

CCA-318

669-153.1:539.172.4:546.15

Original Scientific Paper

Thermal Annealing Reactions in Neutron-irradiated Calcium Iodate*

S. Kaučić and M. Vlatković

Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia

Received December 11, 1963

Thermal annealing of ^{128}I in neutron-irradiated calcium iodate showed the usual increase in the retention as observed earlier with the products of Szilard-Chalmers reactions. A series of systems of calcium iodate with the incorporated »impurity« ^{131}I in the form of I^- was also prepared and the isotopic exchange of IO_3^- - (I, I_2) was studied at higher temperatures (170°–400°C). The results are discussed in view of the possibility that isotopic exchange reactions may participate in the processes of the return of the recoil atoms to the chemical form of the target.

By heating neutron-irradiated potassium chromate Green and Maddock¹ observed an increase of ^{51}Cr -retention**. Since that time many authors have carried out similar treatment (often called thermal annealing) with numerous neutron-bombarded solids, *i.e.* inorganic oxyanions and complexes, and an increase in the yield of the radioactive parent form was almost regularly observed. In spite of the many papers treating the thermal and also radiation annealing² post recoil annealing effects are still difficult to interpret.

Harbottle and Sutin³ have extensively reviewed various types of kinetics of thermal annealing in irradiated material. They mention *inter alia* the thermal exchange model as possible in the case of annealing of Szilard-Chalmers products. According to this model the return of active atoms into the chemical form of the parent compound may be interpreted as a reaction of isotopic exchange of radioactive recoil atoms and neighbouring atoms in parent molecules.

Very serious indications of the existence of such an annealing mechanism were given by several authors who have studied the annealing effects in crystalline systems involving complex ions, such as dichloro-*bis*-(ethylene diamine)cobalt III^{5,6}. On recoil both the cobalt and the chlorine entered the parent configuration. The same recombinations were observed also after thermal annealing, the other isomer being formed only in traces. Such results, no doubt, stress the importance of the original medium (configuration) and lend ground to the assumption that the parent compound reacts directly with the recoil atom.

* Work performed in partial fulfillment of the requirements for the degree of Magister of Chemical Sciences, University of Zagreb, by S. Kaučić.

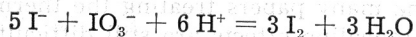
** The percentage of radioactive atoms found in the original chemical form was called retention by Libby⁴.

Our experiments with calcium iodate, which is a completely different and simpler system, were meant to prove the validity of the exchange model. The chemical effects of neutron capture in samples of some solid alkali iodates were studied earlier⁷. An increase of retention was observed on heating of the irradiated samples. It was possible to separate the fraction of radioiodine which did not recombine to give the parent compound, by the addition of an isotopic carrier in the reduced form.

In the course of our experiments the chemical behaviour of iodine-128 was investigated by heating samples of calcium iodate irradiated with thermal neutrons. Then we tried to prepare imitation samples of neutron-irradiated calcium iodate by incorporating an »impurity« of iodine-131 in the reduced form (I⁻) and investigated the possibilities of the exchange of IO₃⁻ and (I⁻, I₂) at higher temperatures. We also prepared a sample of sodium sulphate with incorporated iodine-131, in the form of iodide, in order to find out if any change (oxidation) of the chemical state of radioiodine occurred during the heating.

However, experiments thus conceived can, in an indirect way, give only indications as to the presence of the exchange reaction in the course of thermal annealing of neutron-irradiated calcium iodate.

It has been observed⁸ that the exchange of I⁻ and IO₃⁻ anions in the solutions of their salts did not take place at low temperatures. Zaborenko *et al.*⁹, however, noticed that it could reach as much as 50% in 3.5 hours at 300°C. The isotopic exchange reaction of iodine — iodate was studied in detail by Myers and Kennedy¹⁰ who suggested that the mechanism of the reaction should be understood as a reversible reaction between the iodide and the iodate ions at equilibrium which in overall form is similar to the normal iodide — iodate reaction



EXPERIMENTAL

Materials

Reagent grade chemicals were used throughout.

