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Effect of pH on the Szilard–Chalmers Process in NH_4IO_3

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Abstract

The chemical consequences of neutron capture by iodine in NH_4IO_3 under (n, γ) process was investigated. The influence of pH of dissolution on retention and yields has been also studied. The retention values of recoil iodine in crystalline NH_4IO_3 are found to be greater than in the corresponding solution phase irradiation at different pH. Also, the influence of pH of solution on retention and yields was observed at lower and higher pH range. Contribution of different reactive species formed during irradiation and dissolution is discussed to explain the results.

Introduction

Although a considerable amount of work has been reported for the retention in iodates and periodates both in solid and solution phase irradiation [1], studies for retention in these systems with the pH of dissolution under the nuclear processes have not received the same attention. The production of separable activity by neutron bombardment of the central atoms of an oxygenated anion has been demonstrated in several instances and the behaviour of iodates in these circumstances has been qualitatively determined. Some studies on retention in $KMnO_4$ with the pH of solution due to (n, 2n) reaction has been reported [2–4]. However, there exists only a limited amount of data regarding the pH dependence of the oxidation states of recoil ^{128}I in iodates [5] under (n, γ) process. It was therefore considered of interest to investigate the effect of pH on retention of recoil ^{128}I and to try to correlate the retention and yields of the products on the basis of appropriate mechanisms of local radiolysis due to internal γ-rays associated with the neutron source. In the present study qualitative determinations were made of distribution of recoil iodine activity between various valence states of iodine with the pH of dissolution after neutron bombardment of solid and solution of NH_4IO_3.

Experimental

The ammonium iodate was commercially available reagent of high purity. The neutron bombardment of the samples was performed by two methods: (i) the solid iodate was sealed in soda glass ampoules and irradiated by thermal neutrons. Under the experimental set-up the fast neutrons from the 300 mC_i (Ra–Be) neutron source of integrated flux 3.2×10^6 n/cm^2 sec. were cooled down to thermal neutrons by using paraffin block as a moderator. The thermal neutrons thus obtained were used to induce $^{127}I(n, \gamma)^{128}I$ reaction in crystalline ammonium iodate, and (ii), the solution of NH_4IO_3 was prepared by dissolving in the solution of different pH. The detailed procedure for the irradiation in solution phase has been described [6]. All the irradiations were performed for three hours. For the preparation of buffered solutions of desired pH we used the methods of Clark and Lubes [7] and Sorensen [8], and the exact pH was measured. Double distilled water, freshly prepared was used throughout.

The distribution of recoil iodine activity among the iodine valence states was determined by analysis of the irradiated compound. To the neutron-bombarded solid NH_4IO_3 after dissolving in solution of different pH or the neutron-irradiated solution of ammonium iodate in different pH, 5 ml of 0.1 M potassium iodide was added as carrier for the lower valence states of iodine. Iodide was precipitated as silver iodide by the addition of silver nitrate solution. From the filtrate the precipitate of $AgIO_3$ was produced by neutralizing and acidifying the supernatant with concentrated nitric acid. After separating iodate, the IO_4^- remaining in the solution was reduced with Na_2SO_3 and AgI was precipitated. The precipitate of three radioactive products (*i.e.* iodide, iodate and periodate) was dried and activity was counted by placing the dried precipitate in a standard shelf arrangement

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in front of a mica-window Geiger tube surrounded by a cylindrical lead shield. Radioactive decay corrections, using a value of 25 minutes for the half life of recoil iodine, were applied following the method of Aten [9]. From the corrected activity the retention and yields were calculated.

Results and Discussion

The retention of ^{128}I after $^{127}I(n, \gamma)^{128}I$ reaction was determined in NH_4IO_3 in order to estimate the effects of pH of dissolution on the chemical forms of the recoil iodine atoms. The data obtained are given in Tables I and II, and are plotted in Figs. 1A and B. Each value reported for the salt studies is the average of at least two independent experiments. The data on NH_4IO_3 obtained (25.0%) at room temperature irradiation [10, 11] are in good agreement with the result of the present experiment. Lower retention in ammonium iodate compared to all other iodates (65–70%) may be due to the presence of ammonium ion. According to Cabral and Maddock [12], ammonium ions in the hot-zone produce NH_2 and H radicals which act as donor and acceptor in the crystal lattice [13] and, due to presence of NH_2 and H radicals, give higher fractions of iodide instead of iodate. Also, the radiation chemistry of liquid ammonia has been studied from a view-point of the effect of pH on the molecular and radical yields, as in water, by using NH_4Cl and $NaNH_2$ [14, 15]. The primary species yielded by the radiolysis of liquid ammonia are given in equation:

TABLE I. Distribution of Recoil Iodine-128 Activity in Forms of Iodide, Iodate and Periodate Ions in Crystalline NH_4IO_3 exposed and later dissolved in Solution of Various pH.

pH	% Activity distribution		
	IO_3^-	I^-	IO_4^-
1.5	17.5	78.6	3.9
2.0	19.3	74.7	6.0
3.0	22.5	71.8	5.7
5.0	25.8	70.6	3.6
6.0	25.3	71.6	3.1
7.0	26.0	71.0	3.0
8.0	26.9	70.0	3.1
10.0	27.5	70.3	2.2
11.0	33.1	64.8	2.1
12.0	37.7	60.1	2.2

TABLE II. Distribution of Recoil Iodine-128 Activity in Forms of Iodide, Iodate and Periodate Ions in Thermal Neutron Irradiated NH_4IO_3 Solution of Different pH.

pH	% Activity distribution		
	IO_3^-	I^-	IO_4^-
1.5	10.8	84.2	5.0
2.0	11.9	81.1	7.0
3.0	16.0	73.8	10.2
5.0	18.2	72.7	9.1
6.0	19.6	71.8	8.6
7.0	20.1	71.4	8.5
8.0	18.7	72.6	8.7
10.0	19.2	73.3	7.5
11.0	20.0	74.7	5.3
12.0	29.7	66.2	4.1

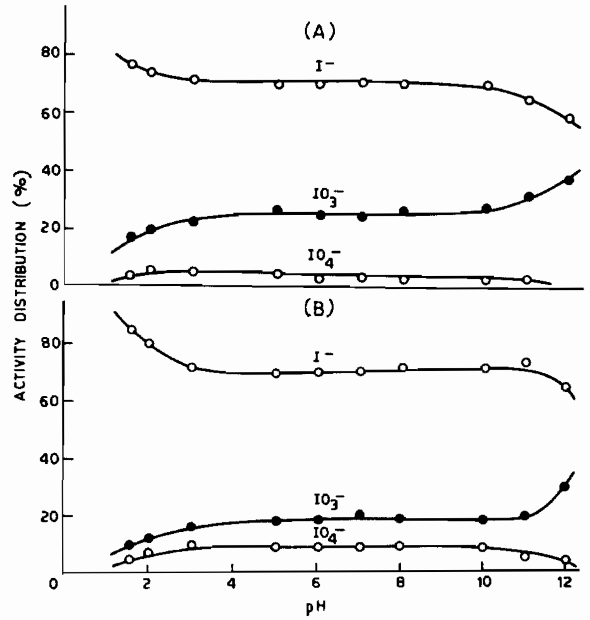

Fig. 1 (A) Activity distitribution *vs.* pH for solid NH_4IO_3 exposed and later dissolved in solutions of various pH values and (B) activity distribution *vs.* pH for NH_4IO_3 solutions.

$$NH_3 \longrightarrow H_2, H, e_{aq}^-, NH_4^+, N_2H_4, NH_2 \text{ and } NH \qquad (1)$$

The stability of solvated electrons causes the increase in the concentration, but may reduce the reactivity. They are scavenged by NH_4^+ as the following reaction:

$$e_{aq}^- + NH_4^+ \longrightarrow NH_3 + H\cdot \qquad (2)$$

in the NH_4 system where the NH_2 radicals became predominant. On the other hand, the NH_2 radicals are scavenged by the solvated electrons.

From Figs. 1 A and B it is observed that the retention and yields found in solution phase irradiation are quite different from those observed in crystalline phase irradiation. With increasing pH of dissolution there is a sharp change in retention in the higher and lower pH range. The values in the higher acidic range fluctuated considerably.

Rapid exchange of iodine activity between I^- and I_2 in aqueous solution has been demonstrated [16], but the exchange of I^- and IO_3^- ion in neutral solution is very slow. Iodide–iodate redox reaction takes place in strongly acid solution producing iodine:

$$5I^- + IO_3^- + 6H^+ \longrightarrow 3I_2 + 3H_2O \qquad (3)$$

The effect of acidity in solution on the I_2 formation has been interpreted by Jortner *et al.* [17]. Radioiodine has not been observed because of its rapid hydrolysis [18] and subsequent disproportionation reaction:

$$I_2 + H_2O \longrightarrow H^+ + I^- + HIO \qquad (4)$$

Therefore, the variation of retention with pH upon dissolution in the lower pH may be partly due to radioiodine exchange between ${}^{128}IO^-$ and inactive IO_3^-. Also, due to molecular iodine, there is a possibility of the formation of IO^- ion in strongly alkaline solution and decomposition into iodate and iodide. 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 and is either oxidized or exchanged with inactive iodate ions during dissolution. Therefore, this assumption requires that any elevation of valence state of iodine fragments must be accomplished by IO_3^- in competition with hydration and reduction reaction with H_2O and its ions. The formation of IO_3^- by an oxidation process depends on the rapid interchange reaction between different valence states of iodine and inactive iodate ions.

