Hot-atom Chemistry of Hexamminechromium(III) Nitrate in the Solid State

By Nagao IKEDA, Kenji YOSHIHARA, Hiroshi EBIHARA and Kiyomi SUZUKI

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The hot-atom effect in trisethylenediaminechromium(III) nitrate[1,2] and hexamminecobalt(III) nitrate[3] has been studied, but the same effect in hexamminechromium(III) nitrate has not yet been reported. Recently, the present authors succeeded in enriching ^{60}Co and ^{60m}Co recoil atoms produced in neutron-irradiated hexamminecobalt(III) nitrate with a high efficiency[4]. The method used by the authors was based on the heterogeneous extraction; the neutron-irradiated fine powders were shaken with a liquid which did not dissolve the target but dissolved the recoil species. As this method is very simple and rapid, it has sometimes been used for the enrichment of radioisotopes produced by (n, p)- and (n, α)-reactions[5,6]. In the case of (n, γ)-reaction[7], however, it does not usually give a high yield because of the short recoil range. Therefore the results in the previous paper were rather striking. In this paper, we investigated a similar heterogeneous extraction method on hexamminechromium(III) nitrate and discussed the mechanism of the extraction process. This complex is insoluble in concentrated nitric acid, but chromic ion and chromate or dichromate ion are soluble in it. Therefore, recoil atoms of ^{51}Cr should be extracted and enriched in the aqueous phase by shaking the target powder with concentrated nitric acid.

On the chemical form of the recoil chromium, some results heve already been reported; e. g., in the case of chromium azo-dye Palatine Fast Blue GGN[8], 83% of the radioactive chromium is present as chromium(III) and 11% of it as chromium(VI)*. In the present paper, chemical forms of recoil chromium atoms were also investigated.

Experimental

Target Material. — Hexamminechromium(III) nitrate was prepared by Mori's method[9].

Irradiation.—The cyclotron at the Institute of Physical and Chemical Research, Tokyo, and the nuclear reactor JRR-1 at the Japan Atomic Energy Research Institute were used for irradiation. The hot-atom effect of ^{55}Cr (half-life: 3.5 min.) was investigated by using the cyclotron, and that of ^{51}Cr (half-life: 27.8 day) by using the nuclear reactor. In the cyclotron, neutrons were generated by bombardment of beryllium with accelerated deuterons, and slowed down by a paraffin block. The neutron flux at the position of irradiation was about $10^6\sim10^7$ n/cm^2 sec.* The reactor, JRR-1 was operated at 50 kW/hr., and the neution flux

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[1] A. Turco and M. Scatena, *Ric. Sci.*, 25, 2651 (1955).

[2] A. Turco, *J. Inorg. Nucl. Chem.*, 13, 200 (1960).

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[4] N. Ikeda, K. Yoshihara and N. Mishio, *Radioisotopes*, 8, 242 (1959).

[5] E. Bleurer and W. Zünti, *Helv. Phys. Acta*, 20, 195 (1947).

[6] P. Jordan, *Helv. Chim. Acta*, 34, 699, 715 (1951).

[7] P. Süe and T. Yuasa, *J. chim. phys.*, 41, 160 (1944).

[8] N. Shibata and K. Yoshihara, This Bulletin, 32, 422 (1959); K. Yoshihara, M. Arai and T. Ishimori, *Proceedings of the 3rd Isotope Conference of Japan*, S18 (1959).

* In this paper, Cr(III) represents chromic ion, and Cr(VI) represent chromate or dichromate ion.

[9] M. Mori, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 74, 253 (1953).

* Contribution of fast neutrons to the radioactivation did not exceed about 5%.

was of the order of 10^{11} n/cm^2 sec. at the irradiation**. Temperature at the position did not exceed about 50°C.

Measurement of Radioactivity.—As ^{55}Cr emitted only β-particles (2.85 MeV.), the radioactivity was measured by a GM-counter made by the Institute of Physical and Chemical Research, (end window type, mica window thickness: 1.4 mg./cm^2). Radioactivity of ^{51}Cr was measured by a single channel γ-ray spectrometer made by the Atomic Instrument Co., Model 810A, (well type, NaI crystal, $1^3/_4{}''\phi\times 2''$). γ-Ray of 0.32 MeV. of ^{51}Cr was measured at the photo-peak by this counter.

