

## Recoil Chemistry of $^{128}\text{I}$ Atoms in Lithium Iodate under $(n, \gamma)$ Process

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Recoil  $^{128}\text{I}$  /  $\text{LiIO}_3$  / Annealing / Phase effect / Additive effect

### Abstract

Kinetics of post-recoil thermal annealing of lithium iodate after  $^{127}\text{I}(n, \gamma)^{128}\text{I}$  nuclear process reveals two first order processes with an associated activation energy of  $6.39 \pm 0.28 \text{ kJ mole}^{-1}$  for the slower component. The observed values of initial retentions in pure crystals are  $63.3 \pm 2\%$  (304 K) and  $39.5 \pm 2\%$  (77 K) while in aqueous (304 K) and frozen aqueous (77 K) solutions the measured values are  $9.4 \pm 1\%$  and  $14.8 \pm 1\%$ , respectively. Modification of target solution with increasing amounts of LiCl additive at 304 K and 77 K shows a moderate initial rise in radio-iodate and periodate yields leading to an apparent plateau. A small but constant radioperiodate yield ( $2.3-3$ )  $\pm 0.5\%$  in all the phases studied signals its origin in the primary event. A mechanism based on the interaction of electron-hole with the recoil atom is proposed for annealing. Importance of  $^6\text{Li}(n, \alpha)t$  reaction and internal conversion events associated with the role of reactive intermediates produced by radiolytic effects are also discussed.

### Introduction

The idea that the stable species formed on dissolution of neutron irradiated crystals come from one or the other precursors has been supported by re-crystallisation studies [1, 2] and theoretical treatments [3].

CLEARY *et al.* [4] were able to deduce the presence of, at least, two radioactive species of intermediate oxidation states (considered to be  $^{128}\text{IO}^-$  and  $^{128}\text{IO}_2^-$ ) in a series of  $(n, \gamma)$  irradiated alkali metal iodates. However BOYD and LARSON [5] failed to observe  $^*\text{IO}^-$  and  $^*\text{IO}_2^-$  in neutron irradiated  $\text{K}^{127}\text{IO}_3$  and  $\text{K}^{129}\text{IO}_3$ . During transfer annealing experiments a stepwise formation of  $^{131}\text{IO}^-$  and  $^{131}\text{IO}_2^-$  has been postulated by BELLIDO and WILES [6]. ATEN *et al.* [7] have given evidence for annealing reaction occurring at temperatures as low as  $-30^\circ\text{C}$  in  $(n, \gamma)$  irradiated  $\text{KIO}_3$ . The variation of retention with pH of dissolution [8] and influence of the presence of chloride and acetate additives [9] on recoil stabilization in neutron irradiated  $\text{KIO}_3$  and  $\text{KIO}_4$  have been explained on the basis of the metastable precursors  $^*\text{IO}^-$  and  $^*\text{IO}_2^-$ .

In solid and liquid targets the  $(n, \gamma)$  recoil ranges are usually short and for  $^{128}\text{I}$  recoil it is estimated to be  $\sim 10 \text{ \AA}$  [8]. Since lithium undergoes  $(n, \alpha)$  reaction with high neutron capture cross section (945 barns) [10] we have chosen  $\text{LiIO}_3$  for the present investigation so that there is an extensive supply of defects in solid and high order of radiolysis in solution near the recoil site. Because of the fact that the radiation effects are largely thermally activated the present study is done at 77 K and 304 K ir-

radiation. Also, the notion that the presence of additive in neutron irradiated solution modifies the population of metastable precursors has motivated us to study the effect of LiCl additive on recoil reactions in solution. By such studies we hope to find, at least in principle, the mechanism which controls the fate of  $^{128}\text{I}$  atoms in  $(n, \gamma)$  irradiated  $\text{LiIO}_3$ .

