The transfer of triplet energy may be formulated as

$$Q'' + A \xrightarrow{k_{10}} A'' + Q \qquad (13)$$

where A and A'' are the ground and triplet states, respectively, of anthracene. With this step, the mechanism furnishes the expression

$$\frac{\Phi}{\Phi_A} = \frac{(QH\cdot)^2}{(QH\cdot)_A{}^2} = 1 + \frac{k_{10}(A)}{k_5[k'' + (RH_2)]} \qquad (14)$$

in which Φ_A and $(QH\cdot)_A$ represent the quantum yield and radical concentration, respectively, in the presence of anthracene in pure 2-propanol. With an anthracene concentration of 1.2×10^{-3} *M* the experimental values of $\Phi/\Phi_A = 1.4$ and $(QH\cdot)^2/(QH\cdot)_A{}^2 = 1.5$ are in satisfactory agreement. Using the value $k_{10} = 3.2 \times 10^9$ l. mole^{-1} sec^{-1} at 25°, which was obtained from the Debye equation with the assumption that the energy transfer proceeds at the diffusion-controlled rate, eq 14 affords the value 7.3×10^5 l. mole^{-1} sec^{-1} for k_5, the rate constant for the abstraction of hydrogen from 2-propanol by triplet PAQ. The effective lifetime of the triplet state in 2-propanol is therefore 1.0×10^{-7} sec, which may be compared with the value of 1.3×10^{-7} sec reported by Wilkinson for the rate of hydrogen abstraction from 2-propanol by the triplet state of α-anthraquinone in a 4:1 mixture of benzene–2-propanol.[11]

Acknowledgment. We are grateful to Drs. J. R. Huber, J. L. Roebber, and R. N. Wiener for many helpful discussions, and to Mr. Alan Dopfel (participant in the National Science Foundation-sponsored Thayer Academy Summer Science Program, 1967) for his experimental contributions to this study.

Chemistry of Iodine-128 and Iodine-130 Recoils in Neutron-Irradiated Crystalline Potassium Iodate and Potassium Periodate[1]

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Abstract: Radioactive iodine-128 and iodine-130 recoils formed by neutron capture in crystalline KIO_3 and KIO_4 appeared as iodide, iodate, and periodate ions on analysis of alkaline aqueous solutions of the irradiated solids. With KIO_3 more than two-thirds of the radioiodine was retained as radioiodate, and small amounts of radioperiodate were found. With KIO_4 nearly 90% of the recoils appeared as radioiodate, while the periodate retention was slightly less than 10%. The relative concentrations of the radioiodine oxidation states varied with the time and temperature of the neutron bombardment. Radioiodide was readily converted to iodate and periodate on heating or on exposing the neutron-irradiated solids to ^{60}Co γ rays. Iodine-131 added in tracer concentrations to crystalline KIO_3 or KIO_4 as iodide ion was rapidly oxidized to iodate and to periodate on heating the solids above room temperature. There was only a small isotopic effect in the yields of the iodine valence states in which ^{128}I and ^{130}I were combined.

This reinvestigation of the chemistry of radioiodine recoils formed in crystalline alkali metal iodate and periodate by thermal neutron capture was inspired by the possibility that careful measurements of the yields of the various iodine valence states might be employed in a test of the "ligand loss" hypothesis.[2a] This hypothesis states that the chemical nature of the fragments created from a molecule–ion by a nuclear transformation is governed by the distribution of bonding electrons in the species prior to the disruptive event. Recent determinations[2b] of the relative concentrations of the radiochlorine valence states produced by thermal neutron capture in $KClO_2$, $KClO_3$, and $KClO_4$ gave a qualitative agreement with the hypothesis. Quantitative information on the distribution of electrons in solid KIO_3 and KIO_4 has become available from Mössbauer effect studies[3] and from chemical shift determinations in high-resolution measurements on the energies of photoelectrons produced by X-rays in these compounds.[4] The positive charge on the iodine atoms in KIO_3 and KIO_4 appears to be significantly larger than that on the chlorine atoms in $KClO_3$ and $KClO_4$, respectively. According to the "ligand loss" hypothesis, the yields of radioiodine recoil valence states should differ from those for the corresponding states of recoil radiochlorine.

A second development further stimulated this research. Neutron irradiation of the very long lived ^{129}I had been known to produce a 12.5-hr iodine activity presumably directly by an (n,γ) reaction. However, recently it has been found[5] that between one-half and two-thirds of the 12.5-hr ^{130}I was formed *via* the decay of a highly internally converted 9.2-min iodine isomer also produced by neutron capture in ^{129}I. In contrast, 25-min ^{128}I which is formed by neutron capture in

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(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) (a) W. F. Libby, *J. Am. Chem. Soc.*, **62**, 1930 (1940); (b) G. E. Boyd and Q. V. Larson, *ibid.*, **90**, 5092 (1968).