Measurement of Solubility of Hexamminechromium(III) Nitrate in Nitric Acid.—The solubility of hexamminechromium(III) nitrate in nitric acid was determined in advance. Each 0.2 g. of the sample was shaken with 25 ml. of nitric acid of various concentrations for two or four minutes at 20°C. Results are listed in Table I. The solubility was about 1 mg./25 ml. for the acidity of 8∼12 N at 20°C, but it was slightly greater for 6 N. Therefore the acidity of 8∼12 N is preferable for this extraction process.

TABLE I. SOLUBILITY OF HEXAMMINECHROMIUM(III) NITRATE IN NITRIC ACID (20°C)

Concentration of HNO_3, N	Shaking time min.	Solubility, mg. $[Cr(NH_3)_6](NO_3)_3$/25 ml.
6	2	3.1
6	4	3.4
8	2	1.2
8	4	1.1
10	2	1.0
10	4	0.91
12	2	0.89
12	4	0.89

Determination of Chromium.—Amounts of extracted chromium in the liquid phase were determined colorimetrically. After the liquid phase was centrifuged, the complex salt in it was destroyed by boiling with concentrated nitric acid repeatedly, and tervalent chromium was oxidized to the sexivalent state with silver peroxide and the amounts of sexivalent chromium were determined by the diphenylcarbazide method[10]. The enrichment factors, E were calculated by the following formula:

$$E=\frac{a}{a_t}=\frac{M}{m}Y$$

where a and a_t denote specific activities in the liquid phase and in the irradiated complex salt before the process, respectively. M and m denote the amounts of chromium in the original salt and in the liquid phase, respectively. Y is the yield of ^{51}Cr in the liquid phase.

Extraction of Enriched ^{55}Cr.—About 1 g. of hexamminechromium(III) nitrate was bombarded with neutrons produced by the cyclotron for about an hour or two. After irradiation, the target was divided into two portions. One was subjected to the measurement of radioactivity by a GM-counter tracing its decay (Sample I), and the other to the extraction of ^{55}Cr with 20∼50 ml. of 8 N nitric acid in an Erlenmeyer flask by being shaken vigorously for 2 min. After the extraction and centrifugal separation, the solid was washed with ethanol and dried in air. Its radioactivity was measured by a GM-counter tracing its decay (Sample II). Samples I and II were weighed, and the retention was calculated from the ratio of the specific activities of the two samples at the same time. The extraction yield was given by subtracting the retention value from 100%. The results are listed in Table II. The extraction yield higher than 60% was obtained and the enrichment factor of 200∼400 was obtained. The enrichment of ^{55}Cr has been attained by these simple and rapid procedures.

Preparation of Enriched ^{51}Cr.—Enrichment of ^{51}Cr was studied in the same way as in the case of ^{55}Cr. About 1 g. of the sample was irradiated in the pneumatic tube in the nuclear reactor for 2 hr. After irradiation, the sample was shaken with 50 ml. of 8 N nitric acid in an Erlenmeyer flask for 2 min. After being centrifuged from the solid, an aliquot of the liquid phase was subjected to the measurement of radioactivity by a γ-ray spectrometer. The solid was dissolved in water, and the radioactivity of an aliquot of the solution was measured by a γ-ray spectrometer. The yield of ^{51}Cr was calculated from these values. The results are shown in Table III. A yield of 57∼73% was obtained. The enrichment factor was 24∼41 which was much lower than the values of ^{55}Cr.

Extraction Curves on Repeated Extraction.—In order to investigate the extraction mechanism, extraction curves on repeated extractions were observed. An outline of the procedures for the repeated extractions is illustrated in Fig. 1. About 0.2 g. of the sample was irradiated in the pneumatic tube in JRR-1, and treated according to the

TABLE II. PREPARATION OF ENRICHED CHROMIUM-55

Amount of target, g.	Irradiation time, hr.	Integrated deuteron current, μA·hr.	Volume of 8 N HNO_3 ml.	Radiochemical yield %	Enrichment factor
1.292	2	20	50	86	230
0.972	2	20	25	66	240
1.270	1	14	20	61	400

** Contribution of fact neutrons to the radioactivation did not exceed about 5%.

[10] M. Tanaka, This Bulletin, 23, 165 (1950); E. B. Sandell, "Colorimetric Determination of Traces of Metals", 2nd Ed., Interscience Pub. (1950), p. 260.