### Experimental

300 mg of crystalline reagent grade  $\text{LiIO}_3$  was taken for the thermal neutron activation and kept in a sealed ampoule in the neutron irradiation facility. The thermal neutrons needed for the  $^{127}\text{I}(n, \gamma)^{128}\text{I}$  reaction in the iodate target were obtained from a 300 mCi (Ra-Be) source having an integral flux of  $3.2 \times 10^6 \text{ cm}^{-2} \text{ sec}^{-1}$ . The neutron source was surrounded by a cylindrical block of paraffin for thermalizing fast neutrons. The concomitant  $\gamma$ -dose associated with the neutron source was  $\sim 172$  rads/hour as estimated by Frick's dosimetry. The dose received from  $^6\text{Li}(n, \alpha)t$  reaction has been calculated [10] to be  $7.62 \times 10^{20} \text{ eV/mole of IO}_3^-$ , the value of cadmium ratio at the irradiation site being 0.1015.

For the irradiation at 77 K, a Dewar flask containing liquid nitrogen was placed in the central hole of the paraffin block and the target material sealed in soda glass tubes were dipped in the flask together with the neutron source.

For solution study, a 0.165 M solution of  $\text{LiIO}_3$  was prepared by addition of 10 ml of doubly distilled water to 300 mg of the sample. The mole fraction of the LiCl additive (AR grade) was varied from 0.00 to  $12.52 \times 10^{-3}$ . Since LiCl is hygroscopic, each time before weighing it was heated at  $60^\circ\text{C}$  in a constant temperature oven and then replaced to a vacuum desiccator. At high temperature it forms oxide or hydroxide and hence heating to higher temperatures was avoided. The solutions with varying concentration of LiCl were irradiated at ambient temperature as well as at 77 K for 3.0 hours.

Chemical separation of the three stable radioactive products i.e.  $^*\text{I}^-$ ,  $^*\text{IO}_3^-$  and  $^*\text{IO}_4^-$  was performed by fractional precipitation and solvent extraction methods similar to that of BOYD and LARSON [5].  $^{128}\text{I}$  radioactivity of all the three fractions was counted with the help of a thin wall end-window G.M. counter having a constant geometry. The half-life of  $^{128}\text{I}$  in the activated iodate target was found to be  $24 \pm 2$  minutes and no other radioactive species was detected in the time-decay analysis and thus the presence of any long lived isotopic impurity was

improbable. The retention value is an average of at least three independent experiments and the reproducibility of individual determination was within  $\pm 2\%$ .

## Results

The retention and yields of different fractions at 304 K and 77 K, both in solid and aqueous solution are presented in Table 1. It is evident (cf. Table 1) that thermal neutron capture in crystalline  $\text{LiIO}_3$  at room temperature produces significantly different pattern of chemical consequences from those observed in chlorate [11] and bromate [11] targets. The retention value obtained for thermal neutron irradiated  $\text{LiIO}_3$  at room temperature ( $63.3 \pm 2\%$ ) is much higher than chlorates (1.5–5.0%) and bromates (12–25%). This may possibly be due to higher enthalpy of formation [5] of iodates than iodides whereas the reverse is the case in bromine and chlorine oxyanion systems. The present room temperature retention value of  $^{128}\text{I}$  in solid  $\text{LiIO}_3$  is in good agreement with the value reported by CLEARY *et al.* [4] 67% and by AMBE and SAITO [12]  $61 \pm 1\%$ . The higher value of retention for  $^{128}\text{I}$  in  $\text{CsIO}_3$   $66 \pm 1\%$  [12] and 68.2% [13] have been explained to be due to the similar masses of Cs and iodine atoms [12]. For crystalline potassium iodate corresponding values reported in the literature are  $60 \pm 1\%$  [12],  $72.7 \pm 0.95\%$  [14]. Similarly for sodium iodate AMBE and SAITO [12] reported a value of  $59 \pm 2\%$  and a value of 67.8% is given by SHARMA [15]. In our experiment the retention value obtained at 77 K irradiation is  $39.5 \pm 2\%$  which is quite less than the room temperature activation value showing that annealing occurs even at room temperature inspite of the fact that an apparent threshold of  $110^\circ\text{C}$  [11] exists for the thermal annealing of bromates. For frozen 0.1 M solution of  $\text{NaIO}_3$  and  $\text{KIO}_3$  AMBE and SAITO [12] found a value of  $38 \pm 1\%$  which is not much different from our present result (cf. Table 1). ARNIKAR *et al.* [16] have reported a higher value of 82.5% for room temperature irradiation of  $\text{LiIO}_3$  crystals as against the value of 70% at 77 K. Since they acidified their solution before the addition of carrier in their separation procedure which favours the  $^*\text{I}^- / ^*\text{IO}_3^-$

