金屬鹽의 原子核變換의 化學的 效果

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Chemical Effects of Nuclear Transformations in Metal Salts

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요 약. 크롬산염, 중크롬산염, 요오드산염 및 과요드산염의 중성자포획에 수반하는 크롬-51 및 요오드-128 반조 화학종의 분배를 거름종이 전기영동법으로 검토하였다. 유효반조에너지 및 내부전환의 관점에서 생각하면 중성자 포획원자가 초기분자중에 잔유하고 반조원자에너지가 결정의 적은 범위를 가열하며 소멸된다고 하기 어렵다. 그러나 거름종이 전기영동결과 더 많은 크롬-51 및 요오드-128 반조원자가 어미분자와 결합되어 있음을 알 수 있었다. 잔류율의 관찰결과 반응 이론을 Disorder Model 로 설명하였다. 양이온 반경이 클수록 2차 cage를 돌파하는 반조원자의 확률이 높다. 암모늄염중 암모늄이온은 disorder zone에서 환원작용을 하며 잔류율이 낮어졌다. 결정구조에서 자유공간이 크면 잔류율이 낮어졌다.

ABSTRACT. The distribution of ^{51}Cr and ^{128}I recoil species following radiative-neutron capture in chromates, dichromates, iodates and periodates has been investigated by using paper-electrophoresis. In view of the effective recoil energy and the effect of the internal conversion, it is unlikely that an atom which has captured a neutron can remain bound in its original molecule. It is also unlikely that the energy of the recoil atom is dissipated in heating a small region of the crystal. However, the results of paper-electrophoresis separation of recoil ^{51}Cr and ^{128}I indicated that many more of the recoil atoms were bound in the parent molecule. The disorder model for the reaction was proposed from observations of retention. In considering cations, the greater their radii, the higher is the probability of the recoil atom breaking through the secondary cage. In ammonium salt, the ammonium ion behaved as a reducing agent in the disorder zone and resulted in low retention. Crystal structures with their greater free space have shown low retention.

INTRODUCTION

The most characteristic quantity associated with the chemical effects of nuclear transformations in solid compounds is retention. Retention is the fraction of the total radioactivity found after the irradiation in the same chemical form as the target substance. The mothods of investigating 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.

For the chemical nature of the recoil atom, Libby[1] proposed the ligand loss model based on the hypothesis that central atoms of complex ions in (n, γ) reactions lose some of their ligands. For the isotopic effect, Müller[2], and Thomson and Cairns[3] suggested that the kinetic energy liberated in the (n, γ) process is removed from the recoil zone through focussing collisions in close-packed crystalline solids. However, if internal conversion occurs a long time after the kinetic energy has been lost, the mode of kinetic energy dissipation is of importance to the excitation and ionization in influencing the chemical form of the stabilized recoil. For the effect of cations, the influence of the ionic radii of cation on retention in hexachloroiridates was investigated by Heine and Herr[4]. They found that the higher stability of the complex compound increases the disintegration and decreases the retention. Harbottle and Sutin[5] suggested that in ammonium salts and in hydrated salts, ammonium ion and water molecule behave as reducing agents in the hot zone and result in low retention. For the effect of the crystal structure, the initial retentions of monoclinic and triclinic potassium dichromate were found to be 82. 4 and 89. 5% respectively[6]. A difference of initial retention between α and β crystals of metal phthalocyanine was investigated[7~10]

This research has been concerned with the chemical consequences of neutron capture in chromium and iodine oxygenated salts; chromates, dichromates, iodates and periodates. The distribution of ^{51}Cr recoil species following radiative-neutron capture in Na_2CrO_4, K_2CrO_4, Rb_2CrO_4, $Na_2Cr_2O_7$, $K_2Cr_2O_7$, $(NH_4)_2Cr_2O_7$, $Rb_2Cr_2O_7$, $Ag_2Cr_2O_7$, and ^{128}I recoil species following radiative-neutron capture in KIO_3, $RbIO_3$, $NaIO_4$, KIO_4 has been investigated. The influence of the ionic radii of cations, and the crystal structure on retention in neutron-irradiated chromates, dichromates, iodates and periodates was investigated.