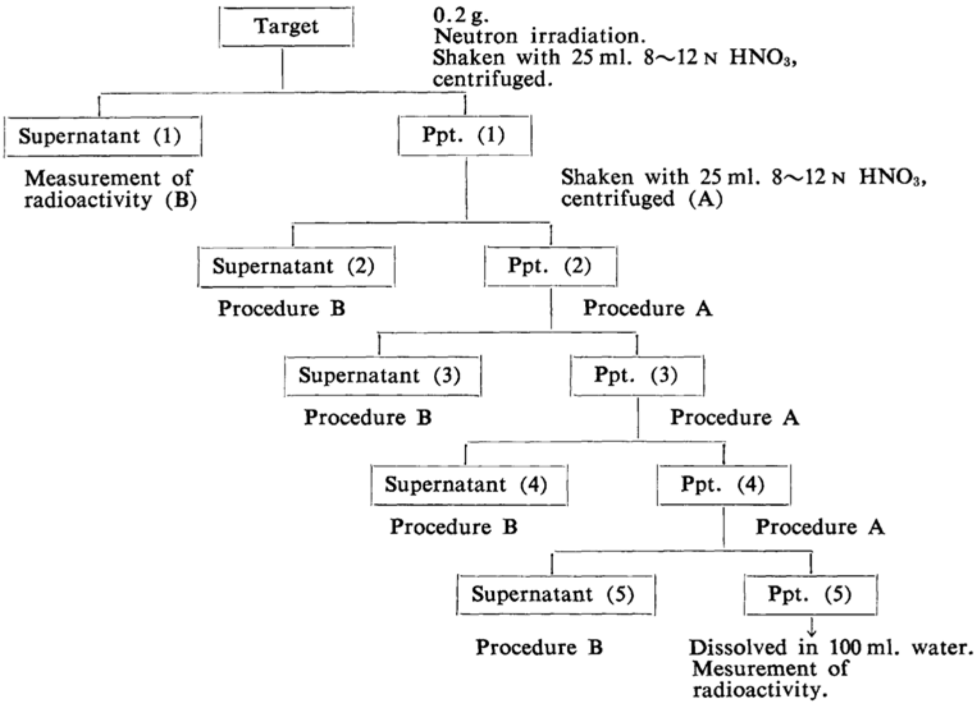

Fig. 1. Procedures in repetition of the extraction.

TABLE III. PREPARATION OF ENRICHED CHROMIUM-51

Amount of target, g	Vol. of 8N HNO_3 ml.	Radiochemical yield %	Enrichment factor
1.0	50	57	24
1.0	50	73	41

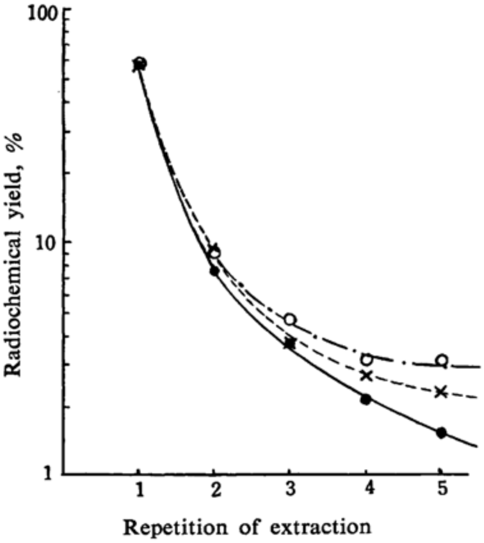

Fig. 2. Relationship between the radiochemical yield and the repetition of extraction (nitric acid only).
—●— 8 N HNO_3 ---○-- 12 N HNO_3
···×··· 10 N HNO_3

