[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Szilard-Chalmers Reaction with Inorganic Compounds of Iodine[1,2]

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The chemical consequences of neutron capture by iodine in various inorganic forms have been investigated. Activation of solid iodates causes the majority of the I^{128} atoms to appear in a reduced chemical state. The retention as iodate increases, however, when the solids are subjected to elevated temperature or ionizing radiations after bombardment. Neutron bombardment of aqueous iodate yields active iodine in reduced form. The retention in neutral solutions is 20%. This can be decreased to 6% by small additions of reductant and increased to 40% by additions of oxidant. The observed variations in retention can be treated semi-quantitatively by a simple kinetic scheme involving iodite as a reaction intermediate. Neutron bombardment of aqueous periodate yields active iodate and reduced forms. Again the distribution between iodate and reduced forms is influenced by solution composition. Similarities in behavior to the iodate system are noted and a unified mechanism indicating the energy spectrum of the recoil atoms is suggested.

The production of separable activity by neutron bombardment of the central atom of an oxygenated anion has been demonstrated in several instances[3] and the behavior of iodates in these circumstances has been qualitatively determined. Since isotopic exchange between iodate and reduced forms of iodine (iodide, iodine and hypoiodite) occurs at an appreciable rate only in strongly acid solutions,[4] there is a wide range of experimental conditions under which the yield of activity in the reduced forms may be determined after bombardment of iodate. Isotopic exchange of iodine between periodate, iodate and reduced forms is equally slow and if the range of acid concentration where oxidation of iodine to iodate by periodate occurs is avoided, a change in the chemical form of the target iodine atoms is possible. In the present study, quantitative determinations have been made of distribution of I^{128} activity between the various valence states of iodine (taking the reduced forms as a group, since isotopic exchange among them is rapid[5]) after neutron bombardments of various solid inorganic compounds and solutions of pentavalent and heptavalent iodine.

Experimental Procedures

Bombardment.—The neutron bombardment of the samples was performed by two general methods: (1) The solid samples were placed in silica test-tubes and immersed in a tank of water at a distance of approximately one inch from a 300-mg. Ra–Be neutron source. (2) The solutions were placed in a wide-mouth bottle and the Ra–Be neutron source placed in a central silica test-tube. Bombardments were continued for at least one half-life of iodine (25 min.) but no attempt was made to reproduce the bombardment conditions with precision, since the activity distribution between the various states was presumed to be independent of the amount of activity produced.

A few experiments were performed using neutrons produced by the action of X-rays from a Van de Graaf generator on metallic beryllium. Appreciable changes in the composition were produced during bombardment by the great X-ray intensity, and therefore this procedure was abandoned.

Separation from Iodate Samples.—To the neutron bombarded solid, after dissolving in water, or to the neutron bombarded solution, 5 ml. of 0.1 *M* sodium iodide was added as a carrier for the lower valence states of iodine. Silver iodide was precipitated by the addition of a slight excess of 0.05 *M* silver nitrate solution. Collection, treatment and counting of precipitates is described later.

The iodate fraction was precipitated by the addition of a slight excess of barium nitrate solution to the filtrate from the preceding operation. The order of these two precipitations had no effect on the observed activities.

In a few cases, periodate carrier was added to the bombarded solution and isolated as potassium periodate. No activity was found in these fractions.

Separation from Periodate Samples.—To the neutron bombarded solid, after dissolving in water, or to the neutron bombarded solution, carrier amounts of iodate and iodide were added, the latter in an amount corresponding to only a few per cent. of the periodate present. The reaction

$$2I^- + 2H^+ + IO_4^- \longrightarrow I_2 + IO_3^- + H_2O$$

occurs rapidly and the iodine produced was isolated by extraction into carbon tetrachloride, from which it was returned to aqueous sodium bisulfite and precipitated as silver iodide. It has been shown[6] that when active iodide is added to inactive periodate, no activity appears as iodate. However, in these experiments a small correction must be made to the observed periodate and iodate activities subsequently observed, due to the reduction by iodide. In the data reported, these corrections have been made.