EXPERIMENTAL

Chemicals. Sodium chromate, potassium chromate, rubidium chromate, sodium dichromate, potassium dichromate, ammonium dichromate, rubidium dichromate, potassium iodate, rubidium iodate, sodium periodate and potassium periodate were used without further purification on account of guaranteed reagents. Silver dichromate was prepared according to recognized method taken from the literature[11]. All other reagents used in the chemical procedure were of A. R. quality.

Neutron Irradiation. Chromates and dichromates were put in a polythene snap-closure capsule and irradiated in a thermal neutron flux of approx. $10^{13} n/cm^2/sec$ at the rotary specimen rack, TRIGA mark III reactor. Iodates and periodates, put in a polythene snap-closure capsule, were irradated in a thermal neutron flux of approx. $10^{13} n/cm^2/sec$ by means of a pneumatic tube at the TRIGA mark III reactor.

Neutron-irradiated samples were stored for a certain period of time to allow decay of sodium-24 ($t\frac{1}{2}$=15. 0 hrs.), potassium-42 ($t\frac{1}{2}$=12. 45 hrs.) and rubidium-86 ($t\frac{1}{2}$=18. 7 d.). After decay, chromates and dichromates were dissolved in 0. 1 M hydrochloric acid solution, and iodates and periodates were dissolved in 0. 1 M sodium hydroxide solution.

Paper Electrophoresis. Paper-electrophoresis apparatus consists of a vertical paper-electrophoresis tank ($45 \times 21 \times 15$ cm), Shandon Co., London, and a power supply, up to 1000 volts.

The strip of Whatman No. 1 filter paper, 38 cm long and 2. 5 cm wide, was wetted in a solu-

tion of 0. 01 M hydrochloric acid for chromates and dichromates, and in a solution of 0. 01 M sodium hydroxide for iodates and periodates. A portion of 10 lambda of the radioactive solution was applied at the fiducial point of each strip as a spot by using a lambda pipette. The strip, placed on the nylon thread, was dipped at its end and positioned in the electrophoresis tank containing about 800 cm³ of electrolyte, 0. 01 M HCl or 0. 01M NaOH, into which were dipped platinum electrodes. The electrodes were connected to the d. c. power supply and a potential of 600 volts was applied for a certain period of time. After the electrophoresis run was over, the strip was removed from the electrophoresis tank, dried, and cut into pieces of one centimeter length. The radioactivity of each paper strip was measured by a NaI(Tl) well-type gamma scintillation counter, The activity on the strips was checked by using a Packard model 7201 radiochromatogram scanner without cutting them into pieces, and the radiochemical purity was determined by using a Hitachi model 400 channel analyzer.

RESULTS and DISCUSSION

Identification of Recoil Species

The nature of the recoil species in condensed states remains unknown in detail, largely 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 often possible to detect such atoms and to investigate their chemical behavior by their radioactivity, all the non-radioactive, 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.

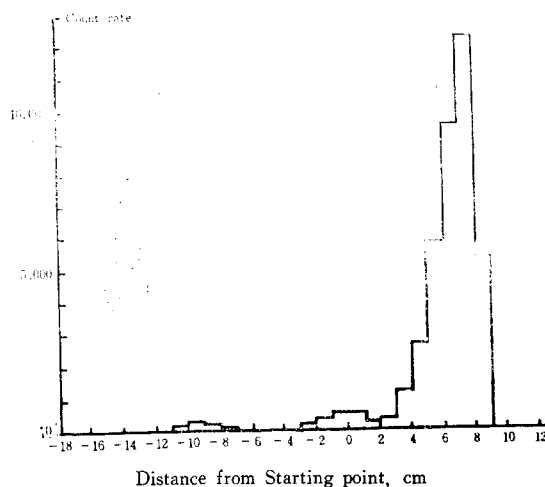The typical paper-electrophoresis histograms of

