TABLE III
EXCHANGE STUDIES

Reactants	Other conditions	Contact time and temp.	% Exchange	Remarks
PCl_3–red P*	20 ml. PCl_3 and 52.3 mg. red P	Room T°, 3 hr., max. bath temp. 78°	<2	Heterogeneous
PCl_3-red P*	20.5 ml. PCl_3 and 67 mg. red P	32 hr., 30°, max. bath temp. 78°	<2	Heterogeneous 20,7000 R. of X-rays ~1 Å.
PCl_3–red P*	6 ml. PCl_3 and 17.9 mg. red P	73 hr., 30°, max. bath temp. 78°	<2	Heterogeneous 62,100 R. of X-rays ~1 Å.
PCl_3–P*SCl_3	2 ml. of each component	2 hr. for distillation, max. bath temp. 163°	<2	Homogeneous
S–PS*Cl_3	4 ml. $PSCl_3$ and 0.16 g. sulfur	1.75 hr. for distillation, max. bath temp. 182°	<2	Homogeneous
S_2Cl_2–PS*Cl_3	5 ml. of each component	3.5 hr. for distillation, max. bath temp. 190°	<2	Homogeneous

inches to determine whether the gamma ray dosage was a factor in recombination. However, from calculations presented by Primak[13] in a recent paper, a 10-hour bombardment would still give a dosage of 5×10^4r to 5×10^5r. Consequently, this approach was not followed.

As exchange reactions and post-bombardment procedure may also affect the proportion of labeled chemical species, certain experiments were performed to check whether exchange of the labeled atom occurred under the given conditions. The results of these studies are given in Table III. The distillation procedures, additions of carriers and analyses were identical with those used for irradiated samples. From the results, it would appear that the reactions studied did not affect the ultimate analyses for the labeled chemical species.

While repeated distillations have been carried out on the $PSCl_3$ fractions and a constant ratio of P^{32} to S^{35} has been observed, it appears quite improbable that the P^{32} is actually present as labeled $PSCl_3$. The reason for this statement is that if the original PCl_3 contained no sulfur, the only sulfur available for the P^{32} to combine with is the S^{35} formed during the irradiation. Hence the 1 to 2% found in the $PSCl_3$ fractions must be associated with unidentified compounds that have boiling points near $PSCl_3$. The residue in the still pot always contained some P^{32} so a small percentage of higher boiling components also is present. In some distillations as much as 5% of the total P^{32} present was in fractions with a b.p. near $POCl_3$ and hence may be identified tentatively as labeled $POCl_3$. The formation of labeled $POCl_3$ may be a result of hydrolysis of PCl_5 in post bombardment handling.

The principal S^{35}-labeled compound was identified as $PSCl_3$ which contains 30 to 40% of the total S^{35}. Repeated distillations were performed to ensure the purity of this fraction. When S_2Cl_2 was used as a carrier, S^{35} was found in most of the distilled fractions due to the dissociation of the monochloride to the dichloride (b.p. 59°) as the distillation progressed. Because of known exchange reactions[14] it is difficult to identify either SCl_2 or S_2Cl_2 as compounds labeled by the primary event.

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MANHATTAN, KANSAS

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(14) R. Cooley and D. Yost, THIS JOURNAL, **62**, 2474 (1940).

[CONTRIBUTION FROM THE INSTITUUT VOOR KERNPHYSISCH ONDERZOEK]

Chemical State of Radio-iodine in Neutron-irradiated Periodate after Thermal Treatment

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The distribution of radioactive iodine over the iodide–iodine, iodate and periodate fractions is determined in neutron-irradiated potassium periodate. The main activity is found in the iodate fraction with minor contributions in the other fractions. If the activated solid is heated, the iodide–iodine activity disappears below 100°. Above this temperature most of the activity goes into the periodate fraction but part of it remains in the iodate fraction.