(3) D. W. Hafemeister, G. DePasquali, and H. deWaard, *Phys. Rev.*, **135B**, 1089 (1964).

(4) (a) C. S. Fadley, S. B. M. Hagström, J. M. Hollander, M. P. Klein, and D. A. Shirley, *Science*, **157**, 1571 (1967); (b) C. S. Fadley, S. B. M. Hagström, M. P. Klein, and D. A. Shirley, *J. Chem. Phys.*, **48**, 3779 (1968); (c) D. A. Shirley, *Science*, **161**, 745 (1968).

(5) D. D. Wilkey and J. E. Willard, *J. Chem. Phys.*, **44**, 970 (1966).

stable ^{127}I does not appear to result from the decay of any isomers. Hence, the possibility existed for comparing the chemistry of radioiodine recoils produced by differing sequences of nuclear events if KIO_3 and KIO_4 containing chemically combined ^{127}I and 1.6 × 10^7 year ^{129}I were irradiated with neutrons. In many instances in condensed phases the yields of products from (n,γ) and (IT) processes have been found to be quite similar despite the large difference in the characters of these two processes. It was of interest, therefore, to determine if an isotopic effect would be observed in KIO_3 and in KIO_4.

Experimental Section

Materials. Reagent grade crystalline KIO_3 and KIO_4 were irradiated with neutrons to produce 25-min ^{128}I recoils. Potassium iodate containing IO_3^- labeled[6] with ^{129}I was prepared by heating a solution of Na^{129}I with a large excess of inactive HIO_3 (prepared by converting a 0.16 *M* KIO_3 solution with H form of Dowex 50X-8) in a closed vessel for several hours at 60°, neutralizing the mixture with KOH, and recrystallizing the KIO_3 three times before isolating and drying the crystals. Crystalline KIO_4 containing $^{129}IO_4^-$ was prepared from $K^{129}IO_3$ following the procedure described by Brauer[7] in which $Cl_2(g)$ was employed to oxidize KIO_3 dissolved in a strongly alkaline KOH solution. The slightly soluble $K^{129}IO_4$ was separated by repeated recrystallization from pure water, dried in air at *ca.* 100°, and then vacuum dried over liquid nitrogen.

Chemical analyses of both isotopically labeled preparations were made. Microtitrations of the $K^{129}IO_3$ indicated that the I^- ion it contained was negligibly small. Analysis of the $K^{129}IO_4$ by precision titrations with standard arsenite and thiosulfate solutions, respectively, indicated that no IO_3^- ion was present. These analyses were essential to establish that the ^{129}I, added as iodide ion, was converted quantitatively to either $^{129}IO_3^-$ or $^{129}IO_4^-$ ions, respectively.

Crystalline KIO_3 and KIO_4 containing ^{131}I tracer as iodide ion for thermal transfer annealing experiments were prepared by dissolving approximately 0.5 g of salt in 10 ml of 4 *M* NH_4OH containing "carrier-free" ^{131}I tracer and isolating the crystalline solid by "freeze-dry" techniques. The "doped" KIO_4 crystals were stored over CO_2-ice to prevent a slow reaction observed at 25°.

Neutron Irradiations. Neutron irradiations were conducted in three reactors,[2,8] the LITR, the ORR, and the BSF. The thermal neutron fluxes in the active lattice positions employed in the LITR and ORR were 1.5 × 10^{13} and 4.9 × 10^{13} cm^{-2} sec^{-1}, respectively. The γ-ray intensities and fast neutron fluxes in both of these reactors were quite large. Irradiations in the BSF were performed in a special facility where a highly thermalized neutron flux and an extremely low intensity of γ rays were maintained.[8] Bombardments of 2–3-min duration were employed to produce 25-min ^{128}I; 1-hr bombardments were made when the 12.5-hr ^{130}I activity was desired. The irradiated crystals in the latter instance were stored in CO_2-ice until their analysis; in the experiments with 25-min ^{128}I, the analysis was performed within a few minutes after removal of the crystals from the reactor. Irradiations at −78° (CO_2-ice) temperatures also were made in the BSF thermal neutron facility.

Analysis. The distribution of ^{128}I and ^{130}I among the iodine valence states was determined by analysis of aqueous solutions of the irradiated compounds. The crystals were dissolved in alkaline media (*i.e.*, 0.1 *N* $NaHCO_3$, 0.1 *N* NaOH, or 6 *M* NH_4OH) to prevent isotopic exchange reactions from occurring between "reduced" iodine (*i.e.*, I^-, I_2, IO^-) and IO_3^- or IO_4^- ions. Rapid exchange of iodine activity between I^- and I_2 in aqueous solutions at 25° has been demonstrated,[9] but the exchange of I^- with IO_3^- ion in neutral solutions is known to be extremely slow.[10] It also seems likely that radioiodine exchange between IO^- and IO_3^- ions in alkaline aqueous solutions (pH 12) is very slow.[11] This assumption was checked experimentally in this research.