After removal of the reduced forms of iodine, the aqueous solution was treated with a slight excess of 6 *M* potassium nitrate and the precipitate of potassium periodate collected. The iodate fraction was isolated from this filtrate by precipitation as barium iodate.

Collection and Counting of Precipitates.—An adaptation of the methods of Armstrong and Schubert[7] was used in preparing precipitates for activity determinations. A cup of filter paper was prepared with the aid of a filter plate and plunger. This cup, together with a second circle of filter paper used below the cup for support on the filter plate, was weighed in a small aluminum dish. After weighing, the paper cup and its support were replaced in the filter plate, the precipitate was collected, washed with water and acetone and dried for 7–10 min. in air, using a water aspirator. Previous tests had shown that constant weight was reached by this procedure.

The precipitates were next counted as collected by placing the filter plate in a standard shelf arrangement in front of a mica-window Geiger tube surrounded by a cylindrical lead shield. Where the procedure permitted, the filtrate was examined for activity in a liquid counter to confirm the efficiency of separation. Radioactive decay corrections, using a value of 25 min. for the half-life of I^{128}, were applied in comparison of samples counted at different times.

After counting, the precipitates and filter papers were dried in air at 110° to remove moisture accumulated while counting and again weighed for determination of the chemical yield in each fraction. The observed activities were corrected by the ratio of iodine added for that fraction to iodine collected for that fraction.

The weights of the silver iodide precipitates were approximately 100 mg., and since this material was spread as uniformly as possible over the area of the filter paper cup (approx. 13 cm.^{2}) no correction for self-absorption was necessary. However, the weights of the barium iodate and potassium periodate precipitated amounted to several grams,

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[1] From the doctoral dissertation of Robert E. Cleary.

[2] Work supported in part by the U. S. Atomic Energy Commission under contract AT (11-1)–38.

[3] W. F. Libby, THIS JOURNAL, **62**, 1930 (1940).

[4] J. W. Kennedy and O. E. Myers, *ibid.*, **72**, 950 (1950).

[5] M. Haissinsky, *J. chim. phys.*, **47**, 957 (1950).

[6] P. Magnier, A. Khrounoff, M. Martin, P. Daudel and R. Daudel, *Bull. soc. chim. France*, 626 (1947).

[7] W. D. Armstrong and J. Schubert, *Anal. Chem.*, **20**, 270 (1948).

and therefore a correction curve for self-absorption was constructed and used.

Experimental Results

Solids.—The retention of activity by the target compound after neutron bombardment has been measured for several crystalline iodates and the results are given in Table I. Each value reported for the untreated salts (items 1, 13, 25–28) is the average of at least two independent experiments, except in the case of $LiIO_3$, where only one determination was made. As stated in the preceding section, experimental tests indicated that no periodate activity is formed in the bombardment of iodates, and therefore the results represent the distribution between the two fractions iodate and reduced forms (iodide, iodine and hypoiodite).

Table I

Retention of Solid Iodates

Compound	Treatment after bombardment	Retention, %
1 $NaIO_3$	None	67^a
2 $NaIO_3$	None	73^b
3 $NaIO_3$	Heated at 80°, 10 min.	69
4 $NaIO_3$	Heated at 80°, 17 min.	73
5 $NaIO_3$	Heated at 80°, 17 min.	75
6 $NaIO_3$	Heated at 116°, 10 min.	78
7 $NaIO_3$	Heated at 116°, 20 min.	87
8 $NaIO_3$	Heated at 110°, 60 min.	86
9 $NaIO_3$	Heated at 170°, 60 min.	90
10 $NaIO_3$	50 Kv. X-rays, 15 min.	78
11 $NaIO_3$	50 Kv. X-rays, 60 min.	82
12 $NaIO_3$	50 Kv. X-rays, 60 min.	75^c
13 NH_4IO_3	None	22
14 NH_4IO_3	None	31^b
15 NH_4IO_3	Heated at 65°, 10 min.	31
16 NH_4IO_3	Heated at 65°, 20 min.	31
17 NH_4IO_3	Heated at 80°, 3 min.	35
18 NH_4IO_3	Heated at 80°, 10 min.	31
19 NH_4IO_3	Heated at 80°, 16 min.	31
20 NH_4IO_3	Heated at 80°, 20 min.	35
21 NH_4IO_3	50 Kv. X-rays, 5 min.	30
22 NH_4IO_3	50 Kv. X-rays, 15 min.	35
23 NH_4IO_3	50 Kv. X-rays, 20 min.	34
24 NH_4IO_3	50 Kv. X-rays, 60 min.	35^b
25 KIO_3	None	67
26 $LiIO_3$	None	66
27 HIO_3	None	60
28 $KHIO_3$	None	53