Distance from Starting point, cm

Fig. 1. Paper-electrophoresis histogram of neutron-irradiated Na_2CrO_4, dissolved in 0. 1 M HCl. Paper wet with 0. 01 M HCl. Irradiation time, 1 week. Running time, 1hr at 600V.
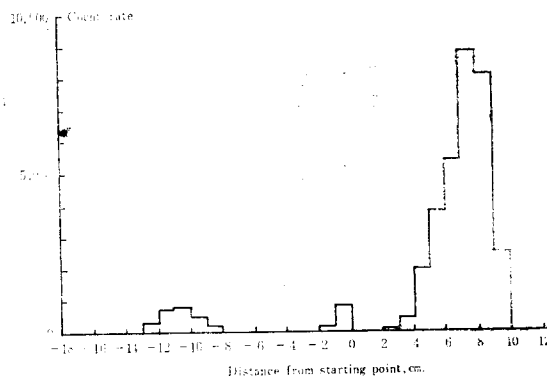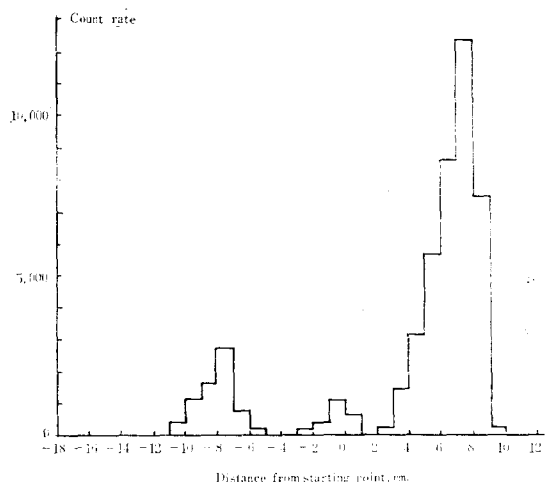

Distance from starting point, cm.

Fig. 2. Paper-electrophoresis histogram of neutron-irradiated K_2CrO_4, dissolved in 0. 1 M HCl. Paper wet with 0. 01 M HCl. Irradiation time, 1 week. Running time, 1 hr at 600 V.

Fig. 3. Paper-electrophoresis histogram of neutron–irradiated Rb_2CrO_4, dissolved in 0. 1 M HCl. Paper wet with 0. 01 M HCl. Irradiation time, 1 week. Running time, 1 hr at 600V.
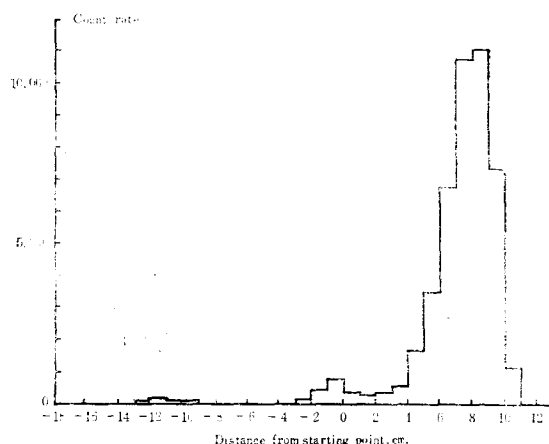

Fig. 5. Paper-electrophoresis histogram of neutron–irradiated $K_2Cr_2O_7$, dissolved in 0. 1 M HCl. Paper wet with 0. 01 M HCl. Irradiation time, 1 week. Running time, 1 hr at 600 V.
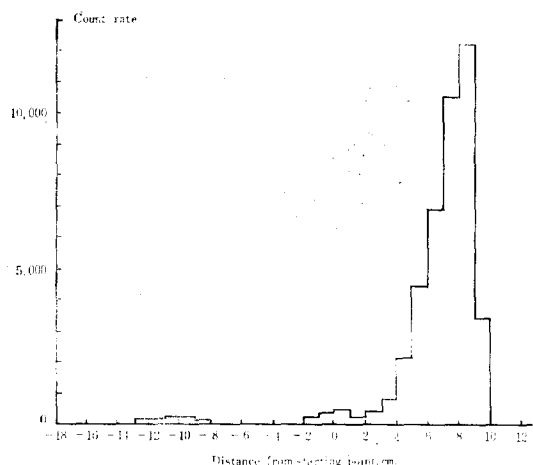