Isotopic exchange and redox reactions of periodate ion also must be considered. Exchange of iodine activity between labeled IO_3^- and IO_4^- ions occurs only in acid solutions and here but slowly.[12] However, the oxidation of iodide by periodate ion even in neutral media occurs rapidly so that alkaline solutions must be employed when these iodine valences occur together.

If molecular iodine is produced, IO^- ion will be formed by hydrolysis in strongly alkaline solutions (*i.e.*, 1 *M* NaOH) and will decompose into iodate and iodide.[13] Iodite ion, IO_2^-, appears to be unknown in aqueous solutions although it has been assumed to occur as an intermediate in the decomposition of hypoiodite. The chemistry of iodine therefore suggests that recoil radioiodine if formed as IO^- or IO_2^- in crystalline iodate or periodate will not be observed when irradiated iodates or periodates are dissolved in alkaline solutions. Radioiodine (*i.e.*, $^*I_2$) will not be observed because of its rapid hydrolysis and subsequent disproportionation reactions.

Three procedures were employed for determining the distribution of recoil iodine between the iodide, iodate, and periodate oxidation states: (a) chromatographic separation of I^- and IO_3^- ions with strong-base anion-exchange columns and alkaline aqueous eluent solutions; (b) separation of I^-, IO_3^-, and IO_4^- ions by fractional precipitations from strongly ammoniacal aqueous solutions;[14] and (c) separation of (I^- + I_2 + IO^-) from IO_3^- ions by solvent extraction with dilute solutions of iodine in CCl_4 followed by back-extraction of the iodine into molar Na_2SO_3 solution.

Unfortunately, none of the foregoing methods gave a direct assay for IO_4^- ion. Unsuccessful attempts were made to effect an anion-exchange column separation of periodate, but the oxidation potential of IO_4^- even in alkaline solution appeared to be sufficiently high that the ion always was reduced by the anion exchanger.

In the ion-exchange procedure, the 12.5-hr ^{42}K activity also induced in the crystals was removed prior to the anion-exchange column separations by passing the solution of irradiated KIO_3 through a shallow bed of Dowex 50 cation exchanger. To obtain the yields of the radioiodine species, the γ-ray activity in the effluent volumes containing the peaks was measured with a 4π geometry ionization chamber and compared with the total activity in the effluent. γ-Ray spectra emitted by the peak fractions were measured with a 3 × 3-in. (Na + Tl)I crystal connected with a 400-channel pulse height analyzer. Lines characteristic of 25-min ^{128}I or of 12.5-hr ^{130}I only were observed. In the experiments with ^{128}I, measurements of the decay of the γ activity in the column fractions gave a pure 25-min half-life.

Chromatographic experiments performed with solutions of $^{131}I^-$ served to establish the identity of the I^- ion peak observed in the separations. The absence of an isotopic exchange reaction between I^- and IO_3^- ions in 0.1 *M* $KHCO_3$ solution was demonstrated in an experiment in which K^{131}I in 5 ml of 0.1 *M* $KHCO_3$ was mixed with 50 mg of inactive KIO_3 and heated at 100° for 3 hr. A chromatographic separation of this mixture gave but one peak, that caused by I^- ion.

In the fractional precipitation method of analysis irradiated KIO_3 or KIO_4 was dissolved in concentrated ammonia (6 *M*) solution containing iodide, iodate, and periodate carriers. Silver iodide was precipitated and separated from the supernatant solution, and then a precipitate of $AgIO_3$ was produced by neutralizing and acidifying the supernatant with concentrated nitric acid and adding Ag^+. A second precipitation of $AgIO_3$ on top of the first was made by the addition of carrier IO_3^- ion and $AgNO_3$. After separating the $AgIO_3$, the IO_4^- ion remaining in solution was reduced with Na_2SO_3 and AgI was precipitated. Because of the slight solubility of $AgIO_3$ and the fact that most of the radioiodine was usually retained as iodate, the determinations of radioperiodate were never as reliable as those for radioiodide. A small "carry-over" of radioiodate, which was reduced with periodate by sulfite, tended to cause a high value for the iodine activity measured in the periodate fraction.

The efficiency of the solvent extraction separation procedure was tested in experiments with ^{131}I tracer which showed that the removal of radioiodide plus iodine from water into CCl_4 was quantitative and that a complete recovery from the organic phase was ob-

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(6) Approximately 0.1 g of 1.6 × 10^7 year ^{129}I, isolated from the uranium fission products, was received as NaI in a basic sodium sulfite solution. The isotopic composition was 86.1% ^{129}I–13.9% ^{127}I.

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(12) M. Cottin and M. Haissinsky, *Compt. Rend.*, **224**, 1636 (1947).

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(14) A. V. Bellido, *Radiochim. Acta*, **7**, 122 (1967).

tained on back-extraction with 1 *M* Na_2SO_3 solution. This method of analysis determines $I^- + I_2$. Periodate will react with iodide ion to give iodine; however, it has been shown[15] that when radioiodide ion is added to inactive IO_4^- no radioactivity appears as IO_3^-. However, radioperiodate is reduced to give radioiodate ion.