[a] 7 expts., average deviation from mean, 0.6%. [b] Neutron bombardment was by Van de Graaf X-Rays on Be. [c] The X-irradiation preceded neutron bombardment, which was as in *b*.

The effect upon retention of heat treatment of the crystals after bombardment has been observed through the following technique: The irradiated crystals were quickly dropped into a small mineral oil-bath surrounded by a boiling liquid. After the desired period at this elevated temperature, the boiling liquid was removed and an organic solvent was added to the oil and crystals to quickly lower the temperature. The crystals were washed with organic solvents to remove oil and then dissolved in water for the usual analysis. Results of this treatment for two compounds are shown in Table I.

The effect upon retention of X-irradiation of the crystals after neutron bombardment has also been observed. The exposures were made with the solid sample uniformly spread in the circular depression of a lucite plate of the same dimensions as the filter plate. This sample holder was clamped in a reproducible position approximately one-half inch from the window of a Machlett AEG 50T X-ray tube, operated at 50 PKV and 20 ma. (*ca.* 10^5 R./min.). The results of these experiments are given in Table I.

Iodate Solutions.—The retention of activity was determined for solutions of sodium iodate in concentrations of 0.01 to 0.5 *M* adjusted to *p*H values from 1 to 12 by use of dilute iodic acid and sodium hydroxide. In seven such determinations, the mean retention was 20% and the average deviation 1%. All experiments on retention in aqueous solutions were performed with the Ra–Be neutron source, since it was observed that higher and irreproducible retentions were obtained when bombardments were with neutrons generated by Van de Graaf X-rays on Be. Simultaneously, a microscopic oxidation of iodide to iodate was observed, indicating that the radiation decomposition effects were superimposed on the nuclear effects. No such indications were present in the work with the Ra–Be neutron source, which has a much lower radiation to neutron intensity ratio.

The retention by iodates in aqueous solution may be altered by the addition of small amounts of oxidizing and reducing agents prior to bombardment. The same reagents added after bombardment have no effect on the retention. The results of these experiments using the reductants iodide ion and methanol, and the oxidant periodate ion, are shown in Figs. 1, 2 and 3. In each case the retention is found to be a regular function of the ratio of reductant (or oxidant) to iodate, rather than the absolute concentrations of these species. Data to illustrate this point are indicated in the figures.

When the added reagent is an iodine compound the contribution of radioactive iodine arising from capture by iodine atoms in the additive must be considered. In the case of iodide, neutron capture was found to produce only reduced forms of iodine activity and the amounts used are small. The correction to the observed iodide activity was therefore simple and usually small. It will be shown later that neutron capture by periodate yields chiefly iodate activity and an appropriate correction on the observed iodate activity was made.

The effect of periodate upon the retention by iodate was found to be a function of the *p*H of the bombarded solution (see Fig. 4). Considerable difficulty was experienced in obtaining reproducible results in the critical region of *p*H. After many experiments it was found that added methanol, equivalent to two mole per cent. of the iodate present, permitted the desired reproducibility. As seen from Fig. 2, this amount by itself would not be expected to affect the retention.

The retention was also measured for several solutions of iodate containing both an oxidizing and a reducing additive. The observed values are given in Table II, together with values calculated from the behavior of each additive by itself in a fashion described in the Discussion.

