Co(II)-species Produced in the (n, γ) Reaction in Cobalt(III) Coordination Compounds

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(Received February 13, 1978)

The yields of ^{57}Fe(II)-species produced after EC-decay were compared with those of ^{60}Co(II)-species produced in the ^{59}Co(n,γ)^{60}Co reaction for twelve cobalt(III) coordination compounds. The results indicate that the radiochemical yield of ^{60}Co(II)-species correlates with the yield of ^{57}Fe(II)-species except in the case of $[Co(NH_3)_6]_2(CrO_4)_3$. The anomalously low yield of ^{57}Fe(II)-species in $[Co(NH_3)_6]_2(CrO_4)_3$ is ascribed to the reaction of chromate anions with ammine ligands initiated by the nuclear transformation in a solid.

A number of studies of the chemical effects of ^{59}Co(n,γ)^{60}Co nuclear reactions in cobalt(III) coordination compounds have thus far been reported. Although several working hypotheses have been proposed in hot-atom chemistry concerning the initial distribution of the transformed nuclides into different chemical states,[1] these hypotheses have all been made on the assumption that radiochemical separation processes have little influence on the analytical results of the transformed nuclides. It is well-known, however, that the results depend on the experimental conditions, such as the time and the temperature both of irradiation and storage, and the chemical and physical state of the sample used for irradiation.[1,2]

Mössbauer emission spectroscopy provides a unique way of studying *in situ* the chemical state of atoms produced as a result of nuclear decay in a solid. The technique has been extensively used in investigations of ^{57}Fe-species produced after the EC-decay of ^{57}Co, but few studies of the Mössbauer emission spectroscopy of cobalt(III) compounds have been concerned with the results of ^{59}Co(n,γ)^{60}Co hot-atom chemistry. We have reported previously that the chemical states of ^{57}Fe produced after the EC-decay of ^{57}Co depend upon the radiolytic character of the ligands or anions surrounding the decaying atoms.[3,4] In the present work, the radiochemical yield of ^{60}Co(II)-species found in the (n,γ) reaction was compared with the yield of ^{57}Fe(II)-species produced after the EC-decay for twelve cobalt(III) coordination compounds, including three compounds reported previously.[4]

Experimental

Target and ^{57}Co-labelled Compounds. $[Co(NH_3)_6]CO_3Cl$,[5] $[Co(NH_3)_6]SO_3Cl$,[6] $[Co(NH_3)_6]_2(CO_3)_3\cdot 3H_2O$,[7] $[Co(NH_3)_6]_2(SO_4)_3\cdot 5H_2O$,[8] $[Co(NH_3)_6]_2(CrO_4)_3$,[9] $[Co(NH_3)_6](NO_3)_3$,[8] $[Co(NH_3)_6]Cl_3$,[8] $[Co(NH_3)_5(OH_2)](NO_3)_3$,[10] and $[Co(NH_3)_5(OH_2)]_2(C_2O_4)_3\cdot 4H_2O$[10] were prepared from soltuions, each containing 50 mg of cobalt(II), by following the methods described in Refs. 5 to 10. The ^{57}Co-labelled compounds were prepared from solutions containing about 1 mCi ^{57}Co, but otherwise in the same way as described above. The purity was checked by elemental analysis and X-ray diffraction and found to be at least 97%.

Neutron Irradiation and Chemical Separation. The samples were irradiated for 10 min at the reactor temperature in a thermal column in a TRIGA Mark II reactor at the Institute for Atomic Energy of Rikkyo University. After being allowed to stand for half an hour, the irradiated sample was dissolved into an aqueous solution containing 10 mg cobalt(II) chloride as a carrier, after which a small amount of diluted hydrochloric acid was added to keep the acidity at pH 3—4. The cobalt(II) species were separated by solvent extraction after adding 1-nitroso-2-naphthol, hydrogen peroxide, and chloroform to the solution. The radiochemical yield of ^{60}Co(II) was determined by counting 1.17 and 1.33 MeV γ-rays with a Ge(Li) semiconductor detector and a multichannel analyser, CANBERRA Model 8100.

Mössbauer Emission Spectroscopic Measurements. The ^{57}Co-labelled compounds were kept in a crysotat, and the Mössbauer spectra were measured against an ^{57}Fe-enriched stainless-steel absorber moving in a constant-acceleration mode at room temperature. The velocity calibrartions were carried out by using an ^{57}Fe-enriched iron foil absorber moving against a stationary ^{57}Co(Pt) source at room temperature.