Calcium iodate with incorporated radioiodine was prepared in two ways. The first method was the precipitation of the salt in the presence of carrier-free iodine-131 previously freshly prepared in the reduced state. To the concentrated solution of calcium hydroxide containing activity an excess of iodic acid was added under constant stirring. The salt doped with radioiodine was also prepared by recrystallization from a saturated solution with accurately adjusted pH to

TABLE I

Sample of Ca(IO ₃) ₂ ¹³¹ I	Method of preparation	Specific activity of samples, microcuries of ¹³¹ I per gram		Percentage of total ¹³¹ I in the iodate fraction	
		of hexa- hydrate	of dehydra- ted salt	in hexa- hydrate	in dehydra- ted salt
a	ppt.	—	0.3	—	20.2
b	„	—	0.8	—	50.5
c	„	—	0.6	—	34.8
d	recryst. (pH 6)	6.7	0.6	0.7	20.9
e	„ (pH 7)	8.1	1.0	1.4	20.5
f	„ (pH 8)	5.0	0.5	1.5	23.0

which first radioiodine and then acetone was added under stirring. The hexahydrate crystals prepared as described above were separated by filtration, washed with cold water, acetone and ether and dehydrated for an hour at 170°C.

The data of the prepared samples of salt are given in Table I.

As can be seen from Table I, a partial transfer of activity into the iodate fraction occurred during the preparation of the salt, *i.e.* still in the aqueous phase and in the course of dehydration of hexahydrate. The method of incorporation of radioiodine by recrystallization gave in this respect better or, rather, more reproducible results. The values given in the last column of Table I did not change by keeping the samples at room temperature.

Inactive calcium iodate was prepared by precipitation as described above without the addition of activity.

Sodium sulphate containing ^{131}I was prepared by recrystallization from a solution to which freshly reduced carrier-free radioiodine had been added. The difference in the preparation of the two samples was that in the case of the sample »b« (see Table II) the solution was adjusted to pH at 7.0 after the addition of activity.

Neutron bombardment

The irradiations of the samples of inactive calcium iodate were performed in the Zagreb cyclotron with neutrons moderated in paraffin. The flux of thermal neutron could amount to about 10^7 – 10^8 $\text{sec}^{-1} \text{cm}^{-2}$ and the irradiation lasted 40 minutes at temperature exceeding the room temperature by a few degrees. For irradiation the salt was cork stoppered in soft glass tubes in the presence of air.

Heating of the samples

The samples were heated in a thermostatically controlled oven or in refluxed boiling liquids. In the course of the heating the samples were in contact with the atmosphere. The heated samples were chilled by dipping the stoppered samples into liquid air.

Analysis

The analysis was performed by precipitation of silver iodide after addition of carrier iodide and silver nitrate in the presence of sufficient ammonia to prevent the precipitation of silver iodate. After filtration the aqueous solution was acidified with sulphuric acid, sulphite was added, sulphur dioxide boiled off and the iodine was precipitated as silver iodide. All precipitates were washed with acetone and ether, dried for a few minutes at 110°C and weighed for the chemical yield. Then the corrections of the activity for the incomplete recovery of the precipitates could be applied.

Radioactivity measurements

The silver iodide precipitates were covered with cellophane tape and counted in aluminium dishes with a β -GM counter. Decay curves of iodine-131 and, in the case of bombarded samples, for iodine-128 were plotted for each sample to determine activities which were used in calculations.

It was observed that a fraction of the activity of iodine-131 was lost during the thermal treatment of samples of salt which contained incorporated radioiodine. Therefore all values for the activity in the iodate and the iodide fractions, obtained from the heated samples, were expressed with reference to the percentage of activities in identical fractions of a similar sample analysed at room temperature.

RESULTS

Thermal annealing of $\text{Ca}(\text{IO}_3)_2$

Calcium iodate irradiated with thermal neutrons at room temperature showed a retention of about 67 per cent. In Fig. 1 classical isothermal annealing curves are given. For each temperature the retention increases to become asymptotic to some characteristic value (pseudo plateau). By plotting

the change in retention from the initial value against the reciprocal of absolute temperature, a straight line is obtained, which has often been reported in cases of the Szilard-Chalmers systems (Fig. 2).