Table II

Retention by Iodate in the Presence of Both Periodate and Methanol

$\frac{\text{Concn. MeOH}}{\text{Concn. } IO_3^-}$	$\frac{\text{Concn. } IO_4^-}{\text{Concn. } IO_3^- \times 10^3}$	Retention, % Obsd.	Retention, % Calcd.
0.985	1	22	18
.985	2	24	23
.985	3	26	26
.985	4	25	28
.192	2	30	31
.497	2	28	27
.693	2	26	25
1.482	2	22	20

Periodate Solutions.—Using the analytical procedure previously described, the distribution of activity between three fractions, periodate, iodate and reduced forms, was measured after neutron bombardments of periodate solutions. The reducing effect of methanol was studied and the effect of *p*H observed (Table III).

Other Experiments.—A few qualitative tests were performed in an attempt to cast some light on the nature of possible intermediates in the reduction reaction brought about by neutron capture.

Vinyl iodide may be an efficient exchange reagent for iodine atoms in the same manner as the bromoölefins.[8] As a test for the existence of iodine activity in atomic form sub-

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(8) W. H. Hamill, R. R. Williams, Jr., and H. A. Schwarz, This Journal, **72**, 2813 (1950).

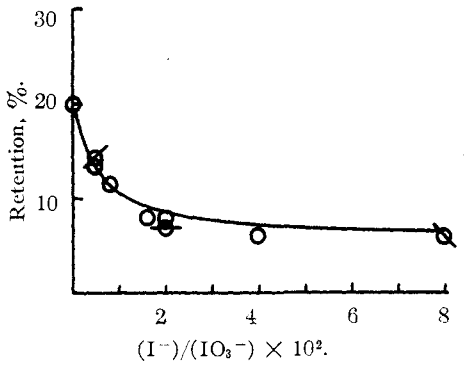

Fig. 1.—Retention by aqueous iodate with iodide: O, iodate = 0.42 *M*; ⊘, iodate = 0.25 *M*; ϕ, iodate = 0.10 *M*; θ, iodate = 0.05 M. Solid line corresponds to $k_7/k_4 = 5 \times 10^2$.

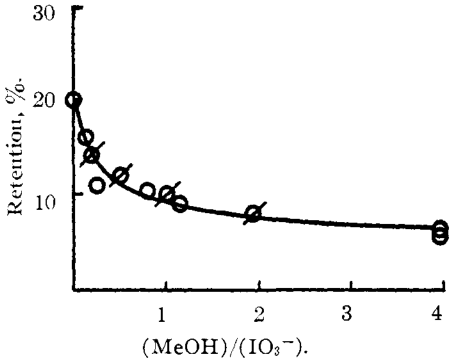

Fig. 2.—Retention by aqueous iodate with methanol; O, iodate = 0.42 *M*; ø, iodate = 0.25 *M*; solid line corresponds to $k_7/k_4 = 8.1$.

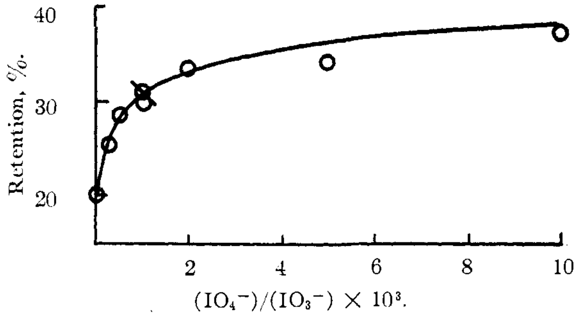

Fig. 3.—Retention by aqueous iodate with periodate: O, iodate = 0.25 *M*; θ, iodate = 0.10 *M*. Additional points not shown at $(IO_4^-)/(IO_3^-) \geq 10^{-1}$: 40, 39, 40, 40, 41% retention. Solid line corresponds to $k_6/k_4 = 2.5 \times 10^{-3}$.