Radiolysis and Radiation Annealing Measurements. Crystalline KIO_3 and KIO_4 were exposed to ^{60}Co γ rays at *ca.* 30° in a constant geometry source arrangement[16] in which the dose rate in water measured with a Fricke dosimeter solution was 1.03×10^{18} eV g^{-1} min^{-1}. Determinations of the radiolytic decomposition of iodate were made by micropotentiometric titration for I^- ion in aqueous solutions of the irradiated KIO_3. Iodate formed in the radiolysis of KIO_4 was determined by dissolution of an aliquot of the irradiated solid in acid solution and titration with standard thiosulfate to determine $IO_3^- + IO_4^-$ followed by dissolution of another aliquot in basic solution and titration with standardized arsenous acid to determine IO_4^-. The difference in titers gave the amount of iodate. Radiation annealing experiments with neutron-irradiated $K^{129}IO_3$ and $K^{129}IO_4$ crystals also were performed in the ^{60}Co γ-ray source.

Thermal Annealing Measurements. Neutron-irradiated $K^{129}IO_3$ and $K^{129}IO_4$ were heated for 1 hr (isochronal anneal) at a series of temperatures up to the melting or decomposition temperature of the compound in an investigation of the effect of heat on the initial distribution of radioiodine activity among the iodine valence states. The crystals, contained in a porcelain boat, were heated in air in a tube furnace maintained at a temperature constant to ±2° which was measured to ±1° with a thermocouple. At the conclusion of the anneal the crystals were cooled abruptly and stored in CO_2-ice until analysis.

Measurements of the thermal transfer of ^{131}I contained as iodide ion in "doped" KIO_3 and KIO_4 crystals prepared by freeze drying were made with the same arrangement. The radioactivity of the crystals was measured before and after heating as, in the case of KIO_4 especially, significant losses of ^{131}I, presumably by volatilization, were observed.

Thermal Decomposition Studies. Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were performed on crystalline KIO_3 and KIO_4. The former salt melted with decomposition at 560° to give potassium iodide, oxygen gas, and small quantities of iodine vapor. The KIO_4 decomposed rapidly and quantitatively at 285° to give KIO_3 and oxygen gas as inferred from the observed weight loss.

Experimental Results

Chemistry of ^{128}I and ^{130}I Recoils in KIO_3. Results from this work (Table I) and from earlier investigations[1,11,14] have revealed that thermal neutron capture in crystalline KIO_3 at room temperature produces a significantly different pattern of chemical consequences from those observed with $KClO_3$ and $KBrO_3$. For example, a much larger fraction (65–70%) of radioactive halogen was retained by the target IO_3^- ion than in ClO_3^- or BrO_3^- ions where retentions of *ca.* 5 and 24% of radiochlorine[2] and radiobromine,[8] respectively, have been observed for similar irradiations. Moreover, no radiohypoiodite ($*IO^-$) or iodite ($*IO_2^-$) was found in KIO_3 compared with $KClO_3$ and $KBrO_3$ where small yields of $^{38}ClO_2^-$ and $^{38}ClO_2$ and $^{82}BrO_2^-$ and $^{82}BrO^-$, respectively, are observed. In contrast with $KClO_3$ and $KBrO_3$, however, a small but significant yield (*ca.* 1.8%) of radioperiodate ion was produced in KIO_3 (*cf.* Table I).

Table I. Radioiodine Recoil Yields Produced by Neutron Capture in Crystalline KIO_3 and KIO_4[a]

Salt irradiated	$R(I^-)$, %	$R(IO_3^-)$, %	$R(IO_4^-)$, %
$K^{127}IO_3$	27.9	69.5	2.6
$K^{129}IO_3$	28.0	70.8	1.2
$K^{127}IO_4$	2.7	87.0	10.1
$K^{129}IO_4$	9.8	83.4	6.7

[a] 2-Min irradiation in ORR at 35°, $\phi_t = 5.9 \times 10^{15}$ cm^{-2}.

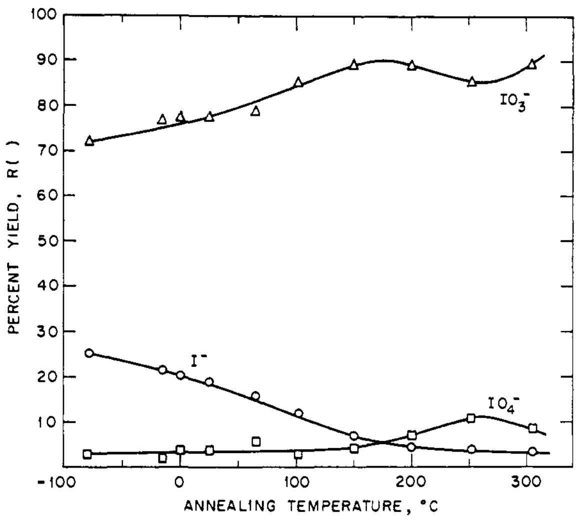

Figure 1. Isochronal thermal annealing of neutron-irradiated $K^{129}IO_3$ (1-hr irradiation at −78° in Bi + D_2O thermal neutron facility).

