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Radiation Effect on Periodate Salts in Solution Phase

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The (n,γ) reactions in aqueous solutions of sodium and potassium periodates have been studied in presence of nitrite additives. It has been found that the retention and yield are remarkably influenced by additives. The yield of radioiodate and radioperiodate decreases and that of radio-iodide increases both at room (25 °C) and at liquid nitrogen (−196 °C) temperatures. The irradiation in frozen aqueous glass leads to retention and yield totally different from those observed in aqueous phase. A suitable mechanism is suggested to explain the results.

Introduction

The chemical effects following (n,γ) recoil have been studied in a large number of halates during past years [1–4]. Studies of thermal annealing effects in neutron irradiated solids were vast as a means of indirect elucidation of the processes following nuclear reactions in the irradiated matrices [5]. However, in spite of a considerable wealth of data on the subject the mechanism of these processes is still very imperfectly understood [6, 7]. A considerable amount of work has been done on the (n,γ) recoil reactions in periodate systems [8, 9]. Arnikar *et al.* [10] have also studied γ-radiolysis in aqueous solution of redox mixtures containing periodates. These results were explained on the basis of oxidizing and reducing properties of the additives over the unstable intermediate formed during recoil. Here we report results of our study of the (n,γ) activation of the periodate and nitrite mixture in solution phase.

Experimental

Compounds and Neutron Source

All the compounds used for the experiment were of B. D. H. and A. R. grade. The targets were irradiated by thermal neutrons from a 300 mCi Ra–Be neutron source of integrated flux 3.2 × 10^6 n/cm^{-2} sec^{-1}. Under the experimental set-up fast neutrons were thermalized by successive collisions with the carbon and hydrogen atoms of the moderator.

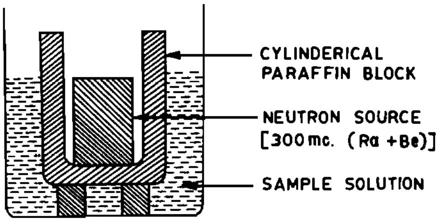

Fig. 1. Arrangement for thermal neutron irradiation of solution.

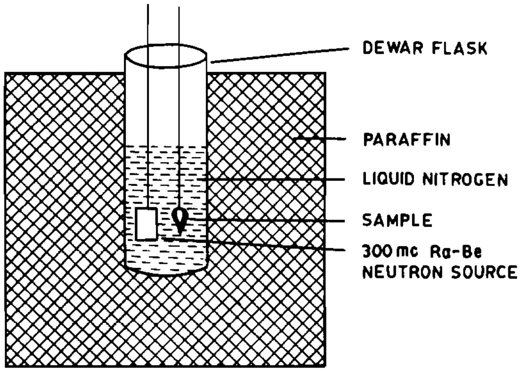

Fig. 2. Arrangement for irradiation at −196 °C.

Thermal Neutron Irradiation of Aqueous Solution

For the irradiation of salts in solution phase, a hollow cylindrical paraffin block of 3 cm thickness was made inside a beaker. The neutron source was placed in the inner hollow portion of the paraffin block. Thermal neutron irradiation in the solution phase of the target materials along with the additives was performed by keeping the solution in the second beaker (Fig. 1). The solutions of the periodates and nitrite were prepared by using double distilled water.

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TABLE 1. Activity Distribution of Recoil ^{128}I in Thermal Neutron Irradiated Aqueous Solution of Pure Sodium and Potassium Periodates at Room Temperature (25 °C).[a]

Target	Concentration (M)	% Activity Distribution		
		IO_4^-	IO_3^-	I^-
$NaIO_4$	0.070	9.9	75.4	14.7
	(0.070)	(14.5)	(61.5)	(24.0)
KIO_4	0.065	11.2	72.2	16.6
	(0.065)	(16.2)	(66.0)	(17.8)

[a] The values given in the parenthesis are at the liquid nitrogen temperature irradiation.

