

Charge Plate Technique in Recoil Study - III. (n,γ) Activation of Dibromomethane in 2-Nitrotoluene*

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Summary: Solutions of dibromomethane (DBM) in 2-nitrotoluene (2-NT) have been irradiated for 30 hours using a 1.11×10^{10} Bq (Ra-Be) neutron source. Charged radioactive bromine species viz. ^{80m}Br , ^{80}Br and ^{82}Br of either sign were collected on charged plates kept at 175 V cm^{-1} (D.C) during the end - 3 hours of irradiation. The anodic yields are invariably greater than the cathodic yields. All the anodic radiobromine activities increase first with increasing mole fraction (mf.) of 2-NT whereas the cathodic bromine activities decrease and then reach plateau values. The cationic deposition was almost zero above 0.37 mf. of 2-NT. The results indicate that Internal Conversion (I.C) and Auger processes are responsible for the formation of charged bromine species and that 2-NT plays an essential role in the electron picking up process leading to the creation of extra anionic bromine activities.

Introduction

The study of the reactions of energetic radio-active bromine atoms, produced by a nuclear transformation is of great utility for gaining insight about the mechanism of hot bromine reactions and subsequent secondary reactions. The effect of additives on the recoil products emerging from (n,γ) reaction in various organic liquid bromo-compounds, has been an interesting study in the whole range of hot atom chemistry. However, the effect of additives on the recoil reactions in liquid phase is not very well understood. The chemical and physical properties of a mixture may differ appreciably from those of the pure components and hence the overall recoil reaction is heavily influenced by the type of target and the nature of the diluent [1-6]. Because of their extraordinary complexity, solution phase hot atom reaction studies have often been lead to disagreements, some of which are yet to be solved [7-9]. The present paper discusses the recoil reactions of ^{80m}Br , ^{80}Br and ^{82}Br nuclides originating from (n,γ) activation of liquid dibromomethane (DBM) in 2-nitrotoluene (2-NT) by the charge plate technique (CPT).

CH_2Br_2 have been computed by time - decay analyses and are shown in Figs. 2 and 3 as a function of 2-NT concentration.

Table 1: Cumulative zero time activities collected on the anode and cathode. Target : Dibromomethane (DBM) + 2-nitrotoluene (2-NT). Duration of neutron activation : 30 hr. Electric field applied : $175 \text{ volts cm}^{-1}$ (D.C) for 3 hr.

Mole fraction of 2-NT	Anode activities (counts/min.)	Cathode activities (counts/min.)	Relative efficiencies (%)	
			Anode (Ec)	Cathode (Ea)
0.0000	10600	1190	89.91	10.09
0.1064	13950	423	97.06	2.94
0.2293	17620	200	98.88	1.12
0.3731	13710	162	98.83	1.17
0.5435	7768	-	100.00	0.00

Origin of charged radiobromines

It is evident from Table 1 that both positive and negative charged radiobromines are present after the thermal neutron activation of DBM or DBM-2-NT solutions as a fraction of these charged species escaping chemical stabilization are deposited on the electrodes kept under a high electric potential gradient (175 V cm^{-1}). It is known that when an organic bromocompound undergoes (n,γ) activation, the gamma rays emitted by the compound nucleus impart recoil energy to the nucleus. As 3-4 gamma quanta emission takes place the mean recoil energy is about 40 - 50 eV which is far in excess of the C-Br bond energy

Results and Discussion

Cumulative zero time activities collected on anode and cathode are given in Table 1. Individual electrode yields for ^{80m}Br , ^{80}Br and ^{82}Br from

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(2.16 eV) [14,15] and as a consequence the recoiling bromine species breaks the C-Br bond (cf. Scheme 1, reaction 1).

Carlson and White [16] pleaded that if an atom X, in a molecule like RX, experiences an isomeric transition (I.T.) and the gamma rays are converted internally, the emission of Auger electrons will cause X to become highly positively charged. Since atom X is bound to R this high positive charge will be driven to the extremities of the molecule by intramolecular electron transfer resulting in two positive centres within the molecule causing it to decompose violently (Auger explosion). The charged fragments will repel each other and can procure considerable translational energies ranging from 10 eV to 100 eV [17]. However, the model was suggested for gaseous systems and the physical and chemical upshot of the Auger explosion are still obscure for condensed phase systems [18,19]. Takida *et al.* [20] opined that there may be some question in connection with the universal applicability of the Auger explosion model. Results from various schools do not confer with the Auger effect coulombic explosion model but do emphasize on other preliminary processes such as ionization and charge neutralization or direct interaction with Auger electrons resulting in (I.T) - activated bromine reactions [18,21-23].