Fragmentary earlier investigations[11,14] with $NaIO_3$ have shown that the retention of recoil ^{128}I increases on heating the irradiated solid in the temperature interval from 80 to 170°, and evidence for the occurrence of annealing reactions at temperatures as low as −30° which increase the iodate retention has been published.[17] The isochronal thermal annealing measurements in this research (Figure 1) confirm the earlier work and further indicate that decreases in the radioiodide and increases in radioiodate yields may begin even at temperatures as low as −80°. Interestingly, conversion of $^{130}IO_3^-$ to $^{130}IO_4^-$ occurred at temperatures above 150°, while above *ca.* 280° thermal decomposition of $^{130}IO_4^-$ to $^{130}IO_3^-$ took place.

The action of energetic ionizing radiations on neutron-irradiated alkali metal iodates might be expected to alter the retention of radioiodide. However, the report[11] that the retention of ^{128}I was increased in $NaIO_3$ by post-neutron irradiation with 50-kV X-rays did not appear to be confirmed by the finding[14] that the relative yields of ^{130}I in the I^-, IO_3^-, and IO_4^- fractions of reactor neutron bombarded salt were independent of the time of bombardment. The data of Table II ob-

Table II. Dependence of ^{130}I Distribution on Time of Reactor Irradiation of $K^{129}IO_3$[a]

LITR irradiation time, min	ϕ_t, cm^{-2}	$R(I^-)$, %	$R(IO_3^-)$, %	$R(IO_4^-)$, %
5	4.5×10^{15}	24.8	74.5	0.6
15	13.5×10^{15}	20.9	78.9	0.2
60	54×10^{15}	15.0	84.5	0.5

[a] Irradiation at ambient temperature of *ca.* 40°.

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(15) P. Magnier, *Bull. Soc. Chim. France*, 626 (1947).

(16) C. J. Hochanadel and J. A. Ghormley, *Radiation Res.*, **16**, 653 (1962).

(17) A. H. W. Aten, Jr., M. Lindner-Groen, and L. Lindner, "Chemical Effects of Nuclear Transformations," Vol. II, IAEA, Vienna, 1965, p 125.

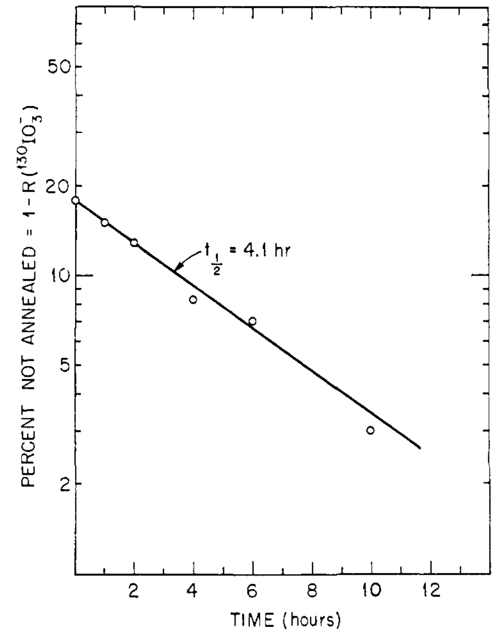

Figure 2. Annealing at *ca.* 30° of recoil ^{130}I in neutron-irradiated $K^{129}IO_3$ by ^{60}Co γ rays.

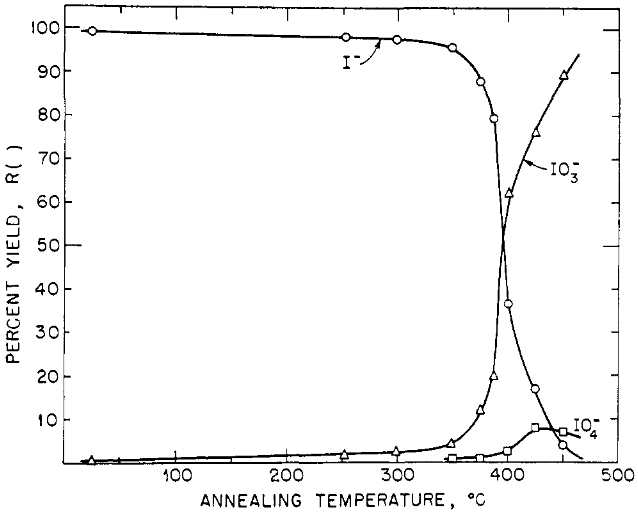

Figure 3. Isochronal thermal transfer annealing of ^{131}I initially present as iodide ion in KIO_3.

tained in this investigation support the view that a radiation annealing may occur during reactor bombardment; further, this annealing may be substantial. Cobalt-60 γ rays also effected a radiation annealing to form $^{130}IO_3^-$ from radioiodide as may be seen from Figure 2. The kinetics of the radiation annealing at the source temperature of *ca.* 35° was first order over a tenfold decrease in the $^{130}I^-$ ion concentration. The rate of the radiation annealing of radioiodide to iodate was significantly greater than the annealing of radiobromate in neutron-irradiated $KBrO_3$ where the half-time was approximately 20 hr.