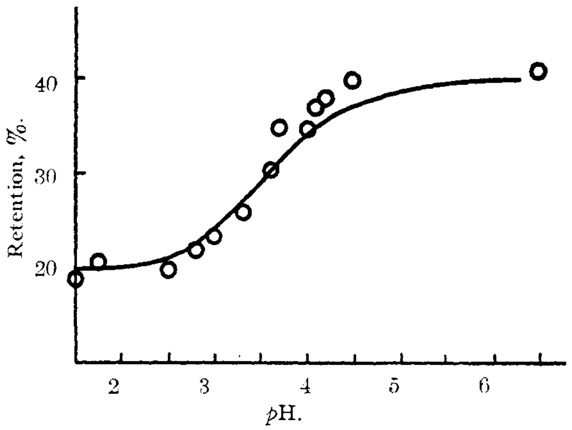

Fig. 4.—Retention by aqueous iodate (0.36 *M*) with periodate (0.031 *M*) at various acidities.

sequent to neutron capture, small amounts of vinyl iodide in alcohol solution were added to solutions of sodium iodide and sodium iodate. After neutron bombardment of these solutions, carbon tetrachloride extracts were made to remove organic iodides, but these extracts were inactive, indicating failure of this test.

Possible importance of the form hypoiodite was tested as follows: A solution of sodium hypoiodite was bombarded with neutrons at −3° (to suppress chemical reaction) and from this solution barium iodate was precipitated and found to be inactive, indicating no oxidation by neutron capture in hypoiodite. In a second experiment molecular iodine was added to a solution of sodium iodate of *p*H 12, containing I^{131}. After 15 minutes iodine was extracted with carbon tetrachloride, returned to aqueous solution with thiosulfate and precipitated as silver iodide. This preparation was inactive, indicating lack of rapid isotopic exchange between hypoiodite and iodate at *p*H 12.

TABLE III

DISTRIBUTION OF ACTIVITY IN NEUTRON BOMBARDMENT OF PERIODATE SOLUTIONS

Concn. IO_4^-	Concn. MeOH / Concn. IO_4^-	*p*H	Activity distribution, % IO_4^-	IO_3^-	I^-
0.187	0	6	8	85	7[a]
.187	0	1.8	5	91	4
.124	1.33	6–7	5	75	20
.124	2.66	6–7	5	60	35
.124	5.31	6–7	8	41	51
.187	14.8	1.8	5	30	65
.187	15.8	6–7	9	28	63
.187	26.7	6–7	5	26	68
.187	39.7	7	7	24	69
.045	82	2.0	5	28	67

[a] Two independent experiments giving the same result.

Summary and Discussion

Retention in Solids.—The data reported in Table I may be summarized as follows: Retention is high and experimentally constant in the crystalline alkali metal iodates. It is successively less in iodic acid, potassium biniodate and ammonium iodate. Heat treatment or the absorption of ionizing radiations after bombardment causes some increase in retention. This effect appears to be greatest in the substance of highest retention (sodium iodate) and in this case a limiting retention of approximately 90% seems to be reached after extensive heat treatment. This is an increase of approximately 23% in retention, while the corresponding increase for ammonium iodate is only about 10%. These effects correspond qualitatively to the retention changes studied by Boyd, *et al.*,[9] in solid sodium bromate.

Retention in Solution.—The retention in aqueous iodate solutions is independent of concentration and *p*H at a value of 20 ± 1%. In Figs. 1 and 2, data are given which demonstrate the decrease in retention brought about by the reducing agents iodide ion and methanol. The limiting lower value of retention appears to be 6% for both reagents. The retention by sodium iodate may also be increased above 20% by addition of periodate (see

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[9] G. E. Boyd, J. W. Cobble and S. Wexler, THIS JOURNAL, **74**, 1282 (1952).

Fig. 3). The upper limit of retention appears to be 40%.

The data summarized above indicate that neutron capture by iodate ions in aqueous solution produces at least three distinguishable products. A small fraction (0.06) of true retention apparently occurs. In this fraction of events the structure of the ion may not be destroyed, possibly through extensive cancellation of gamma recoil momenta. It should be noted that a similar lower limit of retention occurs in the case of periodate bombardment, which strengthens the hypothesis that this value is largely determined by the nuclear reactions rather than by the chemical environment (see Table III).