Results and Discussion

Some typical Mössbauer emission spectra of the source compounds measured at 78 K are shown in Figs. 1 and 2. The peak component ascribed to ^{57}Fe(II)-species was estimated from the isomer-shift and quadrupole-splitting values. The yield of ^{57}Fe(II)-species was evaluated from the area under the component and the total area of the spectrum by assuming that the recoil-free fraction of each ^{57}Fe-species was nearly the same at 78 K, as has previously been described in Ref. 4.

Table 1 summarizes the results concerning the radiochemical yield of ^{60}Co(II), together with the yield of ^{57}Fe(II) evaluated from the Mössbauer emission spectroscopy. It has already been reported that practically the same yield of ^{60}Co(II) is obtained by using either solvent extraction or paper electrophoresis for neutron-irradiated tris(dimethylglyoximato)cobalt(III).[11] Our previous result concerning the radiochemical yield of ^{60}Co(II) obtained for the neutron-irradiated $[Co(NH_3)_6](NO_3)_3$ by means of paper electrophoresis is shown in Table 1 for the sake of comparison.

We have demonstrated repeatedly that the distribution of the decayed atom into the different chemical states depends on the radiolytical property of the species surrounding the decayed atom.[17–19] It was also reported that not only the nearest neighbors of the decayed atom, but also the next nearest neighbors,

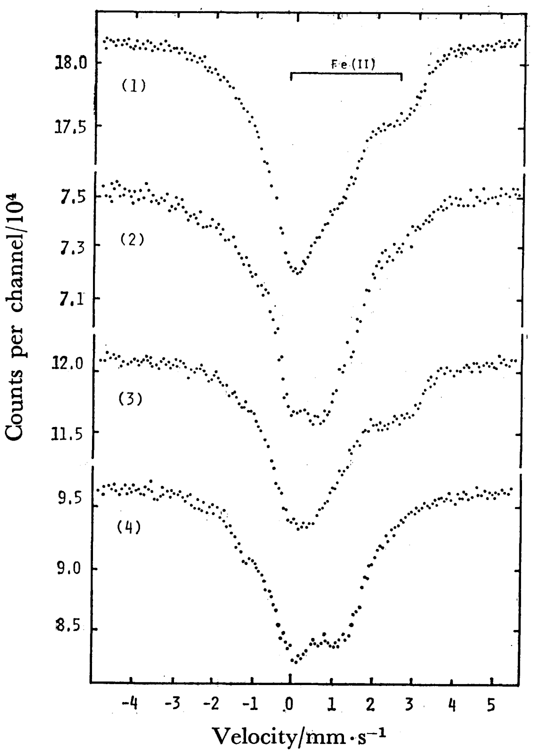

Fig. 1. Mössbauer spectra at 78 K of ^{57}Co-labelled (1) $[Co(NH_3)_6]Cl_3$, (2) $[Co(NH_3)_6]_2(CO_3)_3 \cdot 3H_2O$, (3) $[Co(NH_3)_6]_2(SO_4)_3 \cdot 5H_2O$, and (4) $[Co(NH_3)_6]_2(CrO_4)_3$ sources.
All the velocity scales were normalized with respect to metallic iron.

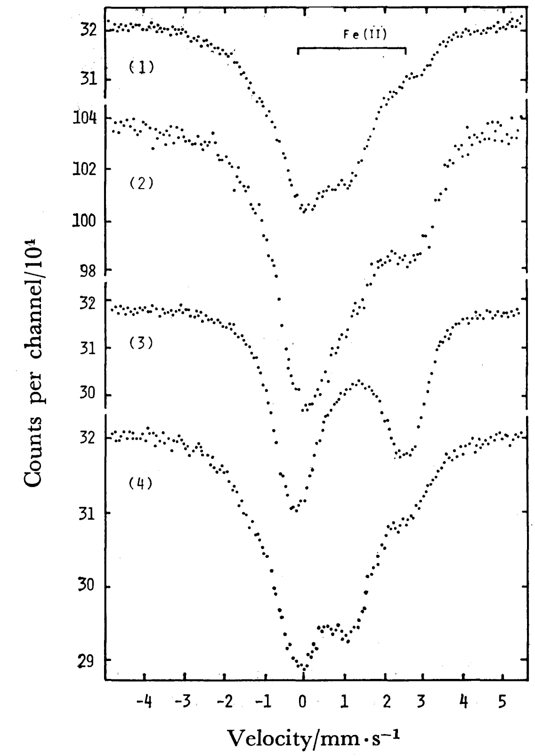

Fig. 2. Mössbauer spectra at 78 K of ^{57}Co-labelled (1) $[Co(NH_3)_6]CO_3Cl$, (2) $[Co(NH_3)_6]SO_3Cl$, (3) $[Co(NH_3)_5OH_2]_2(C_2O_4) \cdot 4H_2O$, and (4) $[Co(NH_3)_5OH_2](NO_3)_3$ sources.
All the velocity scales were normalized with respect to metallic iron.