Fig. 4. Paper-electrophoresis histogram of neutron–irradiated $Na_2Cr_2O_7$, dissolved in 0. 1 M HCl. Paper wet with 0. 01 M HCl. Irradiation time, 1 week. Running time, 1 hr at 600 V.
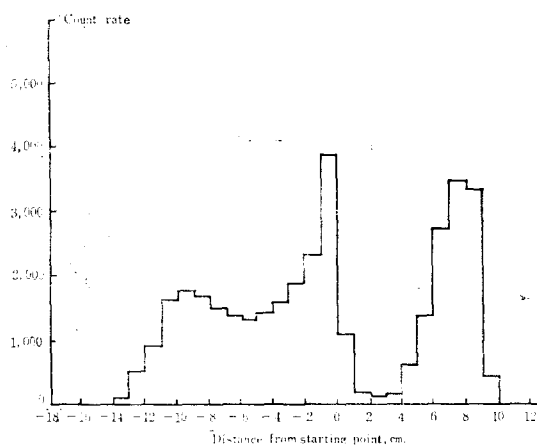

Fig. 6. Paper-electrophoresis histogram of neutron–irradiated $(NH_4)_2Cr_2O_7$, dissolved in 0, 1 M HCl. Paper wet with 0. 01 M HCl. Irradiation time, 1 week. Running time, 1 hr at 600 V.

neutron–irradiated $Na_2{}^{51}CrO_4$, $K_2{}^{51}CrO_4$, $Rb_2{}^{51}CrO_4$, $Na_2{}^{51}Cr_2O_7$, $K_2{}^{51}Cr_2O_7$, $(NH_4)_2{}^{51}Cr_2O_7$, $Rb_2{}^{51}Cr_2O_7$ and $Ag_2{}^{51}Cr_2O_7$ are plotted in Figs. 1, 2, 3, 4, 5, 6, 7 and 8. The whole of the chromium–51 radioactivity appears ⊢in three peaks on the electrophoresis paper, one of which has migrated towards the anode, another migrated towards the cathode, and other remains almost at the starting point. The major part of the activity migrates about 6∼8 cm from the origin towards the anode —Species(I). The smaller part of the activity migrates about 8∼10 cm from the origin towards the cathode—Species(II). A considerable amount of the activity remains at zero point as a neutral species—Species(III). The actual migration distances fluctuate slightly from experiment to experi-
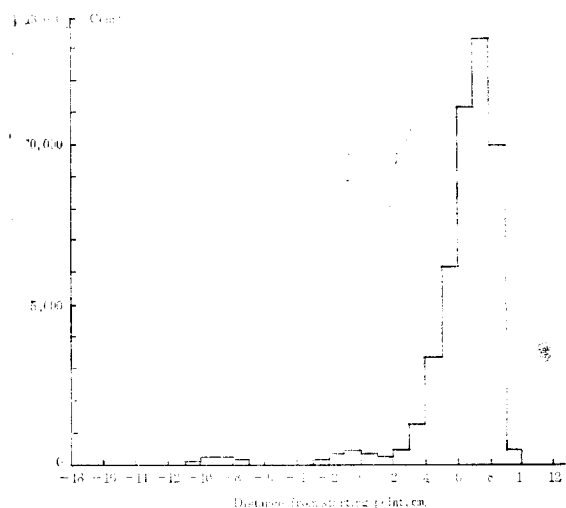
Fig. 7. Paper-electrophoresis histogram of neutron-irradiated $Rb_2Cr_2O_7$, dissolved in $0.1 M$ HCl. Paper wet with $0.01 M$ HCl. Irradiation time. 1 week. Running time, 1 hr at 600 V.
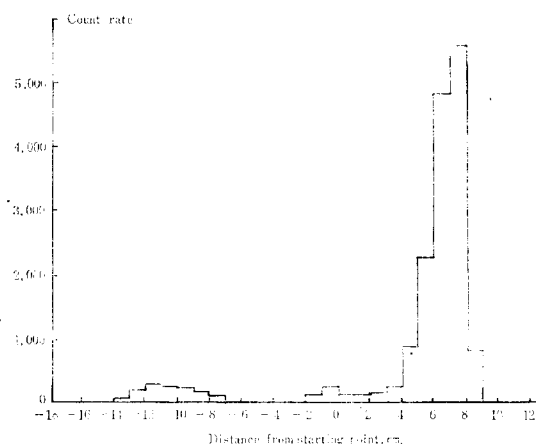

