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Recoil Effects of Neutron-irradiated Metal Salts

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Abstract

The distribution of ^{56}Mn and ^{38}Cl recoil species following radiative neutron capture in permanganates, chlorates and perchlorates has been investigated by using ion-exchange chromatography method. The whole of the ^{56}Mn radioactivity in permanganates appeared in two valence states, the ^{38}Cl radioactivity in chlorates in two valence states and also the ^{38}Cl radioactivity in perchlorates in three valence states. Recoil energy was calculated. The internal conversion of $^{38\text{m}}\text{Cl}$ isomer transition affects the retention value. The greater the radii of the cation, the higher is the probability of the recoil atom breaking through the secondary cage. In ammonium salt, the ammonium ion behaves as a reducing agent. Crystal structures with their greater free space have shown low retention.

요 약

과망간산염, 염소산염 및 과염소산염의 중성자 포획에 수반하는 망간-56 및 염소-38 반조화학종의 분배를 이온교환크로마토그래피법으로 검토하였다. 과망간산염의 망간-56 방사능은 2종의 원자가상태로 나타나며 염소산염의 염소-38은 2종의 원자가상태 그리고 과염소산염의 염소-38은 3종의 원자가상태로 나타난다.

반조에너지는 계산하였다. $^{38\text{m}}\text{Cl}$ 의 핵이성체 전이에 수반하는 내부전환은 잔류율에 영향을 미친다. 양이온반경이 클수록 2차 케이지를 돌파하는 반조원자의 확률이 높다. 암모늄염 중 암모늄이온은 환원제 작용을 한다. 결정구조에서 자유공간이 크면 잔류율은 낮아진다.

Introduction

Retention is the fraction of the total radioactivity found after the irradiation in the same chemical form as the target substance. The methods of investigating the

retention depend on the determination of the final products by means of radioactive atoms, and do not provide any information on the nature of the primary recoil fragments. Therefore, the studies of these processes are confined to measurements of retention and of its dependence on various

factors, which are concluded from experimental results on retention in various chemical systems.

Libby¹⁾ proposed the ligand loss model based on the hypothesis that central atoms of complex ions in (n,γ) reaction lose some of their ligands. In irradiated potassium chromate crystals O^{2-} fragments are lost from the CrO_4^{2-} ions leaving the chromium atom in its original oxidation state of (VI).

For some oxyanions, there is a relationship between the retention and the standard redox potential²⁾. The oxy-anions of higher redox potential take fewer states of oxidation to give a form which oxidizes water on dissolution, and therefore, lower the retention. The central complex-forming ion has an electronegativity similar to that of oxygen. The oxidation state is decreased. The effect is strongest with chlorine, and less with iodine. The ions XO_4^- , XO_3^- , XO_2^- , XO^- and X^- form and react with water to produce the corresponding acids.

In the gamma-radiolysis of $KClO_3$ and $KClO_4$ relatively much larger yields of less degraded oxychlorine anions are produced than in (n,γ) reaction³⁾. The breaking of a single Cl-O bond is much more possible when the ClO_3^- or ClO_4^- ions are excited or ionized by gamma rays than when the nucleus of the chlorine atom is excited by neutron capture.

For the effect of cations, the influence of the ionic radii of cation on retention in hexachloroiridates was investigated by Heine and Herr⁴⁾. They found that the higher stability of the complex compound increases disintegration and rearrangement of excited molecules and decreases the retention. Baba⁵⁾ found that the change of retention as parent form was proportional to the ionic radii of cations. In ammonium salts

and in hydrated salts, ammonium ion and water molecule behave as reducing agents in the hot zone and result in low retention⁶⁾.

The initial retentions of monoclinic and triclinic potassium dichromate, irradiated under the same conditions, were found to be 82.4% and 89.5% respectively⁷⁾. The monoclinic crystals with their greater free space show the lower initial retention. The relationship between the crystallography and the initial retention was studied with four polymorphic forms of copper phthalocyanine, i.e. alpha, beta, gamma and delta⁸⁻¹¹⁾. Ikeda et al.¹²⁾ investigated the effect of the crystal structure on the initial retention in neutron-irradiated cobalt, nickel and copper tetraphenyl-porphines.