A second fraction (0.60) of the neutron capture processes apparently leads to reduced forms of iodine regardless of solution composition, since the retention reaches an upper limit of 40% in the presence of the oxidizing agent periodate. The third fraction (0.34) appears to represent an unstable intermediate formed by the recoil reaction, one which can be oxidized to iodate or reduced to the lower valence states by small amounts of appropriate reagents. In the absence of such reagents, the intermediate appears to be reduced and oxidized in nearly equal amounts. One may postulate it to be the iodite ion.

The formation of three distinct recoil products and the subsequent behavior of the intermediate may be ascribed to variations in the recoil energy in the capture act, probably through partial cancellation of momenta as suggested above. Three primary reactions may be postulated as

$$
\mathrm{IO_3^-} + \mathrm{n} \longrightarrow
\begin{cases}
\mathrm{I^*O_3^-} & (6\%) \quad (1) \\
\mathrm{I^*O_2^-} + \mathrm{O} & (34\%) \quad (2) \\
\mathrm{I^*O^-} + 2\mathrm{O} & (60\%) \quad (3) \\
\text{or } \mathrm{I^{*-}} + 3\mathrm{O} &
\end{cases}
$$

The ultimate fate of the radioactive iodine produced in reactions (1) and (3) is independent of minor variations in solution composition. Reaction (2), however, results in a product which may be sufficiently stable to react in the fashion of free radicals and other reaction intermediates and the following reaction mechanism is proposed to describe the experimental observations

$$\mathrm{I^*O_2^-} + \mathrm{IO_3^-} \longrightarrow \mathrm{I^*O_3^-} + \mathrm{IO_2^-} \qquad (4)$$

$$\mathrm{I^*O_2^-} + \mathrm{IO_3^-} \longrightarrow \mathrm{I^*O^-} + \mathrm{IO_4^-} \qquad (5)$$

$$\mathrm{I^*O_2^-} + \text{oxidant} \longrightarrow \mathrm{I^*O_3^-} \qquad (6)$$

$$\mathrm{I^*O_2^-} + \text{reductant} \longrightarrow \mathrm{I^*O^-} \qquad (7)$$

According to this mechanism, the fraction of activity, f, (referring only to that portion which is subject to variation) found as $\mathrm{IO_3^-}$ will be

$$f_{\mathrm{IO_3^-}} = \frac{k_4(\mathrm{I^*O^-})(\mathrm{IO_3^-}) + k_6(\mathrm{I^*O_2^-})(\text{ox.})}{k_4(\mathrm{I^*O^-})(\mathrm{IO_3^-}) + k_5(\mathrm{I^*O_2^-})(\mathrm{IO_3^-}) + k_6(\mathrm{I^*O_2^-})(\text{ox.}) + k_7(\mathrm{I^*O_2^-})(\text{red.})}$$

which reduces to

$$f = \frac{1}{1 + \dfrac{k_5(\mathrm{IO_3^-}) + k_7\,(\text{red.})}{k_4(\mathrm{IO_3^-}) + k_6\,(\text{ox.})}} \qquad (8)$$

The experiments reported in Table V correspond to three simplified forms of this relation

Case I: (red.) = (ox.) = 0

$$f = \frac{1}{1 + \dfrac{k_5}{k_4}} \qquad (9)$$

Case II: (ox.) = 0, (red.) > 0

$$= \frac{1}{1 + \dfrac{k_5}{k_4} + \dfrac{k_7(\text{red.})}{k_4(\mathrm{IO_3^-})}} \qquad (10)$$

Case III: (red.) = 0, (ox.) > 0

$$f = \frac{1 + k_6(\text{ox.})/k_4(\mathrm{IO_3^-})}{1 + \dfrac{k_5}{k_4} + \dfrac{k_6(\text{ox.})}{k_4(\mathrm{IO_3^-})}} \qquad (11)$$

The value of k_5/k_4 may be obtained from the retention observed in solutions of sodium iodate alone. This value was 20%, while the total range of retention is 34%. The value of k_5/k_4 is therefore 1.43.