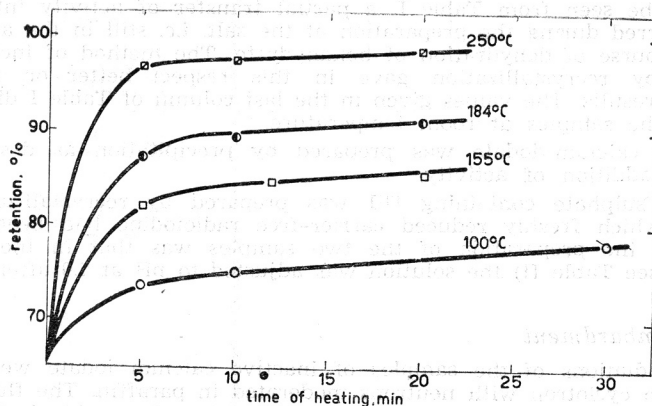


Fig. 1. Effect of thermal annealing upon retention in $\text{Ca}(\text{IO}_3)_2$

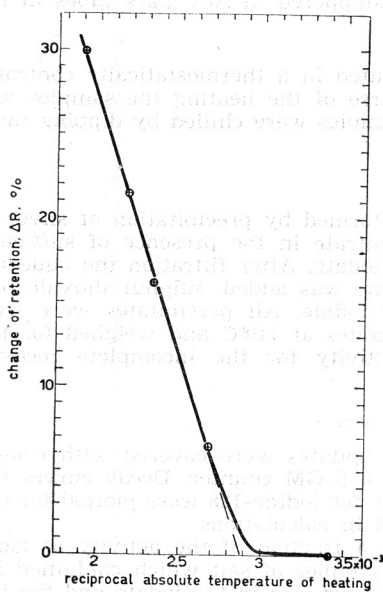


Fig. 2. The increase in retention to the plateau (ΔR) against reciprocal absolute temperature of heating.

Heating of $\text{Ca}(\text{IO}_3)_2$ (^{131}I)

The increase of activity in the iodate fraction was also observed by heating the samples of calcium iodate into which iodine-131 in the reduced form had been incorporated. The results indicate that the reduced carrier-free iodine passes, on heating, into the iodate form, and that at a determined temperature the reaction comes to equilibrium. Heating curves obtained with samples

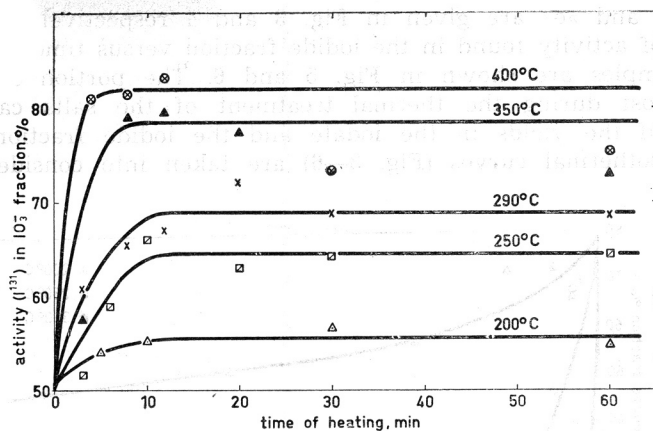


Fig. 3. Heating of $\text{Ca}(\text{IO}_3)_2$ - ^{131}I system (sample b) Activity of ^{131}I in the iodate fraction against time of heating.

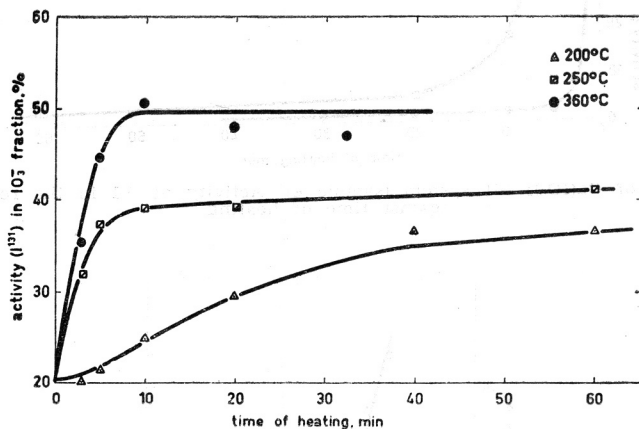


Fig. 4. Heating of $\text{Ca}(\text{IO}_3)_2$ - ^{131}I system (sample e). Activity of ^{131}I in the iodate fraction against time of heating.

