

Separation of ^{51}Cr by Means of the Szilard-Chalmers Effect from Potassium Chromate Irradiated at Low Temperature

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The recombination of ^{51}Cr in K_2CrO_4 at low temperature as well as under dilute conditions has been investigated. Crystals of K_2CrO_4 and a 1 % solution of this compound have been irradiated in a thermal column of a nuclear reactor.

Lowering of the temperature was observed to cause a decrease in retention.

Chemical separations have been carried out both at 0°C and at 20°C .

The degree of enrichment was determined by reactivating one part of the solution after separation of the hexavalent chromium. Irradiation of K_2CrO_4 in the frozen aqueous solution was observed to favour the degree of enrichment.

The fate of the ^{51}Cr recoil nuclide has been discussed in the light of the thermal spike theory.

INTRODUCTION

Hot atoms

The chemical behaviour of atoms formed through nuclear transformations, *i.e.* the so-called "hot atoms"^{1,2} has been the subject of considerable interest. There does not seem to exist any theory which gives definite explanations and a correlation of the great number of observations made in this field. Of the theories proposed in this context we may mention the billiard ball model by Libby,³ the random fragmentation theory by Willard,⁴ the epithermal reaction model by Miller and Dodson,⁵ and the kinetic theory by Estrup and Wolfgang.⁶ A review article by Harbottle and Sutin⁷ gives, moreover, an excellent survey of the field.

A short recapitulation of the course of events for the recoil nuclide produced in the thermal neutron capture process may here be appropriate for the case studied. Let us assume that a prompt gamma-ray of 8 MeV is emitted in the neutron capture process, resulting in a recoil energy of about 0.5 keV imparted to a nuclide in the mass region of 50. In the case of chromium, 29 % of the neutron capture events in ^{50}Cr lead to the emission of a quantum of

8.50 MeV followed by a quantum of 0.76 MeV.⁸ The recoil nuclide then travels a certain distance in the material, losing its energy mainly in elastic encounters. At the end of the particle path the encounters become increasingly inelastic, owing to the transfer of energy to whole molecules. For a heavy particle recoiling in a light medium the path will be an approximately straight line. On the other hand, for a nuclide recoiling in a medium of atoms with heavier mass, the path of the particle will be characterized by diffusion.⁹ Considering the ⁵¹Cr species formed by the irradiation of potassium chromate, this nuclide would have a range of about 40 Å, as calculated from the universal range-energy relationship deduced by Lindhard and Scharff.⁹ In this context it might be mentioned that range measurements become difficult in the recoil energy region of some hundred eV, *e.g.* by (n, γ) reactions. However, the validity of the Lindhard-Scharff theory in this energy region has been confirmed by Skorka *et al.*¹⁰ in their recent nuclear resonance fluorescence scattering study.

T h e r m a l s p i k e s

During the thermalization process (finished within about 10⁻¹³ sec), it has been assumed that the recoil nuclide gives rise to the formation of a hot zone, a so-called "thermal spike".¹¹ In connection with (n, γ) reactions it has been difficult to confirm the existence of such zones experimentally. The interaction of high energy particles with matter has, however, given more significant evidence for the spike theory. Thus Thomson and Nelson¹² have investigated the thermal spikes by studying the high energy sputtering of metals at elevated temperatures. In their study the energy spectrum of ejected atoms from a gold crystal irradiated with 43 keV Xe⁺ ions at 500°C was investigated. They observed a peak in the spectrum corresponding to an energy which was consistent with a spike temperature of about 1750°K. The radius of the spike was 110 Å.

The spike temperature can be estimated,¹³ the case being simplified by assuming the energy dissipated to be equally distributed between the atoms within a "spike" shaped like a sphere. Considering also the atomic oscillations to be characterized by 3 degrees of freedom, we then have:

$$\frac{E}{\frac{4}{3}\pi r^3 d_a} = \frac{3}{2} kT \quad (1)$$

where

E denotes the recoil energy,

r the spike radius,

d_a the atomic density,

k the Boltzmann constant and

T the temperature in the spike in excess of the lattice temperature.

Immediately after the creation of the spike, it will spread and the temperature decreases quickly.