Introduction

It is a well-known fact that the radio-halogens, formed by capture of a neutron in the central atom of halate-ions in solid substances, are found almost entirely as halides in the case of chlorine and bromine.[1] In the case of solid iodates, however, about one third is found as iodide and about two thirds as iodate.[2] If solutions of a periodate are irradiated, about 90% of the activity can be isolated as IO_3^- and the rest as $I^- + I_2$ and as IO_4^-.[2] It seemed to be a matter of some interest to find out the corresponding distribution of the radioactivity in neutron-irradiated solid periodates and

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(1) W. F. Libby, THIS JOURNAL, **62**, 1930 (1940).

(2) R. E. Cleary, W. H. Hamill and R. R. Williams, *ibid.*, **74**, 4675 (1952).

to determine the fate of the radioactivity if the solid is heated before being dissolved.

Experimental

Potassium periodate (KIO_4) was activated by exposure to neutrons (generated in the Philips synchrocyclotron) which had been moderated in paraffin. After the irradiation the sample was heated in an electric furnace at different temperatures and for different periods. (During the second and the third experiment the oven was slightly overheated before the sample was introduced to balance the loss of temperature caused by the introduction of the cold material.)

After the sample had been taken out of the furnace and cooled off, it was dissolved in a solution of iodine and iodate. (In the third experiment the iodine was introduced after the periodate was dissolved. This was done in view of the high rate of exchange of iodine between iodate and periodate ions in the presence of free iodine.[3] It may, however, have resulted in partial loss of the radioactive iodide–iodine fraction.) The iodine (which is known to exchange very rapidly with any iodide ions present in the solution) was extracted several times by means of carbon tetrachloride, back-extracted into a sulfite solution and precipitated as AgI with nitric acid and silver nitrate. In all experiments the iodide–iodine activity was counted as silver iodide.

In the first experiment the iodine extraction was followed by a barium iodate precipitation[4] and finally the periodate was either precipitated as bismuth periodate[4] or reduced with sodium hypophosphite and precipitated as AgI by addition of nitric acid and silver nitrate. In these experiments the iodate activity was counted as barium iodate and the periodate either as bismuth periodate or as silver iodide.

In the second and in the third experiment the iodate fraction was precipitated as silver iodate in a solution containing dilute nitric acid. (0.3 *M* is unsatisfactory, but the concentration of the acid is not critical.) After filtration the periodate remaining in solution was reduced with sulfite and precipitated with more nitric acid and silver nitrate. In these experiments the iodate was counted as silver iodate and the periodate as silver iodide.

All samples were counted in aluminum dishes and corrections were applied for self-absorption.[5] Decay curves were drawn for all samples—which always showed the correct half-life of 25 minutes—and the activities of different samples in each experiment were taken at the same value of the time.

In general it was not possible to isolate the different fractions quantitatively, but corrections were applied for loss of material in each sample. In the first experiment the total activity obtained in this way was much lower than that observed by direct measurement of a sample of the untreated potassium iodate, but in the second and third experiments the difference did not exceed a few per cent. In each case the activities of the chemical forms are given as fractions of the sum of the activities obtained for all three, and not as fractions of the total iodine activity observed in the unseparated potassium periodate.

The unsatisfactory activity balance in the first experiment, which was also observed in preliminary experiments in which similar chemical methods were used, is somewhat difficult to explain. Cross-contamination and uncertain chemical composition of the compounds which were isolated and measured may account for a large part of the discrepancies.

Results

The distribution of the I^{128}-radioactivity in potassium periodate after irradiation with slow neutrons is shown in Table I.

The activity distribution obtained after 15 minutes heating at different temperatures is given in Fig. 1. Observations made on irradiated potassium periodate, kept at 200° for different lengths of time, are shown in Fig. 2.