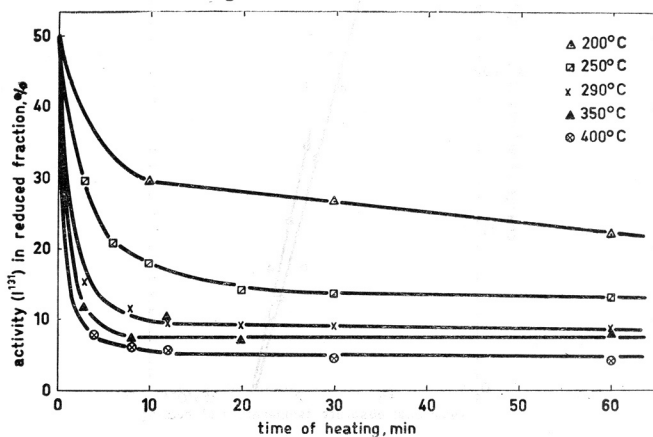


Fig. 5. Heating of $\text{Ca}(\text{IO}_3)_2$ - ^{131}I system (sample b). Activity of ^{131}I in the reduced fraction against time of heating.

of salts »b« and »e« are given in Fig. 3 and 4 respectively. Plots of the percentage of activity found in the iodide fraction versus time of heating for identical samples are shown in Fig. 5 and 6. The portion of activity of iodine-131 lost during the thermal treatment of the salts can be easily established if the yields in the iodate and the iodide fractions given by respective isothermal curves (Fig. 3—6) are taken into consideration. The

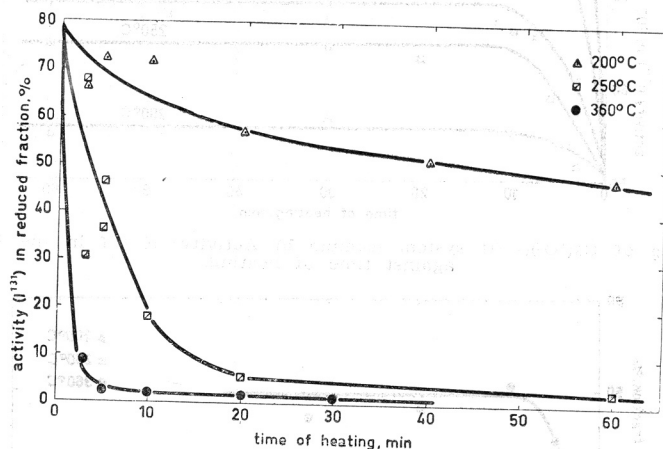


Fig. 6. Heating of $\text{Ca}(\text{IO}_3)_2$ - ^{131}I system (sample e). Activity of ^{131}I in the reduced fraction against time of heating.

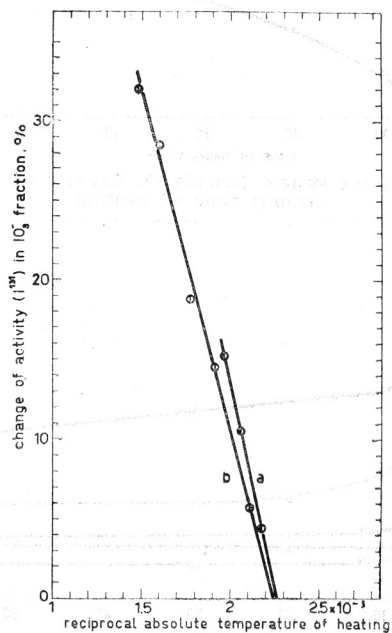


Fig. 7. The increase in activity of ^{131}I to the plateau (samples a and b) against reciprocal absolute temperature of heating.

loss of iodine and the activity yield in the iodate fraction increase simultaneously with the rise of temperature.

A linear relationship was observed between the change of ^{131}I activity in the iodate fraction and the reciprocal absolute temperature (Fig. 7, 8). It is interesting to note that straight lines obtained with corresponding samples of salt intercept the abscissa approximately at the temperature of 170°C . This implies that the samples were exposed to further heating treatment after the reaction had reached equilibrium at drying temperature.