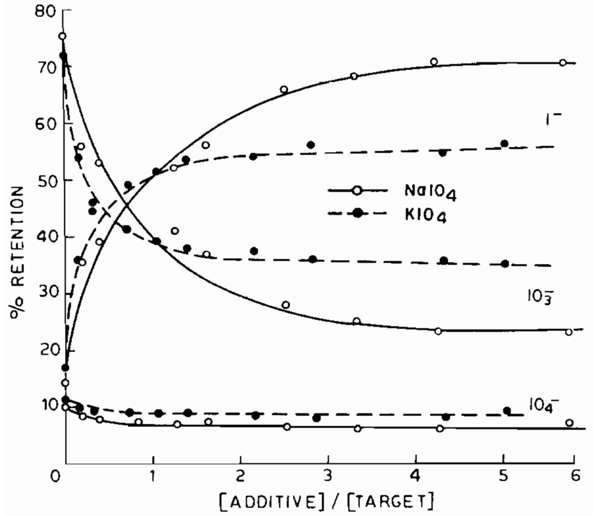

Fig. 3. Distribution of recoil ^{128}I activity in forms of I, IO_3, and IO_4 ions produced during thermal neutron irradiation of periodates solution containing nitrite additive at 25 °C.

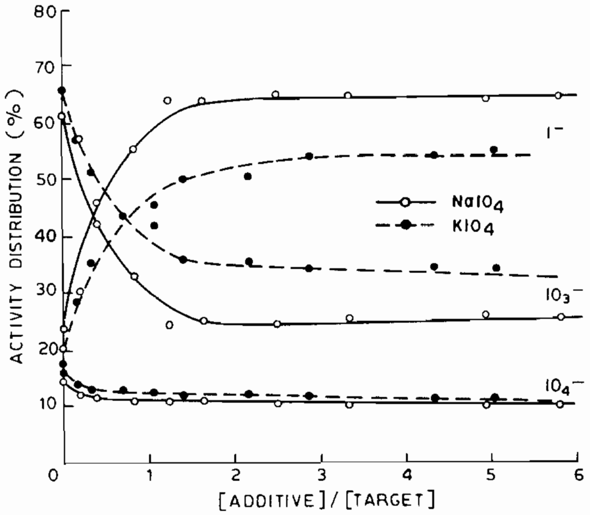

Fig. 4. Distribution of recoil ^{128}I activity in forms of I, IO_3 and IO_4 ions produced during thermal neutron irradiation of periodates solution containing nitrites additive at −196 °C.

Thermal Neutron Irradiation of Frozen Aqueous Glass

The aqueous solutions of the targets were freezed drop by drop in a soda glass test tube at liquid nitrogen temperature and then dipped in liquid nitrogen contained in Dewar-flask, together with neutron source (Fig. 2). The samples were irradiated for three hours.

Chemical Analysis

The distribution of recoil ^{128}I activity in three stable forms *i.e.* radio-iodide, -iodate and -periodate were performed by fractional precipitation and solvent extraction methods [11]. The fractions were collected as their silver salts. The precipitates of the three radioactive products were dried and the activity was counted with an end window G.M. counter. Correction for the decay time and background followed the method of Aten [12].

From the corrected radioactivities in iodide, iodate and periodate fractions the retentions are calculated using the equations which have been described previously [13].

Results

The retention and yields of ^{128}I in solution phase irradiation of pure $NaIO_4$ and KIO_4 without additives at room (25 °C) and at liquid nitrogen temperature (−196 °C) are given in Table I. The observations show that the retention and yield found in liquid and glass phase are quite different from those observed in crystalline matrices [14]. Each value reported is the average of at least three independent experiments, the reproducibility of individual determinations of retention being within ±1%. The presence of an additive causes a marked variation in the distribution of ^{128}I activity. With increasing concentration of the nitrite additives there is a sharp decrease in retention by 4–5% from aqueous solution of periodates. The radio-iodide yield has been found to increase while the corresponding radio-iodate yield decreased (Figs. 3 and 4) with the increase of concentration of nitrite additive. The major observations are:

(i) For the irradiation of aqueous solution of $NaIO_4$ and KIO_4, the retention values at 25 °C irradiation are 9.9 and 11.2%, respectively.

(ii) The changes in retention are fast in the beginning and slow down later leading nearly to constant maximum values.

(iii) Retention decreases with the concentration of nitrite additives in the case of (n,γ) irradiated aqueous solution of periodate.