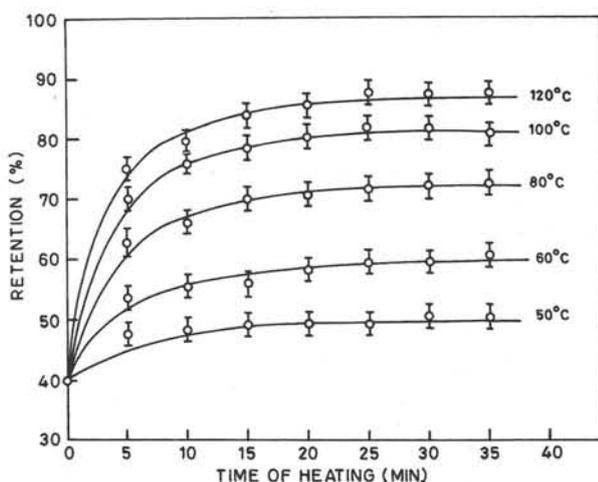


Fig. 1. Effect of thermal annealing on retention of  $^{128}\text{I}$  in  $\text{LiIO}_3$  irradiated by thermal neutrons at 77 K

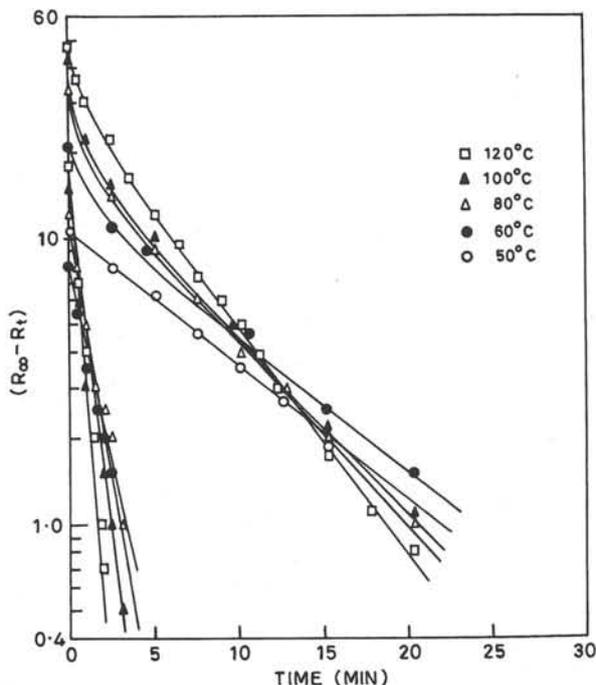


Fig. 2. Plot of  $(R_\infty - R_t)$  vs. time of heating in  $\text{LiIO}_3$  irradiated by thermal neutrons at 77 K

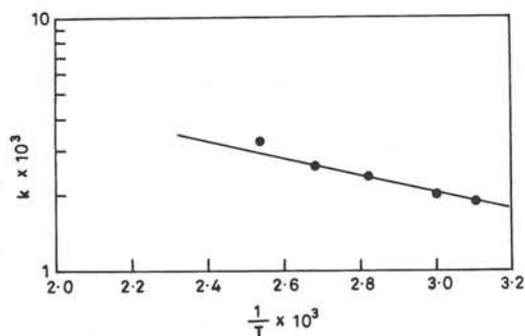


Fig. 3. Arrhenius plot for thermal annealing of solid  $\text{LiIO}_3$  irradiated by thermal neutrons at 77 K

isotopic exchange reaction, it may be a probable reason as to why they got as much as 70% retention even at 77 K.

