ON THE ELECTRODEPOSITION OF ^{80m}BR, ^{80}BR AND ^{82}BR SPECIES FROM (η,γ) ACTIVATED DIBROMOMETHANE - N,N-DIMETHYLANILINE MIXTURE

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Thermal neutron activation has been carried out in dibromomethane (DBM) - N,N-dimethylaniline (N,N-DMA) system and the ^{80m}Br, ^{80}Br and ^{82}Br species have been electrodeposited on Ag/AgBr electrodes under a constant electric field of 175 volts cm^{-1}. With the addition of N,N-DMA in DBM, anodic deposition has been severely decreased for all the radiobromines and cathode plate shows zero activities. Results are critically discussed by explaining the chemical reactivity of the amine. Electrode deposition pattern and the chemical stabilisation mode of the nucleogenic bromine species in this system are deduced to some extent.

Key words: Nucleogenic bromine species, Electrodeposition, Amine scavenger.

Introduction

In a recent study [1], it was observed that aniline failed to exert its scavenging action in dibromomethane-aniline or dibromoethane-aniline mixtures due to the formation of crystals in the systems and the activities of electrodeposited radiobromines fell off sharply. The experiment with dibromomethane (DBM) in N,N-dimethylaniline (N,N-DMA) showed the same decreasing trend regarding the electrode activities. Here, we present the results of our study on energetic bromine reactions in DBM - N,N-DMA mixtures by charge plate collection experiments and discuss the mechanism of stabilisation mode of ^{80m}Br, ^{80}Br and ^{82}Br species in the system.

Experimental

Materials. DBM (Ventron, Alfa Division, USA, 98%), N,N-DMA (E. Merck, India Ltd., 99%, GC) and potassium bromide (E. Merck, India Ltd., 99%) were of highest purity available from suppliers and used without further purification. All the chemicals were stored carefully in a cool and dark chamber to avoid any thermal/photochemical decomposition.

Equipment. Neutron source unit. A Ra-Be (mixed) neutron source (Department of Chemistry, Banaras Hindu University, India) of 11.1 G Bq strength having an integral flux of 3.2 x 10^6 n cm^{-2} sec^{-1} was used for the production of radiobromines. The concomittant gamma dose [2] associated with the neutron source was 1.72 Gy hr^{-1}; the of cadmium ratio [3] at the irradiation site being 0.1015. The source (in SS casings) was kept in an aluminium capsule hinged with a copper string. When not in use, the source was kept in a lead castle.

Nuclear counter. A G.M. counter with mica thin end window type GCS 41, serial 1660, Electronic Corporation of India Ltd., Hyderabad was used. A built-in preset timer with a range of 0.1 sec to 8000 sec 0.01 min^{-1} to 800 minutes selectable in nine steps with the help of preset and multiplier switches was provided. Provision was also made for introducing three known 'dead times' into the system.

D.C. supply unit. A low noise, high voltage regulated D.C. power supply unit (Powertech, Varanasi-5, India or ECIL, Hyderabad) was used for applying a high voltage across the Ag/AgBr electrodes. The output voltage was controlled from 0 - 1500 volts manually through the panel mounted control. It could withstand any overload including a short circuit, with the normal operation resuming after the removal of the overload.

Electrode preparation. Two circular silver electrodes (of dimension 4x0.1 cm) after cleaning, were dried under an infra-red lamp. The electrolytic deposition of bromide ions over the electrodes was carried out separately and successively by the electrolysis of two freshly prepared potassium bromide solutions using a copper electrode as dummy. The electrode assembly was then stored inside a brown bottle in a dark chamber and was ready for the collection of (η,γ) activated radiobromine charged species from the neutron irradiated liquid systems.

Procedure. The experimental technique adopted in the present investigation for the recoil study of bromine charged species generated by thermal neutron capture essentially consists of thin Ag/AgBr electrodes in contact with the liquid/solution being irradiated and the recoil bromine species were collected on the electrodes under the influence of high voltage D.C. field (175 volts cm^{-1}) across the electrodes for 3 hrs during the end of irradiation. The charged species thus col-

lected gave a high specific activity which was measured with the help of the end-window β–γ G.M. counter coupled with necessary electronic accessories. Experimental details are given elsewhere [4].

Results and discussion

It is evident from the Table 1 that both positively and negatively charged bromine species were produced and deposited on charged plates under a constant potential gradient of 175 volts cm^{-1} during (η,γ) reaction in DBM. Prior to thermal neutron activation, the addition of N,N-DMA to DBM caused a severe decrease in the anode activities and no activity was observed on cathode surface. This behaviour is similar to DBM-aniline system [1]; very low activities on anode and virtually none on the cathode.

No crystal formation was detected in the present case but green precipitation is evident in either irradiated or non-irradiated reaction mixtures. These results are somewhat unusual. The yield of extractable radiobromines, obtained on irradiation of organic bromides by thermal neutrons, can be increased by the addition of amines e.g. aniline [5]. During the neutron exposure time paraffin cylinder (used for moderating the fast neutrons to thermal energy range) was attacked by the vapours resulting from DBM - N,N-DMA solution in the reaction vessel and the cylinder was found partially melted. Hence further experiments were not designed with this amine (N,N-DMA) due to this technical difficulty. Another case of paraffin cylinder melting was observed when 4-bromoacetanilide in methanol was irradiated by thermal neutrons. The implications of this melting phenomenon are discussed earlier [6]. Conclusively, we see that N,N-DMA fails to exercise its scavenging action owing to which it would have been possible to collect more efficiently the radiobromine species on the electrodes (Ag/AgBr) from irradiated DBM -N, N-DMA solutions.

TABLE 1. EFFECT OF N,N-DIMETHYLANILINE (N,N-DMA) ON THE ELECTRODEPOSITION OF ^{80m}BR, ^{80}BR AND ^{82}BR SPECIES FROM (η,γ) ACTIVATED DBM - N,N-DMA SOLUTION

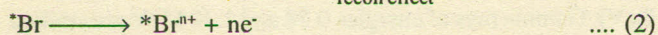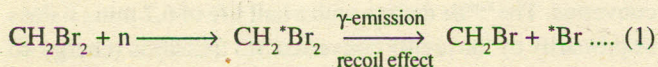| Concentration of N,N-DMA (mf)	Radio active nuclides	Natural abundances (%)	Thermal n capture cross section (b)	Electrode Yields	
				Anodic	Cathodic
0.0000	^{80}Br	50.5	8.5	8000 ± 89	910 ± 30
	^{80m}Br	50.5	2.9	1600 ± 40	170 ± 13
	^{82}Br	49.5	3.3	1000 ± 31	110 ± 10
0.0997	^{80}Br	50.5	8.5	1440 ± 38	-
	^{80m}Br	50.5	2.9	530 ± 23	-
	^{82}Br	49.5	3.3	188 ± 13	-

Target system : Dibromomethane (DBM) + N,N-DMA; Thermal nuetron exposure : 30 hrs Electric field applied across the electrodes : 175 volts cm^{-1} (D.C. field) for 3 hrs.

The following radioisotopes of bromine are obtained when DBM is irradiated with neutrons : ^{80m}Br, ^{80}Br, ^{82m}Br and ^{82}Br. There are differences [7] in the decay modes of ^{80m}Br and ^{82m}Br. In the case of ^{80m}Br there exists a double Auger process; the first transition is 100% and the second transition is 61% converted. The single transition of ^{82m}Br is also 100% converted. The ^{82m}Br decays with a half life of 6.2 min.; it does so primarily by the highly converted M3 transition (energy 46 KeV). Gamma rays of energies 0.78 and 1.48 MeV are emitted during the decay giving the stable product ^{82}Kr. Gamma rays of energies 0.046, 0.78 and 1.46 MeV are emitted from ^{82m}Br where the first is not in coincidence with latter two. As these transitions are extremely internally converted and afterwards followed by Auger process, the resulting atom is left with a high positive charge [8]. These charged radiobromines should be deposited on cathode surface kept under a high potential gradient. However, this deduction is not consistent with our results (Table 1) which lead us to propose that the emergence of negatively charged bromine species in DBM or DBM -N, N-DMA mixtures is due to secondary reactions.
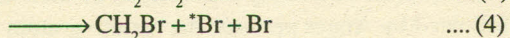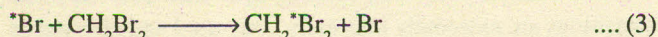
From calculated cross section it has been shown that the tendency for ion-molecule impact and the bimolecular complex formation i.e. [Br-Ar]$^{n+}$ type is exceeded by the capability for Br^{n+} to undergo charge transfer and neutralisation with the aromatic substrate [9]. Hence, multiple charged bromine species is generally expected to undergo sequential charge transfer with neutral molecules because the second ionisation potential is much higher than the first. Eventually a larger fraction of bromonium (Br$^+$) ions may be transmuted to Br$^-$ by capturing necessary electrons from the immediate vicinity during their transit through DBM as recorded in Table 1. ^{80}Br, ^{80m}Br and ^{82}Br recoil reactions that take place in pure DBM are specifically influenced by the presence of N,N-DMA. While there is general compliance that the amine group is primarily responsible for scavenger effect, the general mechanism is not that clear [10]. Agrawal and Rao [11] reported that the two important factors viz. (i) high II-electron density and (ii) the presence of an easily abstractable acidic H (the latter perhaps happen to be of minor importance) seem to explain the efficient scavenging action of aniline and phenol compared to dimethylaniline and anisole respectively. Stoecklin et al. [11] studied the influence of amine scavenger and onium salts on the total retentions of alkyl halides by chemical method and reported that tertiary amines applied as scavenger to alkyl halides lower the retention only if the amine is not, or hardly able to quaternize with the alkyl halide owing to a steric hindrance; iso-propyl bromide -N, N-DMA is such an example. Present results by charge plate collection experiments are similar to that of Stoecklin et al. [12] in the sense that we are getting lower electrode deposition in the DBM - N, N-DMA

system apparently due to the increase in organic yield. With these results and observations the following reaction scheme is proposed that explains the formation of charged radiobromines of both kinds, radicals and stabilisation mode of ^{80m}Br, ^{80}Br and ^{82}Br species in DBM - N,N-DMA mixtures:
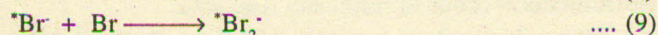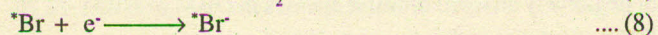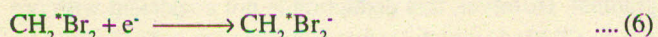
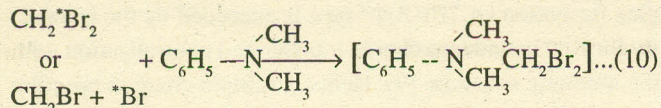(a) Compound nucleus formation [13] and Auger effect [14].

$$CH_2Br_2 + n \longrightarrow CH_2{}^*Br_2 \xrightarrow[\text{recoil effect}]{\gamma\text{-emission}} CH_2Br + {}^*Br \;\dots\; (1)$$

$${}^*Br \longrightarrow {}^*Br^{n+} + ne^- \qquad\qquad \dots (2)$$

(b) Elastic collision reactions and sequential charge neutralisation processes [15,16].

$${}^*Br + CH_2Br_2 \longrightarrow CH_2{}^*Br_2 + Br \qquad \dots (3)$$
$$\longrightarrow CH_2Br + {}^*Br + Br \qquad \dots (4)$$
$$Br^{n+} \longrightarrow {}^*Br^{l+} \longrightarrow {}^*Br \qquad\qquad \dots (5)$$

(c) Electron addition and formation of anions [17,18]

$$CH_2{}^*Br_2 + e^- \longrightarrow CH_2{}^*Br_2^- \qquad \dots (6)$$
$$\longrightarrow CH_2Br + {}^*Br^- \qquad \dots (7)$$
$${}^*Br + e^- \longrightarrow {}^*Br^- \qquad\qquad \dots (8)$$
$${}^*Br^- + Br \longrightarrow {}^*Br_2^- \qquad\qquad \dots (9)$$

(d) Chemical tabilization [12]

$$\begin{matrix} CH_2{}^*Br_2 \\ \text{or} \\ CH_2Br + {}^*Br \end{matrix} + C_6H_5-N\begin{smallmatrix}CH_3\\ \\CH_3\end{smallmatrix} \longrightarrow \left[C_6H_5 -- N\begin{smallmatrix}CH_3\\ \\CH_3\end{smallmatrix} CH_2Br_2 \