Measurements on the thermal transfer annealing of iodine-131 initially incorporated into KIO_3 as iodide ion are presented in Figure 3. The conversion of radioiodide to radioiodate in these experiments contrasted with the behavior of recoil radioiodide shown in Figure 1. The relative concentration of $^{131}I^-$ decreased but little on heating until the temperature exceeded 300°. Between 350 and 450°, however, a rapid conversion to $^{131}IO_3^-$ took place and surprisingly above 400° small amounts of radioperiodate were formed. At 450° approximately 90% of the iodine-131 was combined as iodate and about 8% as periodate with 2% remaining as uncombined iodide. The behavior shown in Figure 3 differs somewhat from observations[18] on the same reaction in $Ca(IO_3)_2$ where the transformation of $^{131}I^-$ to $^{131}IO_3^-$ began near 200° and increased slowly on further heating up to a temperature of 400° where approximately 82% of the iodine-131 activity was transformed to iodate. In the transformation of $^{131}I^-$ in KIO_3 and in $Ca(IO_3)_2$, small amounts of activity were lost from the crystals as was shown by measurements of their total activity before and after heating. This loss suggests that I_2 may be formed as an intermediate in the transformation of iodide to iodate, and the data must therefore be interpreted with caution. The relative concentrations plotted in Figure 3 were based on the total activity in the crystal after thermal treatment.

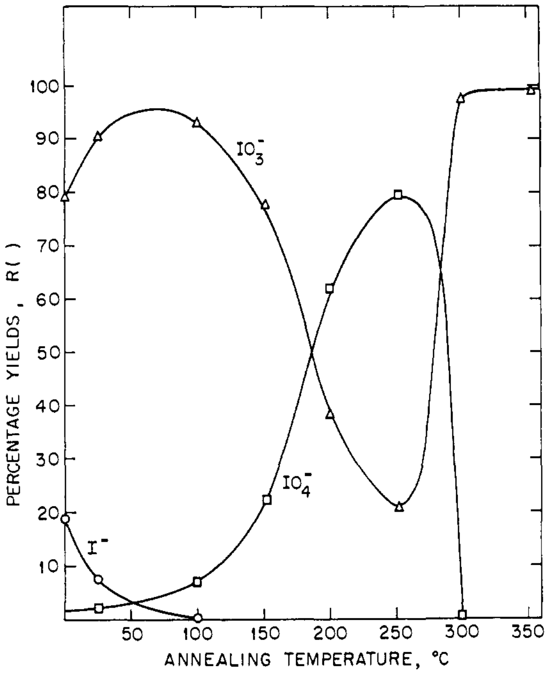

Figure 4. Isochronal thermal annealing of neutron-irradiated $K^{129}IO_4$ (1-hr irradiation at −78° in Bi + D_2O thermal neutron facility).

Chemistry of ^{128}I and ^{130}I Recoils in KIO_4. Previous observations[19] on the distribution of recoil ^{128}I activity among the iodine oxidation states in crystalline KIO_4 have indicated that radioiodate was the dominant species (86%) with smaller amounts of radioiodide (10%) and radioperiodate (4%) also formed. Subsequent investigations,[14] including those from this research given in Table I, have agreed approximately with these observations, although the relative concentration of radioiodide was significantly smaller and that of radioperiodate was larger than quoted. Of further interest is the fact that (Table I) the relative concentrations of ^{130}I activity in the iodine valence states differ from those for ^{128}I.

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[19] A. H. W. Aten, Jr., G. K. Koch, G. A. Wesselink, and A. M. deRoos, *J. Am. Chem. Soc.*, **79**, 63 (1957).

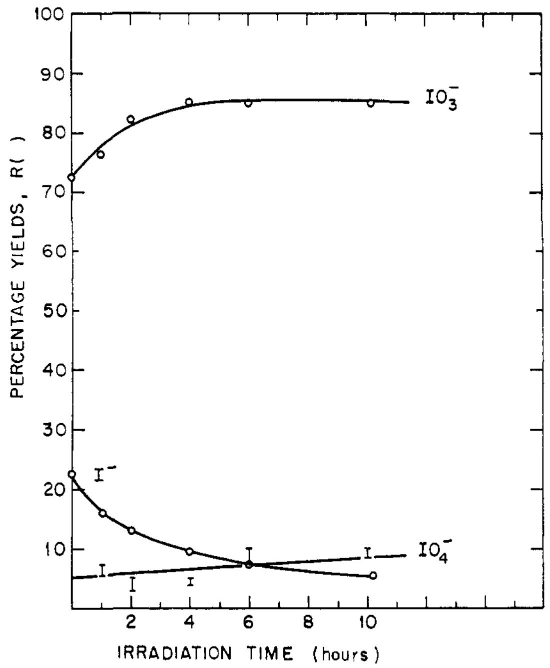

Figure 5. Radiation annealing at *ca.* 30° of neutron-irradiated $K^{129}IO_4$ by ^{60}Co γ rays (1-hr irradiation at −78° in Bi + D_2O thermal neutron facility).