The results on retention of  $^{128}\text{I}$  for different time of heating at different temperatures (i.e.  $50^\circ$ ,  $60^\circ$ ,  $80^\circ$ ,  $100^\circ$ ,  $120^\circ\text{C}$ ) for 77 K irradiated target are shown in Fig. 1. The nature of the isotherms reveal a fast initial rise followed by a temperature dependent pseudo-plateau region. Similar results have been reported by earlier workers on various inorganic halate targets [11]. The rate constants are obtained from the slope of  $\log(R_\infty - R_t)$  (fraction yet to be annealed) vs. time of heating curves (cf. Fig. 2). The energy of activation was computed by using the classical Arrhenius plot (cf. Fig. 3). The kinetic data and the activation energy obtained from the above graphs are recorded (Table 2). Least-square fitting method was applied to determine the values of rate constants and activation energy together with the associated probable errors. The production of small but constant yield of  $^{128}\text{IO}_4^-$  is very interesting.

The observations show that the retention and yields found in aqueous and frozen aqueous solutions are quite

Table 1. Phase and temperature of irradiation dependence of initial yields of  $(n, \gamma)$  activated  $\text{LiIO}_3$ 

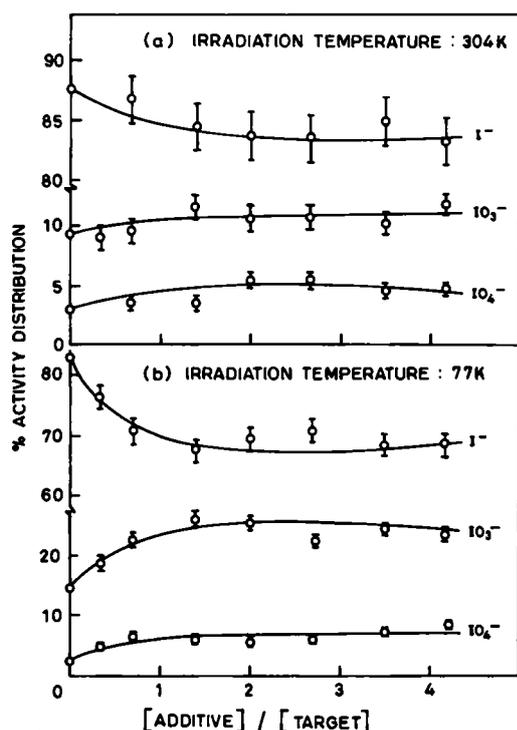
State of the sample during irradiation	Temperature of irradiation K	Concentration	% Yield		
			$\text{IO}_3^-$	$\text{I}^-$	$\text{IO}_4^-$
Crystalline solid	304	—	$63.3 \pm 2\%$	$33.7 \pm 2\%$	$3.0 \pm 0.5\%$
Crystalline solid	77	—	$39.5 \pm 2\%$	$57.8 \pm 2\%$	$2.5 \pm 0.5\%$
Neutral aqueous solution	304	0.165 M	$9.4 \pm 1\%$	$87.6 \pm 2\%$	$3.0 \pm 0.5\%$
Frozen aqueous solution	77	0.165 M	$14.8 \pm 1\%$	$82.9 \pm 2\%$	$2.3 \pm 0.5\%$

Table 2. Isothermal annealing data for thermal neutron irradiated  $\text{LiIO}_3$  at 77 K  
 $R_0 = 39.5\%$ 