Fig. 8. Paper-electrophoresis histogram of neutron-irradiated $Ag_2Cr_2O_7$, dissolved in $0.1 M$ HCl. Paper wet with $0.01 M$ HCl. Irradiation time, 1 week. Running time, 1 hr at 600.

Fig. 9. Paper-electrophoresis histogram of neutron-irradiated KIO_3, dissolved in $0.1 M$ NaOH. Paper wet with $0.01 M$ NaOH. Irradiation time, 2 minute. Running time, 1 hr at 600V.

Fig. 10. Paper-electrophoresis histogram of neutron-irradiated $RbIO_3$, dissolved in $0.1 M$ NaOH. Paper wet with $0.01 M$ NaOH. Irradiation time, 2 minutes. Running time, 1 hr at 600 V.

ment probably because of temperature differences and changes in the amount of electrolyte solution carried by the paper. Species (I) is identified as the parent ion, CrO_4^{2+} or $Cr_2O_7^{2+}$, because its rate of migration is identical with that of a known sample of chromate or dichromate ions. Species (II) co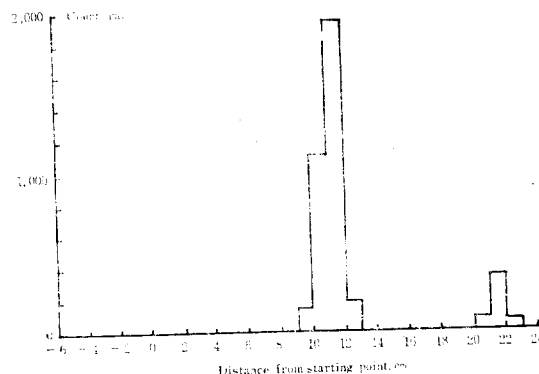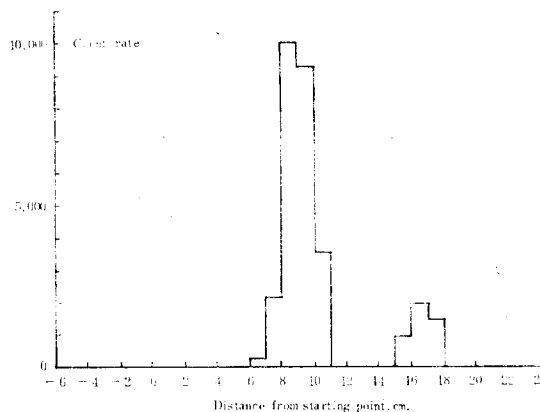rresponds to Cr^{3+} ion, which was formed by breaking the Cr—O bond. The migration distance of Cr^{3+} cation was determined by the paper-electrophoresis on chromium(III) chloride solution. Species (III) at the origin represents either a very insoluble compound, Cr_2O_3, or less likely a polynuclear species, $(Cr_2O_3)_n$.

The typical paper-electrophoresis histograms of neutron-irradiated $K^{128}IO_3$, $Rb^{128}IO_3$, $Na^{128}IO_4$ and $K^{128}IO_4$ are plotted in Figs. 9, 10, 11, and 12. The iodine-128 radioactivity appears in two peaks towards the anode on the electrophoresis paper, except one peak for $Na^{128}IO_4$ and three