procedures shown in Fig. 2, where the values of extraction yield at 20°C are plotted against the repetition number of extraction. The extraction yield was very large at the first extraction, and decreased first rapidly and then slowly. As is shown in Fig. 2, tails of the extraction curves are higher with the increasing concentration of nitric acid. The total extraction yield of five fold extraction is shown in Table IV. These values increase with the increasing concentration of nitric acid. In all experiments mentioned above, nitric acid was used for extraction. Howevere, as the target material is slightly soluble in nitric acid, it is necessary to investigate whether this small solubility plays an important role on the extraction process or not. Nitric acid solution saturated with hexamminechromium(III) nitrate was used as an extracting agent in order to suppress the dissolution of the target. The results are shown in Fig. 3. As a whole, no large difference is found between the results in Figs. 2 and 3, but the tails of the extraction curves seem to be slightly affected by using nitric acid saturated with the complex salt. All the extraction curves in Fig. 3 are similar in shape.

TABLE IV. TOTAL RADIOCHEMICAL YIELD OF CHROMIUM-51 ON REPEATED HETEROGENEOUS EXTRACTIONS

Series	8 N HNO_3 %	10 N HNO_3 %	12 N HNO_3 %
No. 1	71.4	73.8	75.0
No. 2	70.5	71.0	74.5
No. 3	63.6	72.5	78.1

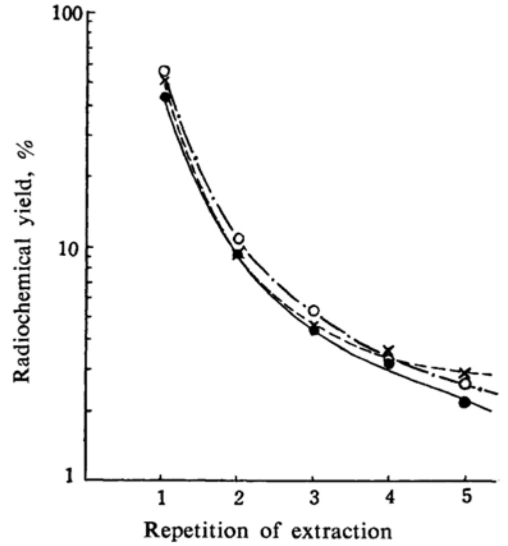

Fig. 3. Relationship between the radiochemical yield and the repetition of extraction (nitric acid saturated with hexamminechromium(III) nitrate).
—●— 8 N HNO_3 ---○-- 12 N HNO_3
···×··· 10 N HNO_3

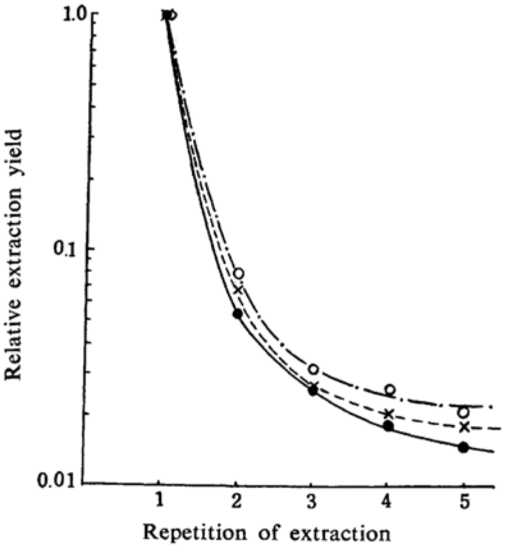

Fig. 4. Effects of shaking time on the extraction. 8 N HNO_3 was used for the extraction; shaking time: —●— 1 min. ---○-- 10 min. ···×··· 6 min.

The effect of shaking time on the extraction yield was investigated, using 8 N nitric acid without addition of the complex salt as the extracting agent. The sample was shaken for 6 or 10 min. The results are shown in Fig. 4. The tails of the extraction curves become higher with the increase of shaking time.