Activity *vs.* pH for solid NH_4IO_3 exposed and later dissolved in solution of various pH values are plotted in Fig. 1A. The similarity of the curves in Figs. 1A and B indicates that more than 80% of the activity in the case of irradiated solid ammonium iodate which later dissolved in the solutions of various pH acts in a way similar to that in which most of the activity behaves in the case of irradiated solutions. The reactions in the case of solid being dissolved after irradiation are certainly thermal. At least several minutes elapsed since the thermal recoil occurred, in all cases. The recoil process itself cannot require more than 10^{-12} seconds, therefore the similarity indicates that even in the case of the solution the reactions determining the variation of retention with pH are thermal in character also. At lower pH range the oxidation of water probably proceeds, causing very small retention. Dissolved oxygen in the case of ammonium iodate solutions may act to oxidize the small amount of reduced iodide in alkaline solution, which might then interchange with inactive iodate to leave to activity in the iodate and so account for the alkaline rise in retention.

In conclusion, the experiment described indicates that (i) the IO_3^- ions in solution are disrupted in nearly every instance to form IO_2^-, IO^-, I^- and IO_3^{2-}, (ii), these ions oxidize H_2O rapidly and in neutral and dilute acid solutions this is the predominant reaction, (iii), in alkaline solutions they may combine with OH^- ions to form IO_3^- again at a rate much faster than H_2O oxidation, and (iv), in strong acid solutions the interchange reactions seem to be able to compete with the oxidation reactions.

During radiolysis there is a formation of different radiolytic products i.e. H, OH, H_2O_2 etc... The trapped electrons released during irradiation are subsequently solvated by water molecules and react with IO_3^-:

$$IO_3^- + e_{aq}^- \longrightarrow IO_3^{2-} \longrightarrow IO_2 + O^{2-} \ldots \qquad (5)$$

Such reactions would be expected on the basis of local radiolysis (apart from a ligand-loss hypothesis) and at the higher pH the OH^- may react with unstable intermediates of irradiated iodate, giving radioiodate as a stable product:

$$*IO_2{}^{1+} + OH^- \longrightarrow *IO_3^- + H^+ \qquad (6)$$

$$*IO_3 + OH^- \longrightarrow *IO_3^- + OH\cdot \qquad (7)$$

Also, the lower value of retention in a lower pH could be explained on the basis of the following reactions:

$$\cdot IO_2 + *IO_3^- \longrightarrow IO_3^- + \overset{*}{\cdot}IO_2 \qquad (8)$$

$$I^- + *IO_3^- \longrightarrow *I^- + IO_3^- \qquad (9)$$

The evident effect of pH on the redox potential is best translated into chemical terms by an example. The disproportionation of halogen in hot alkaline solution shows higher yields of iodate as:

$$3*I_2 + 6OH^- \longrightarrow 5I^- + *IO_3^- + 3H_2O \qquad (10)$$

The equilibrium constant of the above reaction is favourable for iodine (I, I $\times 10^{23}$) and the reaction proceeds (via IO_2^- and IO^-) to completion in a matter of minutes for iodate [19]. However, in acid solution the reverse reaction has a favourable equilibrium constant (I, 6×10^{44}). In the case of bromate and iodate the reaction is almost instantaneous and is used in the analysis of these anions. The rate of reaction is usually faster in acid solution than in alkaline or neutral solutions, although it may be hard to distinguish acid catalysis from other changes brought about by decreasing the pH.

The behaviour of iodate ion in solution is more complex. In aqueous phase, the iodate ion has been considered to be unhydrated. But Nightingale *et al.* [20] provided evidence comparing the limiting equivalent conductance and viscosity coefficient for the presence of some interaction between iodate and water molecules, and this is present with much lesser degree with the periodate ions. In iodate the double bond character is less pronounced and the charge is more efficiently delocalized by the oxygen atoms, permitting more extensive interaction with the solvent. In comparison to solids the probability of recombination reactions is much less pronounced in the solution phase because of the probability of redox reactions. In solids, the minimum displacement energy of a recoil atom has been considered as 25 eV [21]. In solution phase, the minimum displacement energy should be even less comparable to that in solids. The recoil atoms having energy in the range of 0 to 25 eV are only around 2%. This means that in the remaining 98% of the recoil events due to radioactive neutron capture in iodates, the I–O bonds are invariably ruptured, and the number of such cleavages (*i.e.* one, two or three) depends upon the recoil momentum.

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