TABLE 1. SUMMARY OF THE YIELDS OF ^{57}Fe(II)-SPECIES PRODUCED AFTER EC-DECAY AND THE RADIOCHEMICAL YIELDS OF THE ^{60}Co(II)-SPECIES IN THE HOT-ATOM CHEMISTRY OF THE ^{59}Co(n, γ)^{60}Co REACTION

Compound	Yield of ^{57}Fe(II) in EC-decay, %	Yield of ^{60}Co(II) in ^{59}Co(n γ)^{60}Co, %
$[Co(NH_3)_6]Cl_3$	42±1	57.5
$[Co(NH_3)_6]_2(CO_3)_3 \cdot 3H_2O$	34±1	45.1
$[Co(NH_3)_6]_2(SO_4)_3 \cdot 5H_2O$	54±1	96.0[12]
$[Co(NH_3)_6]_2(CrO_4)_3$	1±1	63.2[12]
$[Co(NH_3)_6]CO_3Cl$	41±1	61.0
$[Co(NH_3)_6]SO_3Cl$	52±1	67.8
$[Co(NH_3)_6](NO_3)_3$	38±1; 40±1[14]	66.9; 66.7[12]
$[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$	72±1[14]	91.0[14]
$[Co(NH_3)_5OH_2](NO_3)_3$	34±1	51.3[13]
$[Co(NH_3)_5OH_2]_2(C_2O_4) \cdot 4H_2O$	68±1	82.9[13]
$[Co(NH_2CH_2CH_2NH_2)_3](NO_3)_3$	53±1[14]	69.4[15]
$K_3[Co(C_2O_4)_3] \cdot 3H_2O$	85[16]	98.6[14]

are involved in determining the oxidation state of the decayed atom in the local radiolytic processes initiated by the EC-decay.[3,4] A large amount of ^{57}Fe(II)-species found in the spectrum of $[Co(NH_3)_5(OH_2)]_2(C_2O_4)_3 \cdot 4H_2O$ can be ascribed to the effect of oxalate anions in the second coordination sphere, as was mentioned in the case of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$.[4] Electrons produced in the process:

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

may be involved in enhancing the yield of ^{57}Fe(II)-species.

Including our previous data on $[Co(NH_3)_6](NO_3)_3$, $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$, and $K_3[Co(C_2O_4)_3] \cdot 3H_2O$, Fig. 3 compares the yield of ^{60}Co(II) after the (n,γ) reaction with the yield of ^{57}Fe(II) after the EC-decay. A fairly good correlation may be found between them except for $[Co(NH_3)_6]_2(CrO_4)_3$ which shows a very low yield in the ^{57}Fe(II) state, whereas there is quite large yield in the ^{60}Co(II) state. The correlation between the yield of ^{57}Fe(II) and that of ^{60}Co(II) for the other compounds can be understood by assuming that there should be little irregular influence on the trend of distribution of ^{60}Co atoms produced in the (n,γ) hot-atom reaction through traditional chemical separation.

The results suggest that the fate of the ^{60}Co atoms produced in the (n,γ) reaction is similar, after their slow-down, to that of the ^{57}Fe atoms produced in the EC-decay except for the difference between the chemical behavior of cobalt and iron. The similarlity may be partly explained by the fact that ^{60}Co-species are also produced through the ^{59}Co(n,γ)^{60m}Co reaction and the I. T. (I. C.) process. The large cross-section of the ^{59}Co(n,γ)^{60m}Co reaction (σ : 18 barn), the short ir-