This study has been concerned with the recoil effects of neutron-irradiated permanganates, chlorates and perchlorates. The distribution of ^{56}Mn recoil species following radiative neutron capture in $NaMnO_4$, $KMnO_4$, $Ba(MnO_4)_2$, and ^{38}Cl recoil species following radiative neutron capture in $NaClO_3$, $KClO_3$, $RbClO_3$, $Ba(ClO_3)_2$, $KClO_4$, NH_4ClO_4 and $RbClO_4$ has been investigated. The influence of the ionic radii of cations, and the crystal structure on retention in neutron-irradiated permanganates, chlorates and perchlorates was studied.

Experimental

Chemicals

Sodium permanganate, potassium permanganate, barium permanganate, sodium chlorate, potassium chlorate, rubidium chlorate, barium chlorate, potassium perchlorate, ammonium perchlorate and rubidium perchlorate were used without further purification on account of guaranteed reagents. All other reagents used in the chemical procedure

were of A.R. quality.

Neutron Irradiation

Approximately 5mg of permanganates, 4mg of chlorates and perchlorates were put in polythene snap-closure capsules and irradiated in a thermal neutron flux of approx. 10^{13} n/cm²/sec. This was done by means of a pneumatic tube at the TRIGA mark III reactor for one minute for permanganates and for ten minutes for chlorates and perchlorates. Neutron-irradiated permanganates were dissolved in 10 ml of re-distilled water, neutron-irradiated chlorates and perchlorates in 4ml of re-distilled water, and the solutions were immediately passed through the ion-exchange column.

Analysis of Irradiated Crystals

A cylindrical bed of 200-400 mesh Dowex-50W-x12, 0.8-cm diameter by 3-cm deep, was employed, and the resin was converted to the sodium form by passing with 10ml of 1N-NaOH. Neutron-irradiated permanganates dissolved in water were placed on the top of the bed where all the radioactivity was adsorbed. A selective elution of the radioactive species was accomplished by passing 20ml of re-distilled water and 40ml of 3N-HCl through the bed at 0.5 ml/min, and the radioactivity of 2ml each of the effluent solutions was measured with a well-type gamma scintillation counter.

Anion-exchange resin, Dowex-1-x8 (100-200 mesh) was converted to the nitrate form by placing it into a solution of 2N-HNO₃ for 24 hours. The resin bed, 0.8-cm diameter by 8-cm deep, was prepared by packing as an aqueous slurry into a glass column and was washed with 20 ml of re-distilled water, 20ml of 0.1N-NaOH and 15ml of re-distilled water successively. Neutron-irradi-

ated chlorates dissolved in water were adsorbed on the top of the resin bed. A selective elution of the radioactive species was made by passing 0.01N-HNO₃ and 0.1 N-HNO₃ solutions through the bed at 0.5 ml/min and the ³⁵Cl radioactivity of 2ml each of the effluent solutions was measured with a well-type gamma scintillation counter.

An aqueous solution of neutron-irradiated perchlorates was adsorbed on the bed of anionexchange resin Dowex-1-x8 and was eluted with 0.01N-HNO₃, 0.4N-HNO₃ and 4N-HNO₃ solutions successively through the bed at 0.5ml/min.

The radioactive purity was determined with Hitachi model 400 channel analyzer throughout this work.

The chromatographic analyses were performed five times for each permanganate, four times for each chlorate and perchlorate.

Results and Discussion

Identification of Recoil Species

The nature of the recoil species in condensed state remains unknown in detail, because of the short-lived nature of the compounds and atomic states remaining after the recoil. One difficulty is the actual impossibility of observing the original atom, since the methods of investigation involve dissolution of the sample under observation and subsequent chemical processing. The species observed are those remaining after some vigorous changes have occurred in the physical and chemical surroundings of the recoil atoms. Another difficulty in tracing all the reactions arises from the fact that the number of atoms produced in nuclear reactions is too small for ordinary chemical detection and investigation. Although it is possible to detect such atoms and to invest-

igate their chemical behaviour by their radioactivity, all the non-radioactive and highly energetic atoms, molecular fragments, ions and radicals formed in nuclear processes escape direct observation. Also the influence of lattice defects formed in solids by the nuclear recoil process can hardly be detected by indirect methods.