Figure 1 demonstrates that the experimental data obtained on addition of the reductant iodide ion are satisfactorily described by equation (10). The points represent the observed retention plotted against $(\mathrm{I^-})/\mathrm{IO_3^-}$ and a reasonable range of absolute concentrations is covered. The solid curve is drawn from equation (10), using a value of k_7/k_4 of 5×10^2, chosen for best fit.

Figure 2 repeats this test for equation (10) in the case of a second reductant, methanol, and again the retention is observed to be a function of the ratio of concentrations rather than their absolute values. The value of k_7/k_4 used in this case to obtain the curve shown was 8.1 and its lower value indicates that the specific reaction rate of the intermediate is greater with iodide ion than with methanol.

Figure 3 demonstrates the agreement of the data on the effect of periodate with an equation of the form of (11). The value of k_6/k_4 chosen to give best fit is 2.5×10^{-3}. Again the dependence of the retention on the ratio of concentrations rather than their absolute value is demonstrated by the data.

The retention has been measured in solutions containing both methanol and periodate, a situation to which equation (8), the general form, should apply. Using the values of k_5/k_4, k_7/k_4 and k_6/k_4 found previously, the retention is computed in each case and compared with the experimental value. The agreement, as shown in Table II, is considered adequate.

An effect of the pH of the solution on retention is observed in the presence of periodate, as shown in Fig. 4. Since this effect does not occur in solutions containing iodate alone, or in the presence of reducing agents, it must be attributed to a change in the oxidizing power of periodate with the hydrogen ion concentration. Using equation (11), the value of k_6/k_4 from Fig. 3, and an additional parameter corresponding to an effective equilibrium constant for the process

$$\text{Inert species} \rightleftarrows \mathrm{H^+} + \text{Oxidant}$$

the smooth curve shown in Fig. 4 may be constructed. Best fit of the experimental observations requires a value of approximately 10^{-5} for this constant. Although this value does not correspond with any of the real or apparent dissociation constants of periodic acid, the complications of simultaneous hydrolytic equilibria obscure the situation.[10]

Retention by periodate solutions (Table III) shows some similarities suggestive of the behavior of iodate. The retention as periodate appears to be independent of solution conditions and to have a value (av. = 6%) experimentally indistinguishable from the minimum retention observed with iodate (6%). This observation may be taken to support the previous suggestion that, due to partial cancellation of recoil momenta, insufficient energy is available for rupture of the parent ion. The second similarity is found in the existence of a minimum fraction of reduced form (also 6%) in the presence of an oxidant (periodate itself). That this value should be much smaller than the corresponding value for iodate (60%) is not surprising in view of the greater number of bonds to be broken in periodate. Finally, the third fraction of variable fate again appears, amounting to some 60% (the difference between the two extremes of the iodate or iodide fractions) and could apparently be described by a relation such as equation (8). A fourth fraction, amounting to approximately 28%, is apparently reduced only as far as iodate, regardless of solution conditions. The approximate equality of this fraction with the variable fraction of 34% in the case of iodate suggests the possibility of the following unified description of the consequences of neutron capture by the two species: Due to partial momentum cancellation or other features of the neutron capture process (such as possible internal conversion) the recoil reactions are divided into the following spectrum: 5%, no bond rupture; 28–34%, loss of one O atom (or ion); 60–54%, loss of two O atoms (or ions); 6%, loss of three or more O atoms (or ions). This possibility may be summarized by the scheme

$$\begin{array}{llll}
IO_4^- + n & \longrightarrow I^*O_4^- & (6\%) & \multirow{2}{*}{$\left.\right\}$ retention} \\
 & \longrightarrow I^*O_3^- & (28\%) & \\
 & \longrightarrow I^*O_2^- & (60\%) & \text{variable fraction} \\
 & \longrightarrow I^*O^- & (6\%) & \text{reduced form} \\
 & & & \\
IO_3^- + n & \longrightarrow I^*O_3^- & (6\%) & \text{retention} \\
 & \longrightarrow I^*O_2^- & (34\%) & \text{variable fraction} \\
 & \longrightarrow I^*O^- & (54\%) & \multirow{2}{*}{$\left.\right\}$ reduced forms} \\
 & \longrightarrow I^- & (6\%) &
\end{array}$$

NOTRE DAME, INDIANA

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(10) C. E. Crouthamel, A. M. Hayes and D. S. Martin, THIS JOURNAL, 73, 82 (1951).