As the time for Auger charge build up to take place is shorter 10^{-15} sec) than the molecular vibration period (10^{-14} to 10^{-12} sec.), primarily the multiple positive charge remains only on the bromine atom without affecting the rest of the molecule. Subsequent events depend on the state of aggregation. In the gas phase, where molecules may be considered as isolated and the collisional stabilization is of little significance, the intramolecular charge redistribution is quite possible resulting in an extreme coulombic repulsion causing the molecule to explode. But in liquid systems, molecules are not undisturbed by the other surrounding ones and intermolecular charge redistribution which energetically hinders the molecule from undergoing a so called "Auger explosion" become important.

In our present study the two isomeric nuclides viz. ^{80m}Br and ^{82m}Br offer a specific route to the formation of cationic species. In the case of

^{80m}Br there is a double Auger process as the first transition is for 100% and the second transition for 61% converted; the single transition of ^{82m}Br is also for 100% converted [24]. Due to the Auger processes following the transitions, the resulting Br species posses a high positive charge. Other studies also confirmed that positively charged species results from radiative neutron capture [25], isomeric transition (I.T.) followed by I.C. [26], β -decay [27] and orbital electron capture [28].

While the positively charged radiobromines emerge from loss of orbital electrons, the appearance of negatively charged species in our experiments can be due to electron attachment to neutral species of high electron affinity. Electron addition is highly likely as the electrons from I.C. and Auger cascades in a pure liquid or solutions may be considered to be in a quasi free state [29] distinct from trapped or solvated electrons. As the ionization potential of Br atoms (14.0 eV) is much higher than those of DBM (10.5 eV) and 2-NT (thought to be about 9.7 eV, as the potentials for 3-NT and 4-NT are 9.7 and 9.8 respectively), multiply positively charged bromonium ions (Br^{n+}) will quickly be neutralized in pure DBM or DBM/2-NT mixtures. Hence it is quite reasonable to assume that n+ state will be reduced to 1+ state in the case of all radiobromines under study and this neutralization course will be continuing until the Br^* species is formed. Eventually, a fraction of Br^+ may be transmuted to Br^- by arresting necessary electrons from the immediate vicinity during their transit through DBM/2-NT mixtures (cf. Scheme 1, reaction (4-8)).

The electrode yields

Table 1 shows that cumulative activities deposited on the electrodes follow the order : anode > cathode. Again, from Figs. 2 and 3, it is apparent that anodic activities are invariably greater than the cathodic ones for all the three radiobromine species. Due to the high I.C. coefficients of the transitions $^{80m}\text{Br} \xrightarrow{\text{I.T.}} ^{80}\text{Br}$ and $^{82m}\text{Br} \xrightarrow{\text{I.T.}} ^{82}\text{Br}$ a considerable fraction of the initially formed ^{80}Br and ^{82}Br are expected to be in the positively charged state as stated earlier. Consequently, under a high electric field, there should be a higher enrichment on the cathode. Results obtained in the present investigation, clearly stand against this deduction and indicate that it is not the initial

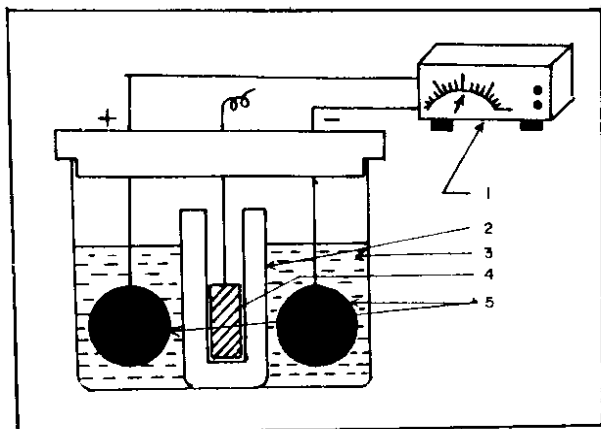
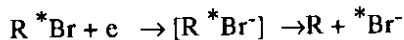


Fig. 1: Arrangement for neutron activation and collection of bromine charged species on electrodes. 1. Stabilized D. C. power supply unit 2. Paraffin cylinder 3. Solution under irradiation 4. Neutron source 5. Ag/AgBr electrodes.

charge of the fragments but their subsequent history that directs on which electrode they will be accumulated.