The typical histogram of cation-exchange chromatographic separation of 2.58hr ^{56}Mn activity in neutron-irradiated permanganates is plotted in Fig.1. The whole of the manganese-56 radioactivity in neutron-irradiated crystalline KMnO_4 appears in two valence states. The identical results were found with neutron-irradiated $\text{Na}^{56}\text{MnO}_4$ and $\text{Ba}^{(56}\text{MnO}_4)_2$. After the neutron-irradiated sample was adsorbed at the top of a bed of Dowex-50, the radioactivity which was obtained by passing 20 ml of distilled

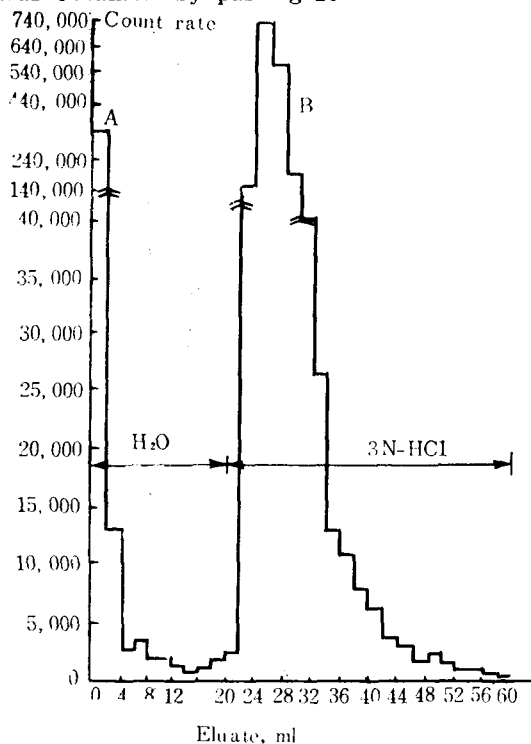
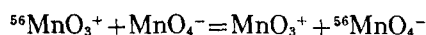
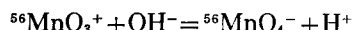


Fig. 1. Cation-exchange Chromatographic Separation of 2.58 hr ^{56}Mn Activity in Neutron-irradiated Crystalline KMnO_4 .

water through the column comes from $^{56}\text{MnO}_4^-$. The radiative species obtained by elution with 40 ml of 3N-HCl is $^{56}\text{Mn}^{2+}$. It will be assumed that in irradiated permanganates O^{2-} fragments are lost from the oxygenate anion, MnO_3^+ radicals are formed, and the retention is increased during the dissolution process due to the following hydrolysis or ion-exchange:



The radioactive concentrations of K^+ , Na^+ or Ba^{++} were almost negligible, and the radioactivities were determined by the difference in half-lives of the nuclides and by the gamma spectra with a NaI (Tl) crystal connected with multichannel analyzer. A test was made for $^{56}\text{Mn}^{2+}$ in neutron-irradiated manganese chloride. The chloride was neutron-irradiated for a certain time and was adsorbed on cation-exchange resin column with the same size of column which was used for the separation of activities in neutron-irradiated KMnO_4 . The column was eluted with 20ml of distilled water and 40ml of 3N-HCl, and the eluate was collected with 0.5 ml/min. The activity was compared with the recoil manganese peak of permanganates.

The typical histogram of anion-exchange chromatographic separation of 37.5 min ^{38}Cl activity in neutron-irradiated chlorates is plotted in Fig. 2. The radioactivity in neutron-irradiated crystalline KClO_3 appears in three peaks. The peak A is identified as cation K^+ , peak B as Cl^- and peak C as parent species, ClO_3^- . K^+ was contained in the initial water solution during elution and was examined with activity of ^{42}K , gamma-ray energy of 1.52 MeV. A test was made for $^{38}\text{Cl}^-$ in neutron-irradiated sodium chloride. The chloride was neutron-irradiated

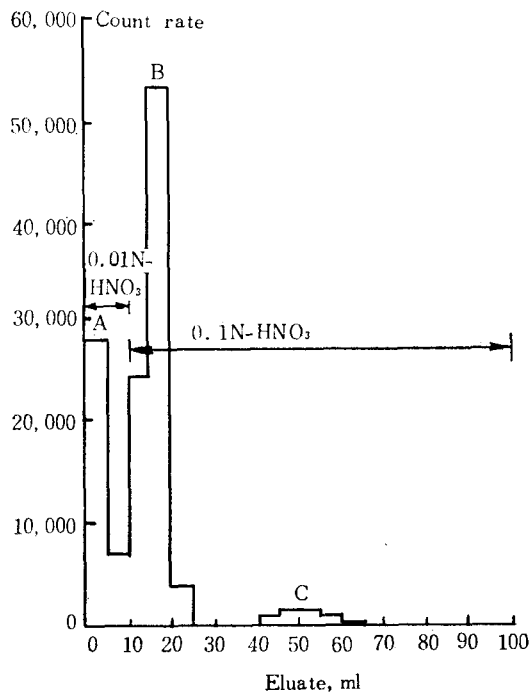


Fig. 2. Anion-exchange Chromatographic Separation of 37.5 min ^{38}Cl Activity in Neutron-irradiated Crystalline KClO_3