peaks for $K^{128}IO_4$ including unknown cationic species. The major part of the activity migrates about 8~10 cm from the origin, and the smaller part of the activity about 16~18 cm. To determine the recoil species, paper-electrophoresis strip of non-irradiated $Na^{131}I$ was measured for iodine-131 radioactivity, and the paper-electrophoresis strips of non-irradiated KIO_3 and KIO_4 were irradiated. The peak at about 8~10 cm is identified as the parent ion, IO_3^- or IO_4^- and the
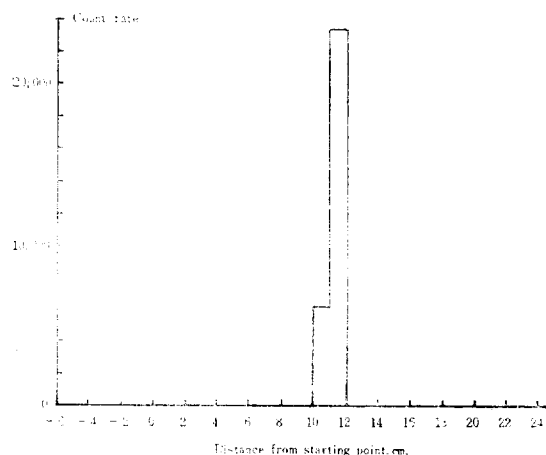

Fig. 11. Paper-electrophoresis histogram of neutron-irradiated $NaIO_4$, dissolved in 0.1 M NaOH. Paper wet with 0.01 M NaOH. Irradiation time, 2 minutes. Running time, 1hr at 600 V.
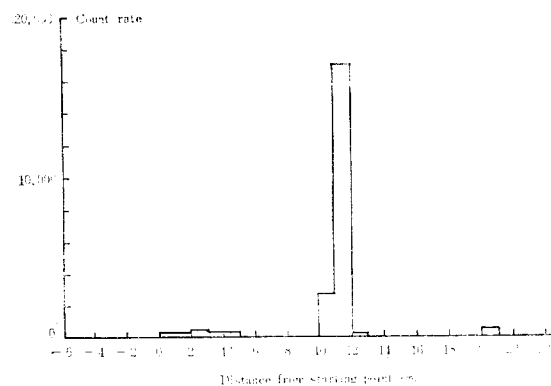

Fig. 12. Paper-electrophoresis histogram of neutron-irradiated KIO_4, dissolved in 0.1 M NaOH. Irradiation time, 2 minutes. Running time, 1 hr at 600 V.

peak at about 16~18 cm as the iodide ion, I^-.

Recoil Reaction

Recoil Energy. The prompt gamma spectra from radioactive capture of thermal neutrons have been determined[12,13]. 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(in MeV), then an atom of mass M(in a. m. u.) recoils with energy E_r(in 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. In oxygenated salts, the recoil energy available for bond rupture depends on the ratio, $R/R+M$, where M is the mass of the recoiling atom and R the rest of the molecule. The effective recoil energy is calculated

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

The recoil energies of nuclides with chromium and iodine oxygenated salts are listed in *Table* 1. These calculations show only the higher recoil

Table 1. Recoil energies of nuclides with chromium and iodine oxygenated salts.

Nuclide	E_γ(MeV)	Recoil energy E_r(eV)	Effective recoil energy E_d(eV)	
^{51}Cr	8.88	831	565	Na_2CrO_4
			606	K_2CrO_4
			681	Rb_2CrO_4
			498	$Na_2Cr_2O_7$
			540	$K_2Cr_2O_7$
			490	$(NH_4)_2Cr_2O_7$
			606	$Rb_2Cr_2O_7$
			631	$Ag_2Cr_2O_7$
^{128}I	5.19	113	45	KIO_3
			57	$RbIO_3$
			45	$NaIO_4$
			49	KIO_4

energies, since several gamma rays are emitted in different directions, which cancel out gamma ray multiplicity and result in a lower recoil energy. Moreover, the threshold displacement energy, estimated as 25~30 eV, of an atom in a crystal lattice reduces the effective recoil energy in the solid salts.