Considering the results of I.T. Geissler and Willard [30] was able to put forward an important hypothesis which describes that the reaction



is quite possible in the liquid phase due to localized radiation chemistry caused by I.C. and Auger electrons. During the successive charge transfer processes it is probable that a larger fraction of Br^+ ions may be converted to Br^- ions and hence the higher anodic yield may be explained by this reaction sequence.

Effect of 2-nitrotoluene (2-NT)

The effect of the addition of 2-NT, a polar diluent on the recoil collection of ^{80m}Br , ^{80}Br and ^{82}Br charged species on the electrodes are depicted in Figs 2 and 3. These figures show that there is an increase in the anodic ^{80}Br yield up to 0.25 mf. and only a slow rise in ^{80m}Br and ^{82}Br yield, whereas the cathodic ^{80}Br yields, decreases exponentially. These findings resemble results reported for mixtures of bromoform and *n*-butyl bromide with aniline which is also a polar solvent [31,32]; a linear rise in the collected activity was observed up to 0.6 or 0.25 mf. for the two mixtures.

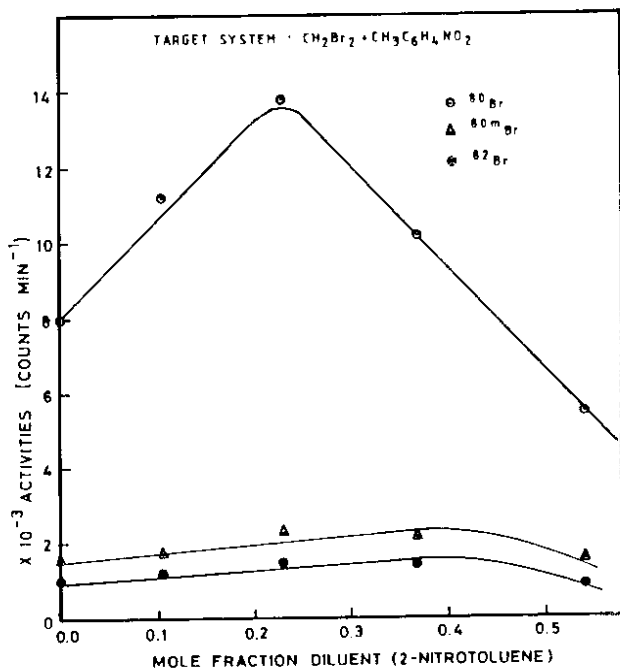


Fig. 2: Effect of presence of 2-nitrotoluene (2-NT) in dibromomethane (DBM) on the anodic collection of radiobromines.

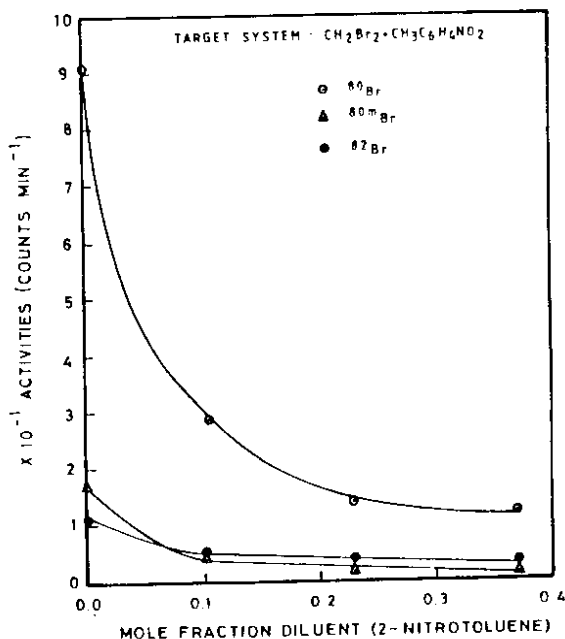
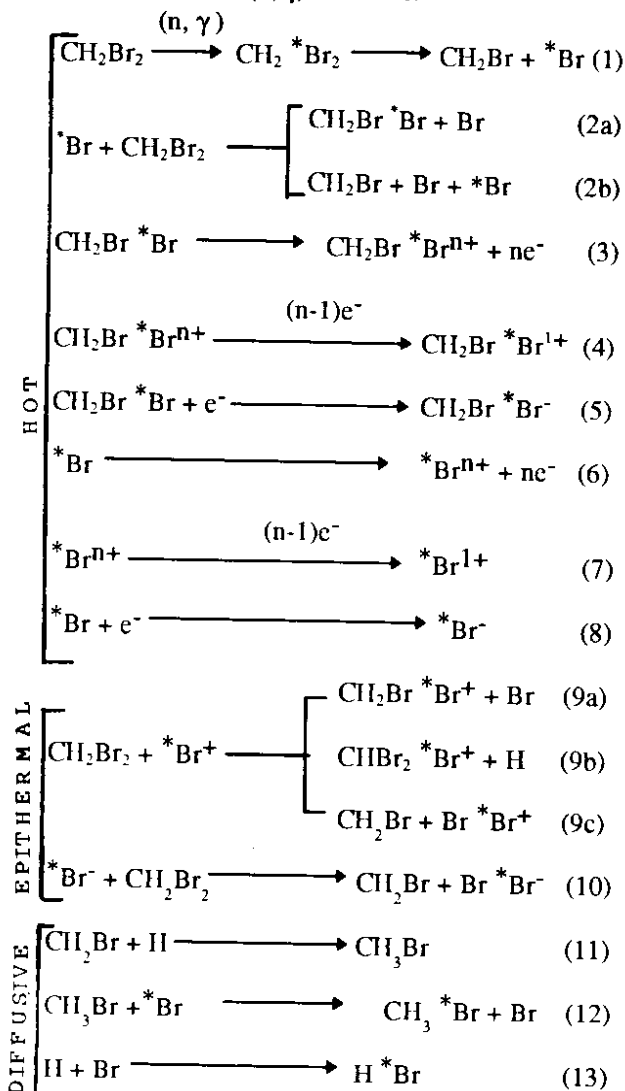