TABLE I

DISTRIBUTION OF RADIOACTIVITY (I^{128}) IN NEUTRON-IRRADIATED POTASSIUM PERIODATE (UNHEATED)

Chemical fraction	Fraction of total radioactivity[a]
$I^- + I_2$	0.10
IO_3^-	.86
IO_4^-	.04

[a] The figures given in this table are from experiment 2, which we considered to be the most reliable for this purpose. If, however, we take the average of six experiments performed in our institute at varying times the figures are not very different: $I^- + I_2 = 0.12$ and $IO_4^- = 0.05$.

Results of experiments 2 and 3, where the temperature control was most efficient and the chemical separation most reliable, are seen to agree quite satisfactorily. The data from experiment 1 scatter in a more disturbing way, but as an average they fully support the more accurate figures. The same is true for some isolated figures obtained in preliminary tests. In experiment 3 tracer iodine was added after the periodate had dissolved. This suggests a possible loss of activity from the iodide–iodine fraction either by absorption or oxidation, and for this reason no values are given for this fraction in Fig. 1. As a matter of fact the values found for this fraction in this experiment were somewhat lower than those in experiment 1 and 2, but the trend of the temperature dependence of the iodide–iodine activity in experiment 3 is in full agreement with that observed in the earlier experiments.

In considering our results we notice that at least two different phenomena take place. First it is evident that at temperatures below 100° the iodide–iodine activity disappears very rapidly. There is no reason to doubt that it enters into the iodate fraction.

The iodate activity is able to resist much higher temperatures, but above 100° a second reaction becomes noticeable, the transfer of radioactivity from the iodate to the periodate fraction. There are indications both in Fig. 1 and in Fig. 2 that this process does not easily reach 100%, but that a fraction of the iodate activity may persist as such for a fairly long time at fairly high temperatures.

One may even conclude that the fraction of the activity which is able to remain in the iodate for a longer time is somewhat temperature dependent. The data in Fig. 2 suggest that at 200° only 60% of the total activity can be brought rapidly into the periodate, but at 240° the corresponding figure is at least 80%.

Discussion

It is tempting to treat the change in the retention in periodates on heating in relation with the corresponding phenomena in permanganates.[6,7] (It is worth pointing out that in the case of potassium permanganate a dependence of the final value of the retention on the temperature of the experiment has been observed,[6] which is quite similar to the difference of the final distribution of radioactivity which we have found in periodates between 200 and 240°.) Our main difficulty is the

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(3) M. Cottin and M. Haïssinski, *Compt. rend.*, **224**, 1636 (1947).

(4) W. H. Burgus and T. H. Davies, in C. D. Coryell and N. Sugarman, "Radiochemical Studies: The Fission Products," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1951, p. 209.

(5) A. H. W. Aten, Jr., *Nucleonics*, **6**, No. 2, 68 (1950); *Natuurwetenschappelijk Tijdschrift*, **32**, 155 (1950); *Chem. Weekblad*, **47**, 553 (1951).

(6) W. Rieder, R. Broda and J. Erber, *Monatsh.*, **81**, 657 (1950).

(7) A. H. W. Aten, Jr., and J. B. M. van Berkum, THIS JOURNAL, **72**, 3273 (1950).