Temp. ( $^{\circ}\text{C}$ )	$R_{\infty}$ %	Slow component			Fast component		Activation energy for slow component	
		$R_{\infty} - R_0$ %	$t_{1/2}$ (min)	$k \times 10^3 \text{ sec}^{-1}$	$R_{\infty} - R_0$ %	$t_{1/2}$ (sec)	KJ/mole	eV
50	$50.1 \pm 2$	$10.6 \pm 2$	6.00	$1.92 \pm 5.1 \times 10^{-3}$	—	—		
60	$60.5 \pm 2$	$21.0 \pm 2$	5.75	$2.00 \pm 5.4 \times 10^{-3}$	$8 \pm 2$	90		
80	$72.5 \pm 2$	$33.0 \pm 2$	5.00	$2.31 \pm 7.9 \times 10^{-3}$	$12 \pm 2$	45	$6.39 \pm 0.28$	$0.066 \pm 0.003$
100	$80.9 \pm 2$	$41.4 \pm 2$	4.50	$2.56 \pm 3.8 \times 10^{-2}$	$15 \pm 2$	40		
120	$87.5 \pm 2$	$40.0 \pm 2$	3.50	$3.30 \pm 3.0 \times 10^{-2}$	$17 \pm 2$	30		

Table 3. Percentage activity distribution of  $^{128}\text{I}$  atoms with varying concentration of  $\text{LiCl}$  additive in  $(n, \gamma)$  irradiated  $\text{LiIO}_3$  solution

Concentration of $\text{LiIO}_3$	Conc. of $\text{LiCl}$ in mole fraction	Conc. of $\text{LiIO}_3$ in mole fraction	Percentage yield					
			77 K			304 K		
			$\text{IO}_3^-$	$\text{I}^-$	$\text{IO}_4^-$	$\text{IO}_3^-$	$\text{I}^-$	$\text{IO}_4^-$
0.165 M	0.34		$18.7 \pm 1\%$	$76.7 \pm 2\%$	$4.9 \pm 0.5\%$	$9.0 \pm 1\%$	$89.9 \pm 2\%$	$1.1 \pm 0.5\%$
	0.69		$22.5 \pm 1\%$	$70.8 \pm 2\%$	$6.6 \pm 0.5\%$	$9.6 \pm 1\%$	$86.9 \pm 2\%$	$3.5 \pm 0.5\%$
	1.39		$26.3 \pm 1\%$	$67.8 \pm 2\%$	$5.9 \pm 0.5\%$	$11.8 \pm 1\%$	$84.8 \pm 2\%$	$3.4 \pm 0.5\%$
	2.09		$25.3 \pm 1\%$	$69.5 \pm 2\%$	$5.1 \pm 0.5\%$	$10.6 \pm 1\%$	$83.8 \pm 2\%$	$5.5 \pm 0.5\%$
	2.79		$22.3 \pm 1\%$	$71.7 \pm 2\%$	$6.0 \pm 0.5\%$	$10.8 \pm 1\%$	$83.8 \pm 2\%$	$5.4 \pm 0.5\%$
	3.49		$24.3 \pm 1\%$	$68.2 \pm 2\%$	$7.5 \pm 0.5\%$	$10.2 \pm 0.5\%$	$85.3 \pm 2\%$	$4.5 \pm 0.5\%$
	4.19		$23.2 \pm 1\%$	$68.5 \pm 2\%$	$8.3 \pm 0.5\%$	$11.8 \pm 1\%$	$83.3 \pm 2\%$	$4.8 \pm 0.5\%$

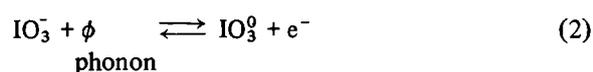
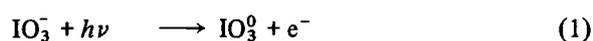
Fig. 4. Effect of  $\text{LiCl}$  additive on  $(n, \gamma)$  activation of  $\text{LiIO}_3$  solution

different from those observed in pure crystalline target (Table 1). Our initial retention value of  $9.4 \pm 1\%$  for thermal neutron irradiated  $\text{LiIO}_3$  solution is less than the value of (25%) reported by ARNIKAR *et al.* [16]. The results on effect of additive ( $\text{LiCl}$ ) concentration are presented in Table 3 and Fig. 4. There is a sharp initial decrease in the radioiodide yield followed by a saturation value on increasing the  $\text{LiCl}$  concentration. Similarly both radioiodate and -periodate fractions increase relatively slowly to attain apparent plateau values. There is a sharp change in activity distribution at 77 K. Lower yield (ca.  $3.0 \pm 1\%$ ) of  $\text{IO}_3^-$  was observed on irradiation of alkaline  $\text{LiIO}_3$  solution at room temperature.