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Oxidation Potentials of the Neptunium(III)-(IV) and the Neptunium(V)-(VI) Couples in Perchloric Acid

BY DONALD COHEN AND J. C. HINDMAN

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The oxidation potentials of the Np(III)–Np(IV) and Np(V)–Np(VI) couples have been measured as a function of temperature in 1 *m* perchloric acid solution. The formal potential for the cell reaction (equation 4) is −0.1551 ± 0.0010 volt at 25°. For this reaction at 25°, $\Delta\bar{H}$ is −5.7 ± 0.2 kcal. and $\Delta\bar{S}$ is −31.2 ± 0.8 e.u. For the reaction (equation 1) the formal potential is −1.1373 ± 0.0010 volts at 25°. $\Delta\bar{H}$ for this reaction at 25° is 28.1 ± 0.2 kcal. and the partial molal entropy change is 6.4 ± 0.6 e.u.

As part of a program to obtain adequate data on which to base calculations of thermodynamic properties of neptunium ions and compounds, measurements have been made of the potentials of the various neptunium couples in 1 *m* perchloric acid as a function of temperature. In this communication the data on the Np(III)–Np(IV) and the Np(V)–Np(VI) couples are summarized. A subsequent publication will deal with the investigation of the Np(IV)–Np(V) couple and the calculations of the partial molal heats and free energies of formation of the neptunium ions.

The oxidation potentials of the neptunium(III)–(IV) and –(V)–(VI) couples in 1.0 *M* HCl at 25° have been measured by Hindman, Magnusson and La Chapelle.[1] They found both couples to be reversible at a platinum electrode. Hindman and Kritchevsky[2] investigated the polarographic behavior of the Np(III)–Np(IV) couple in hydrochloric and perchloric acids at 25°. This couple was found to be polarographically reversible in hydrochloric acid but irreversible in perchloric acid. This irreversible behavior of the Np(III)–Np(IV) couple in perchloric acid is not observed at an inert electrode.

Experimental

E.m.f. measurements were made on cells of the type

$$\text{Pt} : \text{H}_2 : \text{HClO}_4 : \text{HClO}_4, \text{Np(O)}, \text{Np(R)} : \text{Pt}$$

where Np(O) and Np(R) refer to the oxidized and reduced form of the neptunium ion for the particular couple. The potentials of the cells were measured at various neptunium ratios in molal perchloric acid at three temperatures. The ratios of Np(V) to Np(VI) and Np(III) to Np(IV) were prepared electrolytically using a continuous-control type potentiostat. Blank determinations showed that at the potentials used in these electrolyses secondary reactions such as oxygen or hydrogen deposition did not occur. In addition, the coulometer readings agreed with the total neptunium content of the solutions as determined by alpha assay. From this it was concluded that the current efficiency was 100%.

The starting material, in all cases, was a solution of pure Np(V) in 1.0 molal $HClO_4$ prepared by a procedure similar to that previously described.[3] The electrolysis cell and the potentiostat have been described by Wehner and Hindman.[4]

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(1) J. C. Hindman, L. B. Magnusson and T. J. La Chapelle, THIS JOURNAL, 71, 687 (1949).

(2) J. C. Hindman and E. S. Kritchevsky, *ibid.*, 72, 953 (1950).

(3) R. Sjoblom and J. C. Hindman, *ibid.*, 73, 1744 (1951).

(4) P. Wehner and J. C. Hindman, *ibid.*, 72, 3911 (1950).