Determination of Enrichment Factors.—To calculate the enrichment factor of ^{51}Cr in each extract, chromium was determined colorimetrically as described before. The results are listed in Table V. The chromium found in the aqueous phase is derived from the dissolved complex salt or of radiation- and thermal-decomposition of the complex salt in the reactor. In Table V, "amount of chromium" (in 25 ml. extract) represents the amount of chromium calculated in the form of the complex salt. Comparing the amounts of chromium in Table V with those of dissolved chromium in Table I, it is shown that the solubility of the irradiated complex salt was much greater than that of the salt before irradiation. Even if radiation- and thermal-decomposition of the compolex in the reactor was considered, this could not account for the increase of the amount of chromium in the aqueous phase. At the first extraction, the enrichment factor was the largest, and it fell down with the repetition of extraction. The effect of concentration of nitric acid is distinctly seen on the fourth and the fifth extraction in the table.

TABLE V. ENRICHMENT FACTORS OF CHROMIUM-51 ON EACH EXTRACTION

Extraction number		Amount of chromium, mg. $[Cr(NH_3)_6]\cdot(NO_3)_3$	Enrichment factor
8 N HNO_3	1	5.4	20
	2	2.8	5.4
	3	2.7	2.8
	4	3.0	1.5
	5	3.7	0.9
8 N HNO_3	1	5.6	20
	2	2.9	6.5
	3	2.5	3.2
	4	2.4	2.4
	5	2.1	2.3
8 N HNO_3	1	5.8	20
	2	3.0	5.5
	3	1.8	5.5
	4	1.9	3.7
	5	2.0	3.4

As dissolution of a small amount of the target is inevitable, the enrichment factor drops more or less in the heterogeneous extraction. Therefore, the enrichment factor of chromic ion which is the predominant species produced by the hot-atom effect was determined by the following procedures. The irradiated target was dissolved in water and an iron(III) carrier as well as chromate ion as a hold-back carrier was added to the solution. Ammonia was added to the mixture to precipitate ferric hydroxide with which chromic ion coprecipitates. After being washed with a very dilute aqueous ammonia, the precipitate was dissolved in hydrochloric acid and again ferric hydroxide was precipitated with ammonia. After being washed the precipitate was dissolved in 9 N hydrochloric acid, and the solution was extracted twice tri-*n*-butyl phosphate to remove the iron. The aqueous phase was washed twice with benzene to remove tri-*n*-butyl phosphate. The chromium content in the aqueous phase was determined colorimetrically. The enrichment factor of ^{51}Cr(III) thus obtained was 150~230. As an enrichment factor of 20 was obtained at the first extraction in Table V, dissolution of target material plays an important role in diminishing the enrichment factor of ^{51}Cr in the heterogeneous extraction.

Determination of Chemical Forms of Recoil Products.— In the hot-atom effect of chromium complex salts, formation of chromate ion besides chromic ion was observed[8]. Harbottle[11] suggested that ammonium ion might act as a reducing agent on the recoil event in chromate. As hexamminechromium(III) nitrate has six ammonia molecules in it, it was considered interesting to note whether sexivalent chromium was formed in the target or not.

This was investigated in the following way. At first, the percentage of chromium(III) was determined. After adding 10 mg. of iron(III) carrier as well as 20 mg. of chromate as a hold back carrier to the aqueous solution of the irradiated target, ammonia was added to this mixture to precipitate ferric hydroxide. By this procedure, $[Cr(NH_3)_6](NO_3)_3$ and chromium(VI) were not precipitated while chromium(III) was coprecipitated with ferric hydroxide almost completely. The precipitate was separated and the radioactivity was measured by a γ-ray spectrometer.

Next, formation of chromium(VI) was tested by the following two methods; one is based on the precipitation of lead chromate in the presence of chromic ion as a hold-back carrier, and the other on the extraction of chromate with tri-*n*-butyl phosphate[5]. The latter method was preferable because of its exactness, and was adopted to determine the percentage of chromate. The aqueous solution of the irradiated target was made to 1 N by hydrochloric acid, and it was extracted with tri-*n*-butyl phosphate. Chromate was extracted into the tri-*n*-butyl phosphate phase, while the complex salt and chromic ion were left in the aqueous phase. The radioactivity of the organic layer was measured by a γ-ray spectrometer. Thus the distribution of the chemical forms of the recoil products were determined; chromium(III) fraction 98~99%, chromium(VI) fraction $<0.2\%$ and the retention 1~2%.