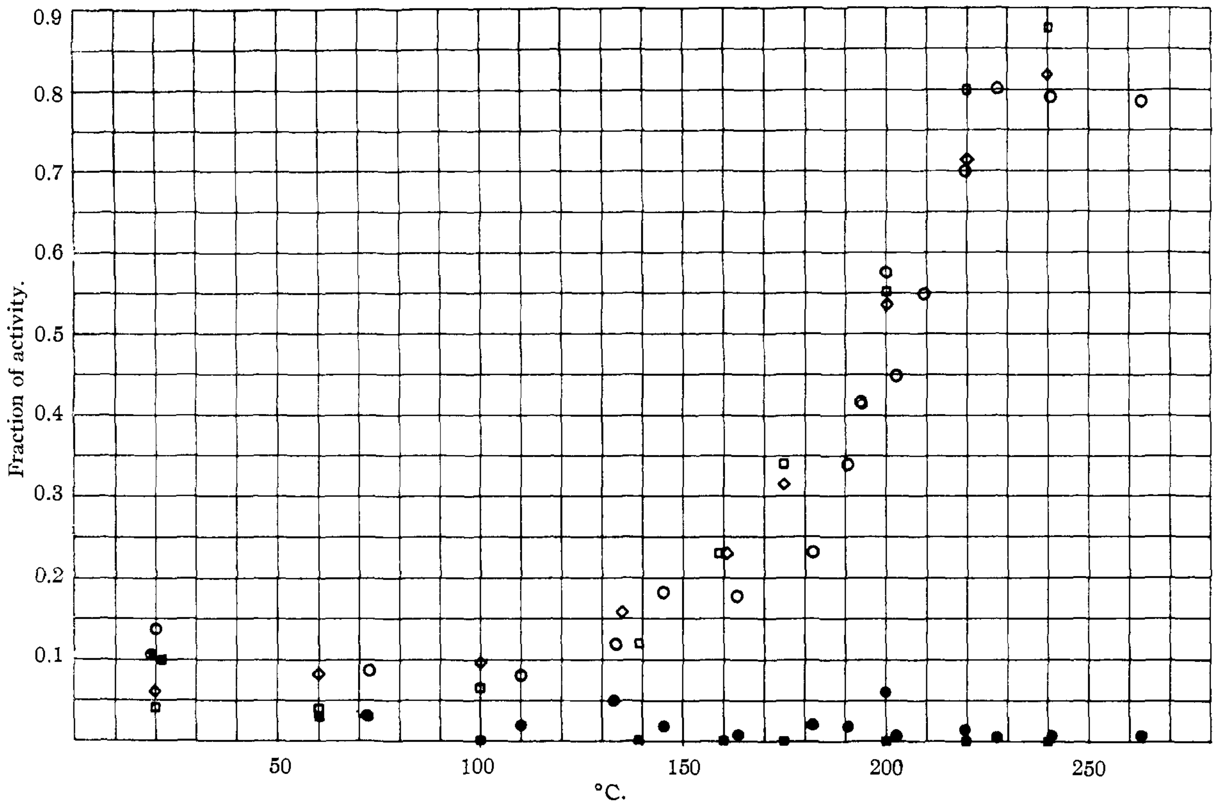

Fig. 1.—Influence of heating at different temperatures on the distribution of iodine radioactivity in neutron-activated potassium periodate. Fraction of the total activity found in the periodate fraction (retention) (○, □ and ◇) and in the iodine fraction (● and ■) after **15** minutes heating at different temperatures. ○ and ● indicate experiment 1, □ and ■ experiment 2 and experiment 3. Experiment 1 is less accurate than 2 and 3.

uncertainty concerning the initial chemical state of the radioactive atoms.

Libby in his fundamental paper about the Szilard–Chalmers process suggests that by neutron activation Mn^{56} is formed mainly in the same oxidation state it had in the MnO_4^- ion before neutron capture, but having electron pair bonds with fewer oxygen atoms. These Mn^{56} atoms enter into a stable chemical state when they are either reduced to a lower oxidation state or hydrated to MnO_4^- ions. To a minor extent Libby recognized the formation of $Mn^{56}O_4^-$ by oxidation of lower valency states of Mn^{56} by MnO_4^- and electron transfer between $MnO_4^=$ and MnO_4^-.

Cleary, Hamill and Williams on the other hand, in their discussion of the Szilard–Chalmers reaction for periodate ions in aqueous solution, suggest that the radioactive I^{128} is formed only as IO_4^-, IO_3^-, IO_2^- and IO^-.