On heating neutron-irradiated KIO_4, the radioiodide concentration decreased and became undetectable above 100° (Figure 4). Initially, radioiodide appeared to be transformed into radioiodate, and at temperatures above 100° the radioiodate was converted to radioperiodate to an increasing extent with increasing temperature until the decomposition temperature (285°) of KIO_4 was approached where the relative concentration of $^{130}IO_4^-$ abruptly decreased to zero and that of $^{130}IO_3^-$ rose to approximately unity. Aten and coworkers[19] had observed the decrease in radioiodide and the increase in radioperiodate shown in Figure 4, but they did not study the change in $^{128}IO_3^-$, nor did they heat irradiated KIO_4 above 250°.

Irradiation of neutron-bombarded $K^{129}IO_4$ with ^{60}Co γ rays caused a decrease in the concentration of radioiodide and an increase in the concentrations of radioiodate and periodate as may be seen in Figure 5. However, the relative concentration of $^{130}I^-$ did not decrease to zero, but rather approached a stationary value after 8–10 hr of γ irradiation. The KIO_4 was estimated to have been radiolytically decomposed to approximately 1.1% after this time.

The measurements (Figure 6) on the thermal transfer annealing of iodine-131 initially incorporated into KIO_4 as iodide ion are of interest in that the relative concentration changes in radioiodide, iodate, and periodate with increasing temperature resembled those observed in the isochronal annealing of neutron-irradiated $K^{129}IO_4$ (Figure 4) except that the transformations of iodide to iodate and to periodate and the decompostion of periodate occurred at a significantly higher temperature in the experiments with ^{131}I. Appreciable quantities of iodine-131 activity were lost from the crystal during the 1-hr heating periods in the transfer annealing studies. Hence, the relative concentrations plotted in Figure 6 were based on the total iodine-131 activity in the KIO_4 at the end of the heating when the solid was quenched to CO_2-ice temperatures before analysis.

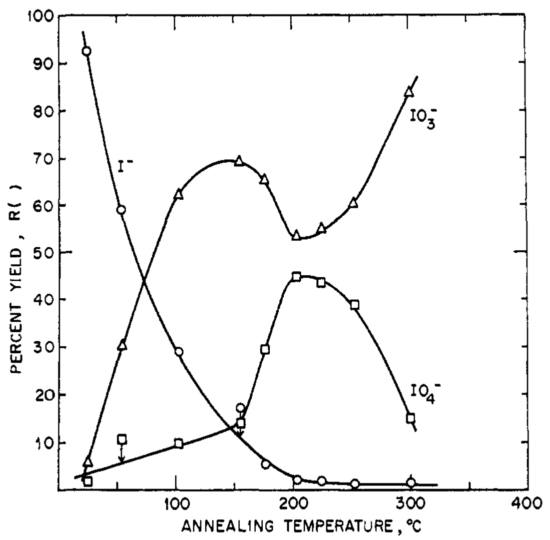

Figure 6. Isochronal thermal transfer annealing of ^{131}I initially present as iodide ion in KIO_4.

Discussion

Three facts of primary importance to an understanding of the chemistry of radioiodine recoils in crystalline KIO_3 and KIO_4 have been brought out in this research: (a) the large relative yields of $^{128}IO_3^-$ and $^{130}IO_3^-$ observed with both salts; (b) the production of small but significant yields of $^{128}IO_4^-$ and $^{130}IO_4^-$ in both salts; and (c) the ease with which thermal and radiation annealing of $^{128}I^-$ and $^{130}I^-$ ions can be induced. Because of the onset of rapid, low-temperature annealing processes in KIO_3 and KIO_4, it seems probable that the "ligand loss" hypothesis will not apply, although the observed relative yields of radioiodide, radioiodate, and radioperiodate are not inconsistent with the hypothesis. The ligand loss hypothesis would predict primary yields unaltered by solid-state reactions when recoil iodine atoms are produced by mechanical recoil following thermal neutron capture. Neither of these conditions appears to be met in the formation of ^{128}I and ^{130}I in the alkali metal iodates and periodates. Recent reports[20] suggest that internal conversion of capture γ radiations occur in the production of ^{128}I.

