FORMATION OF CHARGED SPECIES IN (n, γ) ACTIVATED IODOFORM IN NITROBENZENE

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SUMMARY : Charge Plate Technique (CPT) which essentially applies a high voltage D.C. field across the Ag/AgI electrodes has been used in studying the origin of charged species in (n,γ) activated iodoform - nitrobenzene mixtures. Anode plate shows a fairly high order of radioactivity. No cathodic deposition has been observed. Electrode yields are drastically influenced by the presence of NB. It is concluded that Auger charging and the sequential charge transfer process are responsible for the formation of charged species in (n,γ) activated iodoform (IF) in nitrobenzene (NB).

Key words : Charged ¹²⁸I, recoil reactions, iodoform, nitrobenzene.

INTRODUCTION

Hot atom chemistry concepts and methods are now powerful tools for understanding the nature of high energy reactions (1) and the subject becomes of recent interest to scientists for (i) education and training (ii) research and development with special reference to life, geo-and space sciences and (iii) new energy technology. Some studies on thermal neutron activation of liquid organic iodides have been accomplished by CPT in our laboratory (2, 3). However, (n, γ) activation of solid iodotargets dissolved in solvents of different reactivities have not been studied so far. The physicochemical properties of the solvents are expected to influence the mode of formation of charged species in the target substance and the intermolecular interactions between hot species and the surrounding molecules enter the panorama. Herein are described our findings on (n, γ) activation of iodoform dissolved in nitrobenzene by CPT. For undergraduate studies it has been of interest to apply the CPT for the observation of (n, γ) effects in solid iodocompounds dissolved in suitable solvents with known physical and chemical properties (e.g. + I or -I effective).

MATERIALS AND METHODS

Solutions of iodoform (Burgoyne-Burbidges and Co., Bombay) in nitrobenzene (Ind. Drugs and Pharm., Hyderabad) were prepared by dissolving the requisite quantity of iodoform (IF) in 120 ml. nitrobenzene (NB). Preparation of the solutions were accomplished as quickly as possible and with minimum exposure to light to avoid any photochemical reaction. The solutions were subjected to thermal neutron activation for 3 hours with the help of a 300 mCi (Ra-Be) neutron source (4) having an integral flux of $3.2x10^6$ n cm⁻² sec⁻¹. The experimental procedure was outlined elsewhere (2, 5).

RESULTS AND DISCUSSION

Results obtained are summarized in Table 1. It is apparent from the Table 1 that negatively charged ¹²⁸I species have been deposited on anode surface and show a fairly high order of radioactivity. However, yields on the cathode surface were found nil. This observation is new and striking because previous reports on liquid iodocompounds under (n, γ) process always recorded anodic as well as cathodic activities (2).

Target systems : lodoform - nitrobenzene; Time of irradiation : 3 hours; Electrodes used : Ag/AgI; Electric field applied for collection of charged species : 1050 volts for 1 hour.

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Generation of charged species.- The origin of charged species in the recoil or resulting nucleus are due to (a) adiabatic orbital shake up and shake off and (b) Auger emission. The energetic ¹²⁸I species bear divergent

Table 1: Charge plate collection of $^{128}\mbox{I}$ species orginated from (n,
γ) activated iodoform (IF) in nitrobenzene (NB).

Concentration	Yields on the	Yields on the
of iodoform	anode	anode
(mole fraction)	(counts min ⁻¹ .)	(counts min ⁻¹ .)
0.0051	1100	-
0.0082	1800	-
0.0102	2300	-
0.0152	2800	-
0.0182	4100	-
0.0202	3700	-
(Saturated)		

kinetic energies because the de-energization of the excited iodine nucleus to the ground state proceeds through the emission of a single gamma photon or gamma cascades involving two, three or four or even greater number of intermediate transition steps leading to the ejection of internal conversion (IC) electrons and creation of vacancy in the inner shells. The capture gamma ray spectra for ¹²⁷I (n, γ) ¹²⁸I have been measured by Archer *et al.* (6) and others (7). Besides, it has been reported by Korteling et al. (8) and Schaller et al. (9) that low lying energy levels of 28 KeV 133 KeV in (128) are highly internally converted. Considering the capture phenomena, the ejection of prompt gamma rays which are associated with a 133 KeV level whose existence and life time have been confirmed, is proposed to be an enhanced E2 transition (8) which would correspond to an internal conversion coefficient of ca 0.5. The 133 KeV gamma ray is observed in 42% of neutron capture events and hence at least 21% ionization events will accompany the production of positively charged ¹²⁸I recoil nuclei. The resultant effect of this high conversion of 133 KeV level is the creation of hole in the K shell and emission of characteristic x-ray during the orbital electron reshuffle which cause higher order of Auger charging