The temperature, $T(x,t)$, at a certain distance, x , from the origin at the time, t , after creation ($t = 0$) can be estimated by solving the heat conduction equation.¹⁴

$$T(x,t) = T_0 + \frac{E}{(4\pi)^{3/2} cd(Dt)^{3/2}} \times \exp(-x^2/4Dt) \quad (2)$$

Moreover,

$$D = C/cd \quad (3)$$

The symbols used are:

- T_0 original lattice temperature,
- D the diffusion coefficient,
- C the thermal conductivity,
- c the heat capacity and
- d the density of the material

In the spikes formed in the crystals of K_2CrO_4 a temperature rise of about 2000°K is estimated from eqn. (1), assuming a recoil energy of 0.5 keV and a sphere radius of 20 Å.

Inserting a value of D equal to $0.01 \text{ cm}^2/\text{sec}$ for K_2CrO_4 ¹⁵ in eqn. (2), it will be observed that the spike temperature would have fallen to less than 200°C after the elapse of about 10^{-11} sec.

For the spike formed in the water phase, the estimation of the heat transfer processes seems to be more complicated, owing to the formation of gases through the dissociation of the water.

Recombination of the recoil nuclide by diffusion after stopping

The recoil nuclide may recombine with its parent molecule, its fragments or another molecule of the same kind possessing a chromium vacancy by diffusion during the life-time of the thermal spike or after the decay of the spike.

As regards the first case, the diffusion process to take place within this time interval seems very improbable according to the following estimate.

The mean square displacement, $\overline{\Delta x^2}$, is as well-known related to the diffusion coefficient, D^* , by the expression

$$\overline{\Delta x^2} = 2D^*t \quad (4)$$

Assuming an upper limit for the diffusion coefficient of $10^{-4} \text{ cm}^2/\text{sec}$ ^{16,17} and a value of 40 Å for the mean distance of diffusion for the ^{51}Cr species, the diffusion time would be about 10^{-9} sec according to eqn. (4) which is of an order of magnitude 100 times greater than the life-time of the spike.

Hence, these recombination processes occur after the decay of the spike; the retention may be affected by the temperature of the medium.

Factors influencing the retention

It is well-known that the retention is influenced by factors such as temperature, gamma-dose, and storage time (annealing effects). A reduced retention due to decreasing the sample temperature during irradiation has been observed by several workers; *cf.*, *e.g.*, Refs. 18–20. A dilution of the sample in a suitable solvent or solid diluent may also lead to lower retention values.²¹ Moreover, it has been shown that the retention is influenced by the recoil energy. Thus as regards isomers, the nuclide with the highest recoil energy would have a longer way to diffuse back to its original position which might result in a lower retention. This effect has been verified by, *e.g.* Rosenberg and Sugihara²² who studied the recoil nuclei ⁶⁵Zn and ^{69m}Zn. Also, the isomeric effect is correlated to the chemical constitution of the target.²³

Present investigation

In this study, potassium chromate was chosen as the target material because of its well-known recoil chemistry.^{24–26}

When neutron-irradiated potassium chromate is dissolved in water the ⁵¹Cr activity is distributed among CrO₄²⁻ and Cr(H₂O)₆³⁺ ions as well as among dimers and higher polymers.²⁵ However, in the crystals, Cr²⁺ ions have also been observed, which disappear during the dissolution procedure.²⁸

When the effects of dilution and irradiation at low temperature are combined, reduced retention values may be expected. This can be accomplished by dissolving the target material in water and irradiating the solution under frozen conditions. In this context it should be mentioned that the samples have to be rapidly frozen in, *e.g.*, liquid nitrogen in order to avoid segregations. After the irradiation step the frozen sample should advantageously be brought into intimate contact with a solution containing the actual carriers, unless these are produced in sufficient amounts from the sample itself during irradiation.

Due to the effect of recombination processes taking place during as well as after the dissolution of the irradiated sample, higher retention values should be expected in cases in which carriers are not added.

Moreover, reducing the temperature during the chemical separation procedure might be expected to give rise to a decrease in retention.

EXPERIMENTAL

Sample, irradiation and separation. The samples were irradiated in the thermal column in the reactor R2 (Studsvik) in a flux of 1.1×10^{12} n/cm² sec for periods of 5 min.