In the case of the neutron activated potassium periodate crystals our data are not nearly complete enough to present a reliable picture of the original condition of the radio-iodine. The activity isolated as IO_4^- and as I_2 need not come from a fraction which when dissolving was converted as a whole into the compounds mentioned, but a metastable radio-iodine compound may have disproportionated to form IO_4^- and I_2, although this assumption is not in our opinion very likely. The radio-iodate on the other hand, must come from a radioactive iodine fraction which went into solution entirely as iodate ions. Later we shall give arguments to prove that this fraction did not originally consist mainly of iodate ions, but apart from this little can be said about its chemical constitution. Apart from reduction and hydration—which may have been instrumental in converting it into iodate as explained by Libby—oxidation by periodate may have played a rôle—either in the final solution or in the boundary layer of the crystal during the process of dissolving—and specially a number of

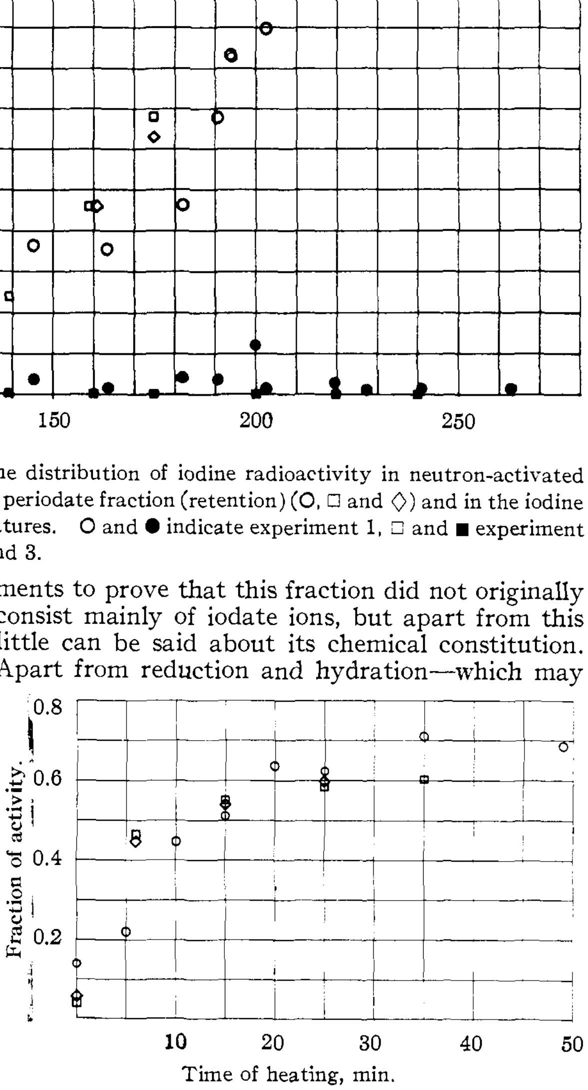

Fig. 2.—Influence of heating for different periods on the distribution of iodine radioactivity in neutron-activated potassium periodate. Fraction of total activity found in the periodate fraction (retention) after keeping at 200° during different times. ○ indicates experiment 1, □ experiment 2 and ◇ experiment 3. Experiment **1** is less accurate than 2 and 3.

possible exchange processes must be taken into consideration. Exchange processes are exceedingly rapid between different units consisting of the same atoms but carrying different charges and they may stabilize combinations of radio-iodine with oxygen atoms both by increasing and by decreasing the negative charge. Under these circumstances it is hardly reasonable to express an opinion concerning the nature of the ions and molecules which may have been converted into radioactive iodate ions, although it must be stated that we have no reason to assume that all of them originally had the same composition.

The situation is much simpler in the periodate that has been subjected to heat treatment. If the heating has been sufficiently long and the temperature sufficiently high most of the radio-iodine is found in the periodate fraction. It is evident that this periodate cannot have been formed by disproportionation. This suggests very strongly, although it does not, of course, prove, that in the heated periodate most of the radio-iodine is present as IO_4^- ions. Although not quite impossible it is hardly likely that the iodine atoms have been oxidized to periodate from an oxidation state lower than or equal to that of iodate.