Internal Conversion. A nucleus that decays by electron-capture results in inner shell electron vacancy, which is filled by another electron dropping in from a less energetically bound level. This reaction is accompanied either by the further ejection of electrons(Auger effect) or by an X-ray(fluorescence). In both cases, vacancies are produced in other shells and these again lead to further Auger or fluorescence processes, yielding an atom with a multiple positive charge. A molecule containing such an Auger atom decomposes as a result of the loss of the bonding electron and Coulomb repulsion following distribution of the positive charge to other atoms of the molecule. The experimental observation by paper-electrophoresis shows that there is no significant evidence for an additional chemical effect in the electron-capture process, $^{127}I(n, \gamma)$ ^{128m}I(EC, 6.3%) in iodates and periodates.

Reaction Mechanism for Recoil Atoms. In view of the effective recoil energy and the internal conversion, it is unlikely that an atom which has captured a neutron can remain bound in its original molecule. It is also unlikely that the energy of the recoil atom is dissipated in heating a small region of the crystal. However, the results of paper-electrophoresis separation of recoil chromium-51 and iodine-128 indicate that many more of the recoil atoms are bound in the parent molecules. The results of the present work affords chemical evidence for the existence of disorder zones as suggested by Müller[2]. The recoil chromium and iodine atoms produced by the (n, γ) reaction generate around their starting point

only small changes in the lattice arrangement without producing a melt. The final fate of the recoil atom is determined by the structure of the immediate environment it has reached after having lost its kinetic energy. Thus, the high initial retention in neutron-irradiated chromates, dichromates, iodates and periodates indicate small and local damage processes during neutron-irradiation. Recoil atoms penetrate the lattice without producing any more damage than small, temporary deviation of atoms from their equilibrium state, replacements, vacancies and interstitials. The recoil atoms stop in the nearly perfect lattice near their starting point and form part of the recoil products of the Szilard-Chalmers process after dissolution or react with the surrounding atoms to form the retention.

Effect of the Cations. The dependence of retention on the radius of the cation was shown in *Table* 2. The stability of the salts formed by one group of metal and a certain complex ion increases as the size of the metal·ion decreases. Therefore, the results explain that the higher stability of the complex compound decreases disintegration and rearrangement of excited molecules, and increases the retention which runs counter to the results of Heine and Herr's experiment[4]. It is proposed that the zone of a displaced atom is formed when an energetic chromium or iodine 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 dichromate, 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 mol-

Table 2. Retention values and crystal structures for chromium and iodine oxygenated salts.

Salt	Recoil atom	Retention (%)	Radius of the cation, Å	Molecular volume, M/D	Crystalline form
Na_2CrO_4	^{51}Cr	92. 1	0. 95	59. 5	Orthorhombic (C_{mcm})
K_2CrO_4		85. 1	1. 33	71. 1	Orthorhombic (P_{mcm})
Rb_2CrO_4		77. 7	1. 48	81. 5	Orthorhombic
$Na_2Cr_2O_7$		94. 7	0. 95	118. 2	Triclinic $(P\bar{1})$
$K_2Cr_2O_7$		94. 4	1. 33	109. 3	Triclinic $(P\bar{1})$
$(NH_4)_2Cr_2O_7$		36. 8	1. 42	117. 2	Monoclinic$(C2/c)$
$Rb_2Cr_2O_7$		94. 3	1. 48	128. 1	Triclinic or Monoclinic
$Ag_2Cr_2O_7$		87. 1	1. 26	90. 5	Triclinic
KIO_3	^{128}I	89. 6	1. 33	55. 0	Monoclinic or Rhombohedral
$RbIO_3$		85. 8	1. 48	60. 1	Rhombohedral$(R3m)$
$NaIO_4$		100	0. 95	55. 4	Tetragonal$(I4_1/a)$
KIO_4		90. 9	1. 33	63. 5	Tetragonal$(I4_1/a)$

ecular volume as well as the ionic radii of cations. K_2CrO_4 is isomorphous with Na_2CrO_4 which is orthorhombic, but the primitive lattice of K_2CrO_4 with its greater free space than the face-centered lattice of Na_2CrO_4 shows the lower initial retention. Although it is difficult to correlate the initial retention with the crystalline forms, it is probable that the monoclinic crystal such as $Rb_2Cr_2O_7$ shows lower initial retention than the triclinic crystal such as sodium and potassium dichromates, due to the greater free space.

ACKNOWLEDGEMENT

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