for a certain time and was adsorbed on anion-exchange resin column with the same size of column which was used for the separation of activities in neutron-irradiated KClO_3 . The column was eluted with 0.01N- and 0.1N- HNO_3 , and the eluate was collected with 0.5 ml/min. The activity was compared with the recoil chlorine peak of chlorates. ClO_3^- was identified as follows: aqueous solution of potassium chlorate was adsorbed on the anion-exchange resin column and the solution of 0.01N- and 0.1N- HNO_3 was passed through the column and the eluate was collected with 0.5 ml/min. 10 ml of each solution was neutron-irradiated and the activity was compared with the peak C. Although the production of ClO^- , ClO_2^- , ClO_4^- or thermal disproportionation reaction, i.e. $4\text{ClO}_3^- = 3\text{ClO}_4^- + \text{Cl}^-$ are suggested by the neutron-irradiation of chlorates, together

with Cl^- and ClO_3^- , the results from the anion-exchange chromatographic separation in neutron-irradiated sodium chlorate, potassium chlorate, rubidium chlorate and barium chlorate were not observed.

The typical histogram of anion-exchange chromatographic separation of 37.5 min ^{38}Cl activity in neutron-irradiated perchlorates is plotted in Fig. 3. The radioactivity in neutron-irradiated crystalline KClO_4 appears in four peaks. The peak A is identified as cation K^+ , peak B as Cl^- , peak C as ClO_3^- and peak D as parent species, ClO_4^- . K^+ , Cl^- and ClO_3^- were identified by the method similar to that of KClO_3 . ClO_4^- was identified as follows: aqueous solution of potassium perchlorate was adsorbed on the anion-exchange resin column and the solution of 0.01N-, 0.4N- and 4N- HNO_3 was passed through the column and the eluate was collected with 0.5 ml/min. 10 ml of each solution was

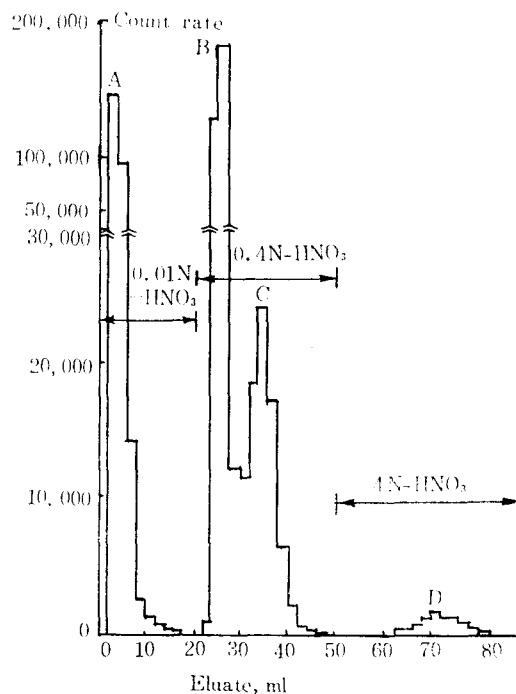


Fig. 3. Anion-exchange Chromatographic Separation of 37.5 min ^{38}Cl Activity in Neutron-irradiated Crystalline KClO_4

neutron-irradiated and the activity was compared with the peak D. The species ClO^- and ClO_2^- were not observed in neutron-irradiated potassium perchlorate, ammonium perchlorate and rubidium perchlorate.

Recoil Energy

In order to calculate the recoil energy distribution, it is necessary to know the intensity of each transition, the energies and angular correlations of the gamma-rays, and the life-times of the corresponding intermediate excited states. There are insufficient data available on nuclear processes following neutron capture to permit detailed investigations but rough calculations of the recoil energies can be made. The prompt gamma-ray spectra from radioactive capture of thermal neutrons have been determined^{13,14}.