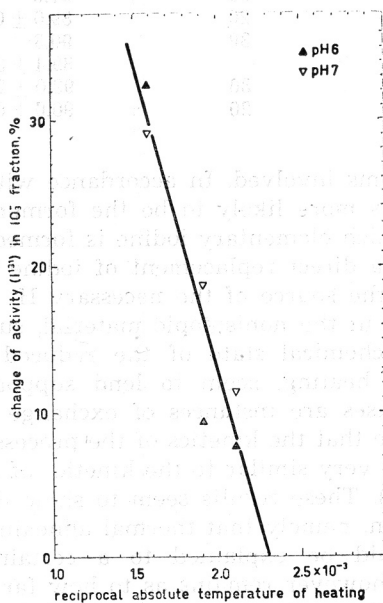


Fig. 8. The increase in activity of ^{131}I to the plateau (samples d and e) against reciprocal absolute temperature of heating.

The heating of Na_2SO_4 (^{131}I)

The heating of sodium sulphate samples incorporating radioiodine did not provoke any change in the initial chemical distribution of activity. It was only at higher temperatures that a decrease of activity in the iodate fraction was observed, probably owing to the thermal instability of sodium iodate, formed in the course of incorporation of activity. Results are given in Table II.

DISCUSSION

There seems to be no difference in the retention obtained at room temperature for calcium iodate, alkali iodates⁷, and iodine pentoxide¹¹.

The heating of calcium iodate containing incorporated ^{131}I »impurity« in the reduced form has shown, to our mind, the possibility of exchange of iodine atoms between the lower and the higher oxidation states. There is little more to be said about the mechanism of this exchange which can be easily measured in spite of the great difference existing in the concentration

TABLE II
 Heating data for Na_2SO_4 (^{131}I)

Sample	Temp., °C	Time of heating, (min)	Iodine-131 activity, %	
			in I^- fraction	in IO_3^- fraction
a	room temp.			
	155	20	85.4 ± 3.2	15.9 ± 3.3
	250	5	91.2 ± 1.0	7.7 ± 0.5
		10	80.0	4.0
		20	91.0	3.4
		30	89.0 ± 0.1	1.7 ± 0.4
b	room temp.			
	100	30	90.3	2.2
	150	20	89.4 ± 3.2	10.7 ± 3.3
			93.0 ± 2.6	6.3 ± 1.5
		90.6 ± 6.9	1.2 ± 0.1	

of the two chemical forms involved. In accordance with the suggestion given by Myers *et al.*¹⁰, this is more likely to be the formerly mentioned iodide — iodate reaction by which elementary iodine is formed and partly lost in the course of heating than a direct replacement of iodine atoms. The rest of the crystal water could be the source of the necessary H^+ ions. The experiments, which have shown that in the nonisotopic material, such as the Na_2SO_4 (^{131}I) system, no change of chemical state of the reduced radioiodine will take place in the course of heating, seem to lend support to the opinion that the above mentioned cases are instances of exchange reactions.

Figures 3—8 indicate that the kinetics of the process in a simulated system $\text{Ca}(\text{IO}_3)_2$ - ^{131}I is formally very similar to the kinetics of annealing in irradiated calcium iodate (Fig. 1, 2). These results seem to show that exchange reactions could affect the retention, namely that thermal annealing reactions in irradiated calcium iodate could be explained to a certain extent by exchange reactions. The question however remains as to how far the simulated systems $\text{Ca}(\text{IO}_3)_2$ - (I^- , I_2) can be taken to be a successful imitation of the irradiated salt.

It might be of interest to mention here that both the retention of radiohalogens and the ability of annealing in oxyhalogens decreases in the direction iodine-bromine-chlorine. It is likewise known¹² that the rate of the halate-halide exchange reactions in solutions decreases in the same order.

With regard to the activation energy, several authors^{3,13,14,15} have successfully adopted the Vand-Primak method of analysis in several cases of thermal annealing of Szilard-Chalmers products. By applying the Vand-Primak expression for energy (in eV)

$$E_0 = k T \ln(B t)$$

where B is a constant having the dimensions of a frequency, t is the time of annealing, k is the Boltzmann constant and T the absolute temperature, the distribution of activation energy has been obtained of the order of 1 eV. The constant B has been used in the wide range from 2.10^6 to 10^{12} sec^{-1} ^{13,14,15}. Owing to insufficiently precise data of exchange in the $\text{Ca}(\text{IO}_3)_2$ (^{131}I) system it was not possible to calculate rigorously the activation energy in a similar way. But considering only the time required to reach the plateau of isothermal curves (Fig. 3, 4) and the absolute temperatures

necessary to stimulate the processes, such a calculation ought to give an apparent activation energy of the same order of magnitude as obtained in the cases of annealing in the bombarded systems.