Discussion

The results obtained in the solution phase irradiation can be explained mainly by chemical reactions. When nuclear reactions are carried out on molecules already in solution, the products observed may be: (a) the result of non breaking of bonds as a result of too low a recoil energy; (b) the rapid reformation of bonds of species held together for a sufficient time by the solvent cage; (c) the interaction of ion radicals and molecules formed in the local hot zone and (d) the interaction of activated species with the bulk of solvent after diffusion out of the local hot zone. From our present experiment it is observed that the periodates reduced to iodate only. No other reduction product is observed so long as an excess of periodate is there in the solution. After complete reduction of periodate to iodate, the iodate formed may undergo decomposition giving iodide as the stable product. In the case of periodate solution the decrease of radio-iodate and radio-periodate in favour of iodide is probably due to stepwise oxidation reaction by oxidizing species formed either from local radiolysis or from additives. The retention and yields are dependent on the initial concentration of periodate and they have tendency to attain a steady value with increasing the concentration of nitrite additives. On the other hand periodate itself being an oxidizing agent oxidizes reduced radio-iodide fragments. The additives prevent these reduced radio-iodine fragments from oxidation by inactive periodate. Therefore, the radio-iodate concentration from aqueous periodate decreased mainly in favour of reduced fragments with increasing concentration of additives.

The change in the retention and yield of product can be explained on the basis of a competing reaction of the solute ions with the primary radiolytic product of water. The radiolytic reduction of periodate in aqueous solution has been a subject of certain controversy. The results reported vary from author to author. The major issue of divergence has been with regard to the role of hydroxyl radical. Bart *et al.* [16] considered OH as an oxidizing agent, while Bhattacharyya and Bardhan [17] considered it as a reducing species and suggested the following reactions:

$$IO_4 + OH \longrightarrow IO_3 + HO_2 \tag{1}$$

$$2IO_3 + H_2O \longrightarrow IO_3 + IO_4^- + 2H^+ \tag{2}$$

$$IO_4^- + HO_2^- \longrightarrow IO_3^- + OH^- + O_2 \tag{3}$$

periodate, being an oxidizing agent, it attacked by the reducing species from local radiolytic products of water. The probable reactions are:

$$IO_4^- + e_{aq}^- \longrightarrow IO_3^- + O^- \tag{4}$$

$$IO_4^- + H \longrightarrow IO_3^- + OH \tag{5}$$

$$O^- + H_2O \longrightarrow OH + OH^- \tag{6}$$

In the above reactions periodate is reduced to iodate and an equivalent amount of OH radical is formed. The OH radical does not react directly with periodate. It forms hydrogen peroxide by,

$$OH + OH \longrightarrow H_2O_2 \tag{7}$$

Hydrogen peroxide is known to be a reductant with respect to periodate,

$$IO_4^- + H_2O_2 \longrightarrow IO_3^- + H_2O + O_2 \tag{8}$$

As well the main reaction that IO^- undergoes to form iodate and periodate is the step wise redox reaction. The oxidizing species is probably the OH radical formed by local radiolysis. The neutron capture γ-rays which have keV to MeV energies, can radiolyse water molecules as only 32.5 eV energy is sufficient to produce an ion pair in water [18]. An ejected electron during radiolysis has a total range upto 3×10^{-9} m [19]. The path resembles a random diffusion walk covering a region with a diameter equal to about one third of its total range. The OH radicals formed by it are concentrated around this region while the H atoms diffuse out to about 1.5×10^{-8} m distance. High internal conversion in ^{128}I is known [20] and the emitted γ-rays and highly positively charged iodine atoms are also expected to produce OH radicals.

As the concentration of nitrite ions increases, the hydroxyl radicals are effectively scavenged by NO_2^- which decreases the retention of ^{128}I as $^{128}IO_4^-$. The decrease in retention of periodate fraction in the mixture of periodate and nitrite is very small due to the presence of nitrite in excess as compared to the concentration of OH radical formed by radiolysis of internal γ-rays. The OH radical may also react with NO_2^- to form nitrogen dioxide, which is then hydrolyzed to nitrate and nitrite as:

$$NO_2^- + OH \longrightarrow NO_2 + OH^- \tag{9}$$

$$2NO_2 + H_2O \longrightarrow NO_3^- + NO_2^- + 2H^+ \tag{10}$$

Even at very low concentration of periodates some periodate is reduced to iodate by e_{aq}^-. Also as the concentration of periodate increases it consumes more e_{aq}^- and H giving iodate and OH radical.

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