Fig. 3: Effect of presence of 2-nitrotoluene (2-NT) in dibromomethane (DBM) on the cathodic collection of radiobromines.

Our results also show that no appreciable amounts of bromine activities are collected on cathode surface; yields fall off up to 0.1 mf. of the diluent

and then become statistically arranged. No cationic charged species have been found to be deposited beyond 0.4 mf. of 2-NT in the target.

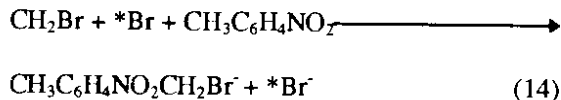
In explaining our present results, we consider here the reactions of nucleogenic radiobromine species investigated by several workers in this field. On the basis of various theories and views [33-40], we propose the following scheme (Scheme 1) which records the probable reactions leading to the formation of charged species, fragments/radicals in pure liquid DBM due to the (n, γ) reactions:



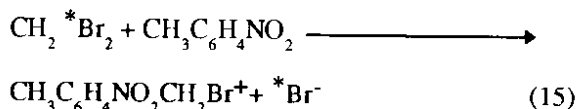
Scheme 1. Production and stabilisation modes of energetic bromine species in pure dibromomethane (DBM)

Some of the radicals, proposed in scheme 1, have been detected by e.s.r. in other studies [41,42]. The above scheme depicts that recoil ^{80m}Br , ^{80}Br and ^{82}Br react to enter organic combination in three successive energy regions: hot, epithermal and thermal. The course of these reactions may be altered by the addition of foreign molecules. Hence, the addition of 2-NT to pure DBM seems to have a strong bearing on the final chemical stabilisation of energetic bromine species due to its moderating efficiency and chemical reactivity.

A proposal [43] that negatively charged radiobromine species are amply produced when a polar diluent is added to the target compound under (n, γ) activation seems to be supported by the present findings. In fact, 2-NT in DBM tends to initiate reaction (14) during the thermal neutron capture process and subsequent processes in which an organic free radical and a recoil bromine atom reacts with the 2-NT molecule and create extra bromide ions (Br^-) as follows:



This three-body encounter is likely, because the cage of solvent molecules (2-NT) holds the radioactive bromine atom, $^*\text{Br}$, and the free radical $^*\text{CH}_2\text{Br}$, together until they can dissipate their excess energy and react with each other or with 2-NT molecules. The probability of reaction (14) increases with increasing concentration of 2-NT. Alternatively, if the R^*Br bond is reformed by way of elastic collision during hot processes (eqn. 2a, Scheme 1), then this excited molecule contains enough vibrational energy to undergo reaction (15):