The fact that in Fig. 2 the activity in the periodate fraction does not go up to 100% indicates that the radio-iodine in the crystal can enter into two different relatively stable chemical states, one which is isolated as periodate and one which is isolated as iodate. If we assume, as seems reasonable, that after the heat treatment has been continued long enough to reach the horizontal part of the graph in Fig. 2 these two fractions occur in the crystal as IO_4^- and as IO_3^-, it follows that before heating most of the radio-iodine was present in the solid in a state which was neither IO_4^- —as we knew already—nor IO_3^-. (The ratio of the activities formed as IO_3^- and as IO_4^- is, of course, determined by the ratio of the rates of the two reactions which convert the radioactive iodine into the two stabilized products.)

It is of interest to point out that the radio-iodine fraction which follows I_2 in the analysis is oxidized in the periodate crystal at a very low temperature, lower than required for the oxidation of the radioactive iodide–iodine fraction in neutron activated sodium iodate.[2] It seems reasonable to ascribe this difference to the strong oxidizing power of the periodate ion. It is not impossible that the oxidation of this radio-iodine fraction gives rise to the formation of normal IO_3^- ions. In this case this radio-iodine fraction would end up in the iodate fraction of the solid after heat treatment. However, nothing definite can be said about this possibility at present. From a chemical point of view it is not difficult to explain that the oxidation of the radio-iodine which follows the iodate fraction requires a much higher temperature, as this fraction is almost certainly in a higher oxidation state. It is not unreasonable to assume that this higher oxidation state needs a higher activation energy to react with the periodate ions.

It seems worth pointing out that the temperature needed to cause an appreciable rise in the retention in potassium periodate is not very different from the temperature needed to bring about a corresponding process in sodium iodate,[2] potassium permanganate[6] or potassium bromate.[8]

We do not want to omit pointing out that the description we have given here may be oversimplified to a very serious degree. What is probably formed by the reaction of the neutron with an iodine nucleus is a region in the crystal where its structure is more or less disturbed and where a number of energy-rich lattice-faults are frozen in very close together. The neutron-irradiated solid contains a great many of these regions and each of them has one radio-iodine atom in one of a number of different possible situations. When the crystals are dissolved these radio-iodine atoms accommodate themselves in the aqueous solution, each in the way which is most suitable for the position it occupies in the irregular lattice structure.

It is evident that this picture—which is fairly close to the treatment presented by Cobble and Boyd[8]—can describe the actual situation much more accurately than is possible with the chemical theory. On the other hand its lack of simplification makes it of little value for the establishment of general rules for the description of a phenomenon as complicated as the Szilard–Chalmers effect. Thus the disturbed lattice theory does not even provide us with a clear argument to explain why the disappearance of radioactivity from the "iodide–iodine fraction" does not take place at the same time as the disappearance from the "iodate fraction."

From this point of view we are tempted to assume that the reconstruction of the disturbed parts of the crystal into the approximately normal lattice is indicated by the transition of radioactivity from the iodate to the periodate fraction. If this is correct the rebuilding starts at temperatures around 100° and does not need more than a few minutes to approach completion at 200°. Then the oxidation of the iodide–iodine activity to iodate does not seem to require the transition of the disturbed crystal to the normal one. This conclusion makes it seem a bit doubtful whether it is correct to assume that the formation of the radioactive periodate coincides with that of the normal crystal lattice. If, on the other hand, we suppose that the recrystallization takes place at the same time as the oxidation of the iodide–iodine fraction, it is equally astonishing that the fraction which is to furnish the radioactive iodide would survive in the annealed lattice without being changed into either iodate or periodate ions. As it is, neither picture seems to be satisfactory.

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Amsterdam, Holland

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[8] J. W. Cobble and G. E. Boyd, This Journal, **74**, 1282 (1952).