While the ¹²⁸I⁺ species result from loss of orbital electrons through internal conversion (IC)/electron shake off, the appearance of negatively charged species in our results is assumed only due to secondary reactions as electron attachment to neutral species/positively charged fragments of high electron affinity. Electron attachment is highly likely as the electrons from IC and Auger charging in a condensed system of a molecular liquid may be considered to be in a quasi free state (10) distinct from trapped or solvated electrons. Assuming not more than one iodine atom undergoes (n, γ) process in the same molecule of iodoform, we propose the following reaction scheme which accounts for the formation of both ¹²⁸I⁺ and ¹²⁸I⁻ species in pure iodoform.

Electrode yields and effect of nitrobenzene .- Due to a high order of Auger charging, production of multiple charged ¹²⁸I+ for ¹²⁸I are highly probable. The charge dis-

Scheme 1: Formation of charged species in iodoform pure.

$CHI_3 + n \rightarrow CH \ {}^{\star}I_3 \xrightarrow{\qquad \gamma \qquad} \mathring{C}HI_2 + {}^{\star}I_{(1)}$
${}^{\star}\mathrm{I}+\mathrm{CHI}_{3}\rightarrow\mathrm{CH}{}^{\star}\mathrm{I}_{3}+\mathrm{I}_{\cdots}$
$CH~^{*}I_{3} \rightarrow CHI_{2}~^{*}I^{n+} + ne^{-} \dots \dots \dots \dots (3)$
$CHI_2 \ {}^*I^{IH} \to CHI_2 \ {}^*I^{IH} \to CHI_2 \ {}^*I \dots \dots \dots (4)$
$CH~^{*}I_{3}~^{*}~e^{-}\rightarrowCH~^{*}I_{3}^{-}~\dots\dots(5)$
$CH~^{*}I_{3}^{-} \rightarrow CHI_{2}~+ \overset{*}I^{-}~\dots\dots(6)$
${}^{\star}I \rightarrow {}^{\star}I^{n+} + {}^{\star}I^{n+} \dots \dots$
$^{\star}I^{1+}\rightarrow \ ^{\star}I_{\ldots}$
${}^{\star}I + e^{-} \rightarrow {}^{\star}I^{-} \dots \dots (9)$
$CH^{*}I_{3}^{1+} + CH_{3} \rightarrow \left(CH^{*}I_{3} - CHI_{3}\right)^{1+} \dots \dots (10)$

tribution ranges from 1+ to 11+ with 5+ as the most abundant state (11). This Auger and secondary electron cascades create a spectrum of positively charged ions which may rapidly undergo charge transfer with the molecules of the medium until the ¹²⁸I⁺ species exists :

CHI₂ *Iⁿ⁺ + MCHI2 *I¹⁺ + M⁽ⁿ⁻¹⁾⁺ (11)

As to the absence of cathodic deposition, it is assumed that due to the extreme instability of multiple positive iodine species, either they have undergone stable chemical combination or have been converted to anionic species by arresting necessary electrons from the immedi-

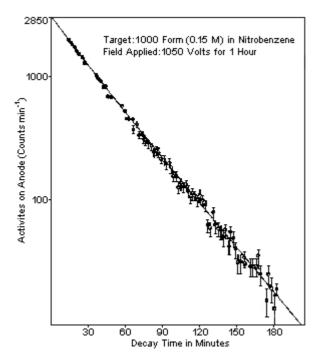
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ate surrounding - [equs. (4-9), Scheme 1] which is possible due to localized radiation chemistry as proposed in Auger electron reaction hypothesis (12). The primary reactions that take place in pure iodoform (Scheme 1) are specifically influenced to a certain extent by the addition of NB, a solvent of high polarity. NB may exert its scavenging action by undergoing following type of reactions which also account for the abundancy of anionic species, originally proposed for explaining the behavior of radio bromine species in aniline (13).

CH₂+^{*}I + C₆H₅NO₂→ C₆H₅NO₂CHI₂)⁺ *I⁻.....(12) or, CH *I₃ + C₆H₅NO₂→ C₆H₅NO₂CHI₂)+ *I⁻.....(13)

Half life of ¹²⁸I.- The recorded anode activities after necessary corrections (viz. background) were platted on a semi log graph paper which yielded a straight line (Figure 1). This line was extrapolated to zero time and half life of ¹²⁸I was determined. All experiments in the present investigation gave the half life of ¹²⁸I as ~ 25 minutes.

Figure 1: Time decay analysis of the activity of ¹²⁸I species collected on anode.



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