The crystal samples consisted of 50 mg K₂CrO₄ of *pro analysi* quality (E. Merck, Germany) while the 2 ml aqueous samples consisted of a 1% K₂CrO₄ solution.

The low temperature irradiations were accomplished by cooling the samples in liquid nitrogen (–196°C) before irradiation. A temperature of –10°C was measured in the frozen aqueous samples after the end of irradiation.

The gamma-dose rate in the actual irradiation position used was 2 Mrad/h and the temperature about 40°C.

The samples were stored for about 4 days at room temperature (samples irradiated at 40°C) and at –5°C (samples irradiated at low temperature) in order to allow the ⁴²K

activity to decay before the chemical separations were undertaken. The ^{51}Cr activity was measured by means of gamma-spectrometric analysis.

The frozen aqueous samples were dissolved in a solution containing 5 mg Cr^{3+} as carrier at a pH of about 3 (carriers were not added in all series).

Chromic ions were separated from hexavalent chromium by retaining the latter on a 10 ml anion exchanger (Dowex 2) in chloride form²⁶ at a temperature of 20°C. However, in one series of investigations the separations were carried out at 0°C. The anion exchangers were contained in Quickfit (G-2) glass filters.

Determination of the enrichment factor. The enrichment factor was determined as follows. After the irradiation of the sample and the subsequent separation of the chromium in the hexavalent state with the anion exchanger in chloride form, the solution was divided into two parts. One part of the chromic fraction was reactivated for 2 h in a flux of 2×10^{13} n/cm² sec. These samples were irradiated in sealed ampoules which were cooled with water in perforated aluminum containers.

The ^{51}Cr activity induced by reactivation was then compared with the ^{51}Cr activity in the part not reactivated, thus giving the "reactivation" factor, which is, moreover, the inverse value of the enrichment factor.*,²⁸

RESULTS

Table 1 gives the distribution of the ^{51}Cr activity in the hexavalent and the reduced states, respectively, after dissolving the samples in water with or without carrier after irradiating crystals of K_2CrO_4 as well as the 1 % solution of K_2CrO_4 at low temperature or at 40°C.

Table 1. Distribution of ^{51}Cr in neutron irradiated K_2CrO_4 . Separation at 0°C and 20°C.

Neutron irradiation of	CrO_4^{2-} ($\text{Cr}_2\text{O}_7^{2-}$) (in % with standard error of 5 or 10 measurements)	$\text{Cr}(\text{H}_2\text{O})_6^{3+}$, dimers, ^a higher polymers ^a (in % with standard error of 5 or 10 measurements)
Crystals of K_2CrO_4 low temperature		
Cr^{3+} carrier added	48 ± 1	52 ± 1
Cr^{3+} carrier not added	78 ± 2	22 ± 2
Cr^{3+} carrier not added	77 ± 2 ^b	23 ± 2 ^b
1 % solution of K_2CrO_4 frozen		
Cr^{3+} carrier added	37 ± 2	63 ± 2
Cr^{3+} carrier not added	71 ± 4	29 ± 4
Cr^{3+} carrier not added	76 ± 2 ^b	24 ± 2 ^b
1 % solution of K_2CrO_4 40°C		
Cr^{3+} carrier added	87 ± 1	13 ± 1

^a It has been assumed that the dimers and higher polymers would pass quantitatively through the anion exchanger in chloride form because of their positively charge distributions,³⁰ and that the activity distribution given in the two columns would amount to 100 %. According to Gütlich and Harbottle this activity distribution is nearly equal to 100 %.²⁵

^b Separation carried out at 0°C.

* The enrichment factor is defined as follows:

$$\frac{\text{Specific activity of } ^{51}\text{Cr} \text{ in eluate}}{\text{Specific activity of } ^{51}\text{Cr} \text{ in irradiated potassium chromate}}$$

Table 2 gives the retention of ^{51}Cr in the hexavalent state when irradiating $\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{ aq.}$

Table 3 gives the enrichment factors for ^{51}Cr (reduced states) obtained when irradiating crystals of K_2CrO_4 and the 1 % solution of K_2CrO_4 at low temperature. Retentions are also included in this table.

Table 2. Retention of ^{51}Cr . Neutron irradiation of $\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{ aq}$ at 40°C . Separation at 20°C .

Sample No.	CrO_4^{2-} ($\text{Cr}_2\text{O}_7^{2-}$) in %
1	4.9
2	3.6
3	4.8

Table 3. Retention and the corresponding enrichment factor for ^{51}Cr . Neutron irradiation of K_2CrO_4 as well as the 1 % solution of K_2CrO_4 at low temperature. Separation at 20°C . (Carrier not added.)

Sample No.	K_2CrO_4		1 % solution of K_2CrO_4	
	Retention in %	Enrichment factor ^a	Retention in %	Enrichment factor ^a
1	80	29	70	149
2	78	49	69	168
3	79	66	73	189
4	79	76	75	190
5	79	113	72	219
	Mean value: 79 Stand. error: 1	Mean value: 67 Stand. error: 14	Mean value: 72 Stand. error: 1	Mean value: 183 Stand. error: 12

^a 10–20 % of the ^{51}Cr activity was in this case found to be adsorbed on the glass filters.

DISCUSSION

In previous investigations the ^{51}Cr activity, formed by neutron capture in K_2CrO_4 , which is associated with the hexavalent chromium, amounted to 50 %¹⁸ and to about 60 % (*cf.*, *e.g.* Refs. 24, 25) when irradiating the samples at dry-ice temperature and at $40\text{--}50^\circ\text{C}$, respectively.

In the present investigation the retention observed when irradiating crystals of K_2CrO_4 at low temperature, amounting to $(48 \pm 1)\%$, is in close agreement with the value obtained by Veljković and Harbottle.¹⁸

The decrease in retention caused by lowering the temperature confirms the assumption that the recombination processes after stopping the recoil

nuclide may take place after the decay of the spike, and may thus be influenced by the temperature of the surrounding medium.

Irradiation of the 1 % solution of K_2CrO_4 at about 40°C gave rise to a high retention, $(87 \pm 1)\%$. This effect may be ascribed to radiation chemical reactions occurring in the aqueous phase. However, the irradiation of these samples in the solid phase (frozen aqueous samples) diminishes the radiation chemical effects, and a markedly reduced retention was consequently observed, $(37 \pm 2)\%$.

In these cases the frozen samples had been in intimate contact with Cr^{3+} carrier during their melting and dissolution procedures. However, in one series the investigation was performed without addition of carrier. In this case the retention values obtained were $(71 \pm 4)\%$ and $(78 \pm 2)\%$ for the frozen 1 % solution and the cooled crystals, respectively. These high values are probably due to recombination processes taking place after the dissolution of the samples in the carrier-free solutions.

A temperature reduction from 20°C to 0°C during the chemical separation gave no significant change of the retention values.

Irradiation of the frozen 1 % K_2CrO_4 solution was observed to favour the degree of enrichment as compared to irradiation of the cooled crystals of K_2CrO_4 . Thus, enrichment factors in the range of 149–219 with a mean value of 183 were obtained for the frozen aqueous samples. In the case of the cooled crystals the corresponding range was 29–113 and the mean value 67. In the investigation by Birkelund *et al.*²⁶ who studied the influence of neutron dose upon the enrichment factor for crystals at K_2CrO_4 , values in the range of 98–400 with a median value of 143, were obtained. The samples amounted in most cases to 7.8 g, and these were irradiated for several days. In their investigation an irradiation period of about 20 days was found to yield the highest specific activity. However, as the degree of enrichment is influenced by the time of irradiation, the results of Birkelund *et al.*²⁶ and those obtained in the present work can not be directly compared.

The separation of chromic and hexavalent chromium was accomplished by means of an anion exchanger in chloride form previously reported to yield a recovery of 94 % for the adsorption of the hexavalent chromium.²⁶ However, in the present investigation, this recovery was found to amount to $(99.9 \pm 0.1\%)$ in neutral as well as slightly acid solution. Cr^{3+} was recovered in the eluate to $(99.4 \pm 0.5\%)$ when passing the same anion exchanger in a slightly acid solution.

In the preparation of $^{51}\text{Cr}^{3+}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{ aq}$ was used as target material. In this connection the retention of ^{51}Cr in the hexavalent form was also investigated. Retentions amounting to 3–5 % were obtained, which are in agreement with the results of Gütlich and Harbottle.²⁵

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* Standard deviation of a single value.

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