Finally, it seems that in considerations of this kind the chemical identity of recoil atoms and of inactive atoms in the parent compounds should be taken into consideration as well as the possibility of reversible exchange reactions under specific conditions of annealing.

REFERENCES

1. J. H. Green and A. G. Maddock, *Nature* **164** (1949) 788.
2. For references see G. Harbottle, *Chemistry Research and Chemical Techniques Based on Research Reactors*, IAEA, Vienna 1963, p. 149.
3. G. Harbottle and N. Sutin, *Advances in Inorganic Chemistry and Radiochemistry* **1**, Eds. H. J. Emeleus and A. G. Sharpe, Academic Press in., New York 1959, p. 267.
4. W. F. Libby, *J. Am. Chem. Soc.* **62** (1940) 1930.
5. H. B. Rauscher, N. Sutin, and J. M. Miller, *J. Inorg. Nucl. Chem.* **12** (1960) 378.
6. A. V. Zuber, H. B. Rauscher, J. M. Miller, and N. Sutin, *Chemical Effects of Nuclear Transformations* **1**, IAEA, Vienna 1961, p. 359.
7. R. E. Cleary, W. E. Hamill, and R. R. Williams, Jr., *J. Am. Chem. Soc.* **74** (1952) 4675.
8. D. Hull, C. Shiftett, and S. Lind, *J. Am. Chem. Soc.* **58** (1936) 535; A. Polesitsky, *Compt. Rend. Acad. Sci., U.R.S.S.* **24** (1939) 540; M. Cottin and M. Haissinsky, *Compt. rend.* **224** (1947) 1536.
9. K. B. Zaborenko, M. B. Nejman, and V. K. Samsonova, *Dokl. Akad. Nauk SSSR* **64** (1949) 541.
10. O. E. Myers and J. W. Kennedy, *J. Am. Chem. Soc.* **72** (1950) 897.
11. M. Vlatković and A. H. W. Aten Jr., *Chemical Effects of Nuclear Transformations* **1**, IAEA, Vienna 1961, p. 551.
12. A. C. Wahl and N. A. Bonner, *Radioactivity Applied to Chemistry*, John Wiley and Sons, Inc., New York, 1958 p. 32.
13. J. Shankar, K. S. Venkateswarlu, and A. Nath, *Chemical Effects of Nuclear Transformations* **1**, IAEA, Vienna 1961, p. 309.
14. T. Costea, *J. Inorg. Nucl. Chem.* **19** (1961) 27.
15. K. Yoshihara and G. Harbottle, *Radiochim. Acta* **1** (1963) 68.

IZVOD

Reakcije termičkog napuštanja u kalcijevu jodatu ozračenem neutronima

S. Kaučić i M. Vlatković

Ispitan je kemizam joda-128 nastalog bombardiranjem kalcijeva jodata sporim neutronima na ciklotronu. Termičkim napuštanjem ozračenih uzoraka soli u temperaturnom intervalu 100°–250°C dobiven je porast retencije, što je već ranije opaženo kod produkata Szilard-Chalmersovih reakcija. Također je priređeno nekoliko sistema kalcijeva jodata s ugrađenim jodom-131 u kemijski reduciranom obliku, kao nečistoćom. Zagrijavanjem uzoraka soli označene s ^{131}J praćene su reakcije izotopne izmjene JO_3^- (J_2 , J^-) u čvrstoj fazi kod povišene temperature (250°–400°C). Budući da je kinetika procesa u simuliranom sistemu formalno vrlo slična kinetici napuštanja bombardiranog kalcijeva jodata, ukazuje se na mogućnost, da reakcije izmjene sudjeluju u procesu vraćanja vrućih atoma joda u kemijski oblik mete.

INSTITUT »RUDER BOŠKOVIĆ«
ZAGREB

Primljeno 11. prosinca 1963.