2-NT does not react appreciably with the bulk of the CH_2Br_2 because the molecules are cold but does react with the freshly reformed CH_2^*Br_2 molecules before they can cool [33]. Thus, in the presence of 2-NT, a considerable fraction of DBM can be ionised by reaction (15). These separated active bromine species, under the applied electric

field will be deposited on the electrodes and in fact such reactions are responsible for the increase in the extractable activity of recoil bromine species with increasing mf. of 2-NT as is evident from Fig. 2. Energetic bromine atoms after being slowed down to thermal energy range become stabilized exclusively by diffusion controlled reactions (eqns. 11-13 Scheme 1). However, beyond 0.25 or 0.40 mf. of 2-NT all the anodic radiobromine activities go on decreasing. This may be due to the sufficient decrement in the number of bromine atoms available to undergo (n, γ) reaction in the target system.

Another important point to be noted here is that, the ^{80m}Br and ^{82}Br activities collected on both anode and cathode are in close proximity but ^{80}Br activities are much higher than the other two. As the natural abundance, n, of ^{79}Br and ^{81}Br are almost same [44] (50.69% and 49.31% respectively), it is perhaps the neutron capture cross section that is responsible for the higher ^{80}Br yield. The neutron capture cross section (σ_i) for ^{80}Br nuclide is 8.5 b whereas the same for ^{80m}Br and ^{82}Br are 2.9 and 3.3 b respectively [45]. In our present study, time of irradiation, t, and the neutron flux, ϕ were constant for a given irradiation.

The most interesting findings of the present study is the gradual decrease of cathode activities which finally lead to zero (cf. Table 1). This may be due to the transmutation of bromonium ions ($^*\text{Br}^+$) to bromide ions ($^*\text{Br}^-$) in the new chemical environment created by the addition of 2-NT which plays an effective role in expediting the electron picking up process in the medium (cf. eqns. 5 and 8, Scheme 1).

Experimental

Materials

DBM (Ventron, Alpha, Division, 98%), 2-NT (Thomas Baker & Co., London) and potassium bromide (E. Merck, 99%) were of highest available purity and used as received.

Electrode preparation

The electrolytic deposition of bromide ions over the two silver electrodes was accomplished separately and successively by the electrolysis of

two freshly prepared 3% aqueous KBr solution using a copper electrode as dummy. The dimension of silver electrodes was 4x0.1 cm and the dummy copper electrode was of same dimension. A ca. 100 mA current for 3 minutes was passed through the electrolyte with the help of a battery eliminator (Monex, India) kept at 9 volts D. C. The deposition was carefully performed in a dark chamber to avoid any photochemical reaction.

Irradiation facility

Experimental set-up and irradiation arrangement are shown in Fig. 1. About 120 ml. of each target liquid/solution was taken in a 400 ml glass beaker for thermal neutron bombardment from a 1.11×10^{10} Bq ($R_a\text{-B}_e$) neutron source unit kept inside a paraffin cylinder. The target substance was subjected to irradiation for a period of 30 h in each experiment so as to ensure the condition of saturation irradiation [10,11]. The radiolytic effect produced by the concomitant gamma dose associated with the neutron source [12,13] is negligible. The mouth of the 400 ml. glass beaker containing the neutron source and the target for irradiation was enveloped with a circular wooden plate which helped well to protect the liquid from evaporation. The irradiation assembly was completely surrounded from all sides successively by 4 cm. thick paraffin blocks and ~ 2 cm. thick lead bricks for checking the escaping neutrons and gamma rays respectively.

Collection of charged species

An electric field of the order of 175 V cm^{-1} (optimum voltage obtained through several experiments) was applied across the electrodes during the last 3 hours of irradiation. Great care in operation permitted a reproducible geometry for irradiation. Irradiation and collection were performed in an underground dark room (neutron cellar).

Counting and analysis

After collection, the electrodes were quickly removed from the irradiated liquid systems, dried under an infrared lamp; the cooled electrodes were then put successively beneath the tube of a G. M. Counter (end - window type, EC, Hyderabad, India Ltd., serial 1660) for measurement of activities. The counting (counts/minute) of both positive and negative electrodes were continued up to 70 h for

each target; counting geometry was kept constant throughout the measurement. The counting assembly was found to have a reproducible low background counts of 180-190 counts per 20 minutes and were frequently measured 2-3 times for each target during the measurement. The corrected activities were then plotted on a semilog graph paper and time-decay analyses were performed for obtaining the relative yields of ^{80m}Br , ^{80}Br and ^{82}Br for both anode and cathode.

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