#### Discussion

In spite of greater supply of additional defects due to the self-radiation damage produced both by emitted  $\alpha$ -rays (LET:  $34.7 \text{ eV}/\text{\AA}$ ) and high triton recoils (LET:  $9.4 \text{ eV}/\text{\AA}$ ) [10] originating from  $^6\text{Li}(n, \alpha)t$  reaction [ $G(-\text{IO}_3^-) = 2.85$ ] [17] the low initial retention in  $(n, \gamma)$  activated crystalline  $\text{LiIO}_3$  at 77 K compared to ambient temperature value supports the fact that radiation annealing is thermally activated.

As ligand loss hypothesis would predict unaltered primary yields due to solid state reaction when recoil atoms are produced by purely mechanical ( $n, \gamma$ ) recoil the observation of higher retention at 304 K compared to 77 K would not fit into this hypothesis. Binary collision approximation of collision cascades in computer simulation of ( $n, \gamma$ ) irradiated  $\text{KIO}_3$  has given a value of 9% retention to be due to direct replacement reactions [8]. Hence such a direct replacement reaction may contribute as much as  $\sim 9\%$  in the present study. It has been agreed that recoil  $^{128}\text{I}$  exists in the irradiated solid either in  $^{128}\text{I}^0$  state or in  $^{128}\text{I}^+$  state [18] which may be assumed to be precursors for lower valence state. If annealing were due to migration of ionic species as the rate determining step its activation energy would lie between 1–2 eV [19]. The present observation of first order annealing with  $0.066 \pm 0.003$  eV activation energy tempts us to explain our results on the basis of defect mechanism involving a combination of electronic and thermal steps in the manner suggested by BAUMGÄRTNER and MADDOCK [20], COSTEA [21], ANDERSEN [22], and later on by LIN and WILES [14].

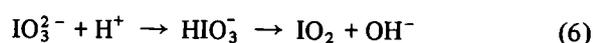


Reaction (2) which releases trapped electron holes is an important step in thermal annealing. Creation of a mobile electron hole ( $\text{IO}_3^0$ ) which oxidizes the recoil atom followed by the transfer of oxygen ions to the oxidized atom is the basis of the above mechanism. Alternating series of reactions 3, 3, 4, 3, 3, 4 . . . etc. gives rise to the parent form [14].

ANBAR and NETA [23] observed the rates of reaction of halate ions with hydrated electrons by pulse radiolysis and found the specific rate constant for iodate ions of the order of  $10^9 - 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ :

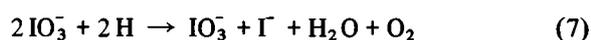


This paramagnetic centre has also been detected by e.s.r. even at room temperature [24] in high energy irradiated solid iodate. The reactive intermediate  $\text{IO}_3^{\cdot -}$  formed may be responsible for the oxidation of  $^{128}\text{I}^-$  and its protonated form may undergo dehydration to yield  $\text{IO}_2$  (cf. reaction 6):



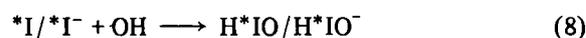
It would be worth mentioning that a comparatively stable species (most probably  $\text{HIO}_3$ ) has been detected by e.s.r. in  $\gamma$ -irradiated iodic acid [25].

In pure iodate solutions the yield of  $\text{I}^-$  can be explained by the reaction of  $\text{IO}_3^-$  ions with primary reducing species H,

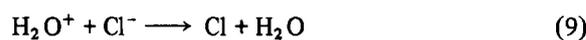


Notwithstanding that  $\text{I}^-$  is also formed as a result of successive ligand loss of  $\text{IO}_3^-$  under ( $n, \gamma$ ) activation of iodates.