The production of radioperiodate both in the neutron irradiations and subsequently by thermal annealing is in striking contrast with what is known about the recoil chemistry of radiochlorine in $KClO_3$ and about radiobromine in $KBrO_3$. With neutron-irradiated $KClO_3$, a yield of only 0.05% $^{38}ClO_4^-$ was found,[2] while with $KBrO_3$ no $^{82}BrO_4^-$ whatsoever could be detected.[21] The retentions of recoil radioactivity by the perhalates also show an interesting difference: with $KClO_4$ the relative concentration of $^{38}ClO_4^-$ was but 0.8%, whereas with KIO_4 the relative yields of $^{128}IO_4^-$ and $^{130}IO_4^-$ were 10.1 and 6.7%, respectively. The foregoing facts

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(20) Recent capture γ-ray data (*cf.* L. V. Groshev, G. A. Bartholomew, *et al.*, *Nucl. Data*, 5 (1–2), 76 (1968)) indicate, however, that a 132-keV γ ray is present in high relative abundance (42%) in the decay of the compound nucleus ^{128}I. This low-energy transition may be appreciably internally converted, and the recoil of ^{128}I may occur *via* "Coulomb explosion."

(21) L. C. Brown, G. M. Begun, and G. E. Boyd, *J. Am. Chem. Soc.*, **91**, 2250 (1969).

and the observed rapid oxidation of radioiodide by thermal or radiation annealing suggest that the valence distribution of the radiohalogen recoils may be determined by the intracrystalline oxidizing potential of the halate and perhalate crystal lattices. Another factor of undoubted importance is the great stability of the iodate ion as revealed by its high decomposition temperature and by its unusually small susceptibility to radiolysis. Among the halates only KIO_3 is stable thermodynamically toward decomposition to halide plus oxygen gas at 298.2°K.

The thermal annealing of radioiodide to radioiodate in neutron-irradiated KIO_3 and KIO_4 occurred at temperatures significantly lower than in the transfer annealing of iodine-131 added as iodide ion to the same, but nonirradiated, salts. This difference would appear to be explicable in terms of the differing local environment of the radioiodide in the two cases. The $^{128}I^-$ and $^{130}I^-$ recoils produced by neutron capture will reside initially in small, highly damaged regions of the crystal containing the fragments of the disrupted target IO_3^- or IO_4^- ions as well as products from the radiolysis of adjacent molecular ions resulting from the recoil halogen and oxygen atoms and from ionizing radiations arising from isomeric transitions, etc. (Auger radiolysis). The likelihood of a rapid recombination between the correlated fragments in a damage center should be high and may explain the low-temperature oxidation of iodide, particularly since it is unstable thermodynamically relative to iodate ion. The transfer annealing reaction (oxidation or exchange) of $^{131}I^-$ to form iodate ion which occurs only at much higher temperatures must result from quite a different set of circumstances in the crystal lattice than does the low-temperature annealing of radioiodine recoil species.

A small isotopic effect was observed between ^{128}I and ^{130}I in KIO_3 and KIO_4 although the difference changed sign between the two salts. The cause of the effect, as with ^{80m}Br and ^{82}Br, resides in the differing sequence of nuclear events leading to the formation of the radiohalogen recoils. With ^{128}I mechanical recoil arising from the emission of neutron capture γ rays is probably the chief process,[20] whereas with ^{130}I at least 50% of the events involve the complex effects of an IT process following the mechanical recoil of ^{130m}I by the capture γ rays emitted when the latter is produced. The observed small isotope effect appears consistent with the model of small, widely spaced damage centers in the crystal which contain the recoiled radioactive species. The fact that there is a difference between ^{128}I and ^{130}I and that, at least with the bromine isotopes, this difference persists during a thermal annealing suggests that the details of the structure of the damage center may differ for isotopes formed by (n,γ) and by (IT) processes, respectively.

The relative ease of the annealing of recoil radioiodide in KIO_3 and KIO_4 by energetic ionizing radiations indicated that electronic as well as thermal excitation in the damage center must occur. Presumably the electronic excitation is dependent on the long-range migration of energy (exciton) to the damage centers. According to this picture radiation annealing will be a first-order process in its early stages as is observed.[22]

The unusual stability of the iodate ion toward thermal or radiolytic decomposition deserves final mention because of its obvious bearing on the chemistry of radioiodine recoils in both KIO_3 and KIO_4. The latter salt, in contrast to KIO_3, is not exceptionally stable; it readily decomposes on heating to KIO_3 and oxygen gas and to the same products in good yield on exposure to ^{60}Co γ-rays. An hypothesis to account for the behavior of KIO_3 might be that a highly efficient back reaction (annealing reaction) acts to restore transitorily disrupted iodate ions. This same reaction would also account for the relative large retention of recoil iodine as iodate in KIO_3 and for the rapidity with which recoil iodine may be converted to iodate either by heat or by energetic ionizing radiations.

(22) A. G. Maddock, F. E. Treloar, and J. I. Vargas, *Trans. Faraday Soc.*, **59**, 924 (1963).