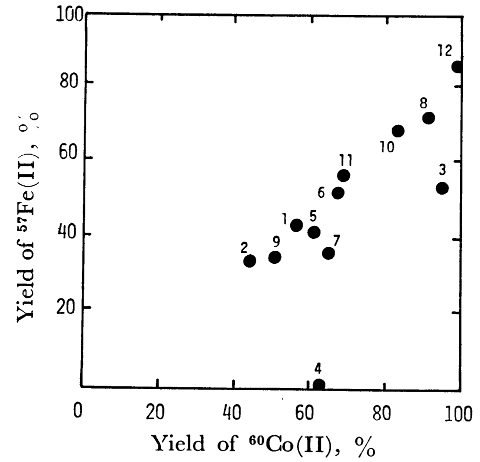

Fig. 3. Comparison of the radiochmiecal yield of ^{60}Co(II)-species in the ^{59}Co(n, γ)^{60}Co hot-atom chemistry with the yield of ^{57}Fe(II)-species produced after EC-decay.
1: $[Co(NH_3)_6]Cl_3$, 2: $[Co(NH_3)_6]_2(CO_3)_3 \cdot 3H_2O$, 3: $[Co(NH_3)_6]_2(SO_4)_3 \cdot 5H_2O$, 4: $[Co(NH_3)_6]_2(CrO_4)_3$, 5: $[Co(NH_3)_6]CO_3Cl$, 6: $[Co(NH_3)_6]SO_3Cl$, 7: $[Co(NH_3)_6](NO_3)_3$, 8: $[Co(NH_3)_6]_2(C_2O_4) \cdot 4H_2O$, 9: $[Co(NH_3)_5OH_2](NO_3)_3$, 10: $[Co(NH_3)_5OH_2]_2(C_2O_4)_3 \cdot 4H_2O$, 11: $[Co(NH_2CH_2CH_2NH_2)_3](NO_3)_3$, and 12: $K_3[Co(C_2O_4)_3] \cdot 3H_2O$.

radiation time, and the large internal conversion coefficient ($\alpha_k : 41$) provide the conditions necessary to produce multi-charge decayed atoms just like those provided by the EC-decay process.[21] The fate of the so-called hot-atoms may be determined through the chemical interaction with the host material—local radiolytic process—either after the (n,γ) reaction or after the EC-decay. The distribution of ^{60}Co atoms in the reduced state, Co(II), may depend upon the local radiolytic property of the host cobalt(III) coordination compound, which determines the yield of the ^{57}Fe atoms produced in the EC-decay into the reduced ferrous state as well.

The anomalous results found in the case of $[Co(NH_3)_6]_2(CrO_4)_3$ indicate that the decayed ^{57}Fe atoms remain in the ligand-deficient Fe(III) state after the EC-decay process. It seems reasonable to assume that the following process:

$$CrO_4^{2-} + 2e^- \longrightarrow CrO_4^{4-}$$

consumes electrons and keeps the decaying atoms in a higher oxidation state, since chromate(IV) anions are known to be stable in Ba_2CrO_4 and Ca_2CrO_4.[20] Chromate(VI) anions may also be supposed to react with ammine lignads in the following processes:

$$CrO_4^{2-} + NH_3 \rightarrow \frac{1}{2}Cr_2O_3 + \frac{1}{2}N_2 + \frac{1}{2}H_2O + OH^-$$

$$Cr_4O^{2-} + \frac{2}{3}NH_3 \rightarrow CrO_2 + \frac{1}{3}N_2 + 2OH^-$$

through the local radiolytic process triggered by the nuclear transformation, giving reduced Cr(IV) or Cr(III) species, nitrogen, and hydroxide ions. The ligand-deficient species produced through the nuclear transformation may decompose into a reduced species, giving a large radiochemical yield of the reduced species—the ^{60}Co(II)-species in the present case—after the sample has been dissolved for the traditional radiochemical analysis, whereas the ligand-deficient ^{57}Fe-species remaining in the original oxidation state can be observed as ^{57}Fe(III)-species by the Mössbauer emission spectroscopy. A similar trend is also found slightly in the case of $[Co(NH_3)_6]_2(SO_4)_3$, although here the effect of sulfate anions seems not so remarkable as that of chromate(VI) anions.

The present results indicate that the trends observed in the traditional hot-atom chemistry correlate with those observed in the Mössbauer emission experiments, if there are no or few addtional effects through the chemical analyses, and that the comparison of the results obtained for the hot-atom chemistry of the (n,γ) process in cobalt compounds with those of the Mössbauer emission spectroscopic studies of the same compounds can provide clues for use in clarifying the reaction mechanism which may occur around the "hot-atoms" in a solid.

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