Measurement of the Surface Area of the Target*.— The surface area of the target was measured by the nitrogen adsorption method before and after irradiation. Before irradiation, the mean grain size of 140~300 mμ was obtained, and this value was not substantially changed by irradiation.

Discussion

On heterogeneous extraction of recoil atoms in hexammimechromium(III) nitrate, extraction curves were affectd neither by concentration of nitric acid, nor by the extraction time. Therefore the extraction mechanism in this method is considered to be mainly due to the surface process, because if the leaching process from the interior part of the target were a principal feature, great changes would be brought about in the extraction curve by changing the concentration of nitric acid or the extraction time. However, the tail of the extraction curve becomes higher at the higher concentration of nitric acid or at the longer extraction time. These results may be interprete by assuming that the leaching process more or less contributes to the whole process.

If the surface process were a predominant one, the following problems would arise. (1) How does the slight dissolution of hexamminechromium(III) nitrate into nitric acid affect the whole process? The previous experiment will furnish an answer to this problem. The extraction curve is not markedly changed even though the extraction is done with the use of nitric acid saturated with the complex salt. Perhaps this shows that slight dissolution of the target in the aqueous phase does not markedly affect the whole process of the extraction. (2) In order to obtain a large extraction yield such as several times ten per cent by the surface process, the grain size of the target must be vevy small and must be of the comparable order to the recoil range[12]. However, the mean grain size of the target used in these experiments was 140~300 mμ (This value was not substantially changed by irradiation.). This value is much greater than the value of 10 mμ or less which is considered to be a recoil range of the (n, γ)-reaction. How is this fact interpreted?

It is difficult to solve this problem clearly, but we may assume as follows: Hexamminechromium(III) nitrate is relatively unstable to heat and is apt to be decomposed beyond 100°C. In the case of the ^{50}Cr (n, γ) ^{51}Cr reaction, the recoil energy of the order of 300 eV. is dissipated in the neighborhood of the recoil atom, and therefore high temperature appears locally around it. For example, Harbottle[13] suggested that several thousands of atoms around the recoil atom attain to several hundred degrees in a molecular crystal. The thermal decomposition by heat liberated locally is considered to be very probable in this case. Chromium nitrate and ammonia molecules would be irregularly present in this "thermal spike". This part would be easily dissolved into the aqueous phase on contact with nitric acid. This part may be considered to be the path to nitric acid. A recoil atom present in this "thermal spike" would be expected to be carried into the nitric acid solution on extraction, and a crack which reaches the

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11) G. Harbottle, *J. Chem. Phys.*, **22**, 1083 (1954).

* This measurement was carried out by Dr. Izumi Higuchi of the Tohoku University.

12) J. Pauley and P. Süe, *J. phys. radium*, **18**, 22 (1957).

13) G. Harbottle and N. Sutin, *J. Phys. Chem.*, **62**, 1344 (1958).

surface after irradiation or on the extraction may be possible. Since ammonia is produced by decomposition of the complex salt, local high pressure may appear in the neighborhood of the "thermal spike". Calculating from the data of the recoil energy of the (n, γ)-reaction and the dissociation energy of the complex salt, ammonia molecules of the order of 10^4 must be present around the "thermal spike". This high pressure may be apt to make a crack at the time of the extraction.

Owing to a thermal spike and/or a crack, the recoil atom would be extractable beyond the recoil range. A similar explanation is possible in the case of the hot-atom effect in hexamminecobalt(III) nitrate.

The heterogeneous extraction is applicale to the rapid separation of recoil atoms. Especially, it is very effective to separate the radioisotope such as ^{55}Cr which has a very short half-life. However, a very high enrichment factor is not expected by this method.

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Tokyo University of Education
Otsuka, Tokyo (*N. I. & K. S.*)

Japan Atomic Energy Research Institute
Tokai-mura, Ibaragi-ken (*K. Y. & H. E.*)