However, in presence of  $\text{Cl}^-$  ions the yield of  $\text{I}^-$  ions decreases at the expense of increasing amounts of  $\text{I}^{\text{O}^-}$  and  $\text{I}^{\text{O}^+}$  fractions formed. The increase in the retention of  $\text{I}^{\text{O}^-}$  with an increase in  $\text{Cl}^-$  concentration in the target as observed in the present investigation is explicable in the light of increasing yields of oxidizing radicals like OH and  $\text{Cl}_2^{\cdot -}$  formed as a result of radiolysis of LiCl solution. It is well known that  $\text{Cl}^-$  is a OH radical scavenger [26] and as the  $\text{Cl}^-$  concentration increases, all the OH radicals are scavenged. But during ( $n, \gamma$ ) process in  $\text{LiIO}_3$  solution, there is high probability of internal conversion of  $^{128}\text{I}$  species [27, 28]. So inspite of emitted X-rays and the highly positively charged iodine atoms the  $\alpha$ -rays and the high energy recoil tritons produced in concomitant  $^6\text{Li}(n, \alpha)t$  reaction are also expected to produce OH radicals. Hence reaction (8) could be operative:



Since  $\text{H}^*\text{IO}/\text{H}^*\text{IO}^-$  is itself a strong oxidizing agent it would result in an increase in the retention of  $\text{I}^{\text{O}^-}$  by oxidizing the recoil species.  $\text{Cl}_2^{\cdot -}$  is formed only in acidic medium through the oxidation of  $\text{Cl}^-$  ions by OH radicals. According to HAMILL *et al.* [29–31] the formation of  $\text{Cl}_2^{\cdot -}$  ions by irradiation of neutral solution can not be accounted for by the theory of diffusion from spurs. In the light of this model of isolated pairs of positive holes and dry electrons ( $\text{H}_2\text{O}^+$ ,  $e^-$ ), the  $\text{Cl}^-$  ions present in large concentration in the iodate/chloride target may react directly with  $\text{H}_2\text{O}^+$  (reaction 9) and also produce  $\text{Cl}_2^{\cdot -}$  (reaction 10):



The oxidation potential of the OH–OH $^-$  couple ( $-2.0$  V) is very high [32]. The chloride additive may be oxidized by OH radicals to hypochlorites which are also strong oxidizing agents and can even oxidize iodate to periodate and this would account for  $\text{I}^{\text{O}^+}$  observed in the present work. The enhanced cage effect in frozen aqueous solution might possibly be the main clue to the enhanced variation in  $^{128}\text{IO}_3^-$  retentions as compared to the liquid phase in the present study.

A small but constant  $(2.28 - 3.00) \pm 0.5\%$  initial radio-periodate yield in frozen aqueous, aqueous and in crystalline solid phases both at ambient temperature and 77 K irradiations seems to show their origin around the primary events. This may possibly be ascribed to Auger process because of the fact that 2.39% of the neutron capture events lead to pure Auger charging of the 50% converted 133 keV level of  $^{128}\text{I}$ . Since this delayed state occurs in 42% of neutron capture events [33], 21% of the events lead to internal conversion. For an atom with  $Z = 53$  the probability for Auger electron emission against X-ray fluorescence is 14.5% [34]. Therefore in about

$2 \cdot 39\% \left( \frac{21 \times 14.5}{100} \right) \%$  of neutron capture events radio-periodate may be expected to be formed by short term annealing in the electronic spike [35] produced as a result of Auger process. This electronic spike has to be characterized by a lack of coupling to atomic motion due to much higher heat diffusivity.

Auger charge neutralization of  $(^{128}\text{IO}_3^+)^n$  in insulating solids like  $\text{LiIO}_3$  is delayed and so we can expect, in addition to Auger electrons, formation of oxygen atoms by the Auger electron radiolysis of immediate surrounding lattice which would contribute in the neutralization process giving rise to small fraction of periodate. In the case of irradiations in aqueous and frozen aqueous phases we can expect that in addition to dry electrons some  $\text{OH}^-/\text{OH}^\cdot$  radicals present in the electronic spike together with  $e_{\text{aq}}^-$  contribute in the neutralization of  $^*\text{IO}_3^+{}^n$  and its subsequent stabilization as periodate.

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