If the whole of the gamma-ray energy emitted in an (n,γ) reaction is concentrated into a single gamma-ray of energy E_γ (MeV) and the energy is equivalent to the neutron binding energy, then it will cause an atom of mass M (a.m.u.) to recoil with energy E_r (eV) given by

$$E_r = \frac{537 E_\gamma^2}{M}$$

The recoil energy available for bond rupture, E_d , depends on the type of bonding

and on the distribution of mass in the molecule. If the molecule containing the newly formed atom is not dissociated immediately as a result of the (n,γ) reaction, the whole molecule will suffer recoil. The molecular recoil energy is distributed between the internal energy available for bond rupture and the energy of translation. In oxygenated salts, the recoil energy available for bond rupture depends on the ratio of $R/(R+M)$, where M is the mass of the recoiling atom, and R the rest of the molecule¹⁵. The effective recoil energy is calculated such as

$$E_d = E_r \frac{R}{R+M}$$

Table 1. Recoil Energies of Nuclides with Manganese and Chlorine Oxygenated Salts.

Nuclide	E_γ (MeV)	Recoil energy E_r (eV)	Effective recoil energy, E_d (eV)
⁵⁶ Mn	7.0	470	288 NaMnO ₄
			306 KMnO ₄
			332 Ba(MnO ₄) ₂
³⁸ Cl	7.72	842	547 NaClO ₃
			586 KClO ₃
			655 RbClO ₃
			635 Ba(ClO ₃) ₂
			615 KClO ₄
			575 NH ₄ ClO ₄
			671 RbClO ₄

Table 2. Retention Values and Crystal Structures for Manganese and Chlorine Oxygenated Salts.

Salt	Recoil atom	Retention %	Radius of cation, Å	Molecular volume, M/D	Crystalline form
NaMnO ₄	⁵⁶ Mn	14.3	0.95	55.4	Orthorhombic
KMnO ₄		13.8	1.33	58.4	Orthorhombic (Pnma)
Ba(MnO ₄) ₂		14.2	1.35	50.0	Orthorhombic (Fddd)
NaClO ₃	³⁸ Cl	5.8	0.95	42.8	Cubic or Trigonal (P2 ₁ 3)
KClO ₃		5.7	1.33	52.8	Monoclinic (P2 ₁ m)
RbClO ₃		6.1	1.48	53.0	Rhombohedral (R3m)
Ba(ClO ₃) ₂		7.9	1.35	101.3	Monoclinic
KClO ₄		2.4	1.33	54.9	Orthorhombic (Pnma)
NH ₄ ClO ₄		6.5	1.42	60.3	Orthorhombic
RbClO ₄		1.1	1.48	63.8	Orthorhombic

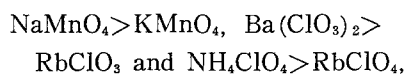
The recoil energies of γ nuclides with manganese and chlorine oxygenated salts are listed in Table 1.

The retention values found by the ion-exchange chromatography of permanganates, chlorates and perchlorates are shown in Table 2.

In addition to recoil energy, the internal conversion of ^{38m}Cl isomer transition from ^{37}Cl (n, γ) ^{38m}Cl (I.T.) ^{38}Cl in neutron-irradiated chlorates and perchlorates may also have some influence on the retention values which are relatively low.

Effect of the Cations

The dependence of retention on the radius of the cation was shown in Table 2. The results explain that the higher stability of the complex compound decreases disintegration and rearrangement of excited molecules, and increases the retention, i.e.



which runs counter to the results of Heine and Herr's experiment⁴).

It is proposed that the zone of a displaced atom is formed when an energetic manganese or chlorine atom breaks through first the primary cage of an oxygenated ion and then the secondary cage of cations. The greater the radius of the cation, the higher is the probability of the recoil atom breaking through the secondary cage.

In ammonium perchlorate, the ammonium ion behaves as a reducing agent in the disorder zone and results in low retention.

Effect of the Crystal Structure

The dependence of retention on the crystal structure was shown in Table 2. It is

observed that the change of retention is inversely proportional to the molecular volume as well as the ionic radii of cations. KMnO_4 is isomorphous with $\text{Ba}(\text{MnO}_4)_2$ which is orthorhombic, but the primitive lattice of KMnO_4 with its free space greater than the face-centered lattice of $\text{Ba}(\text{MnO}_4)_2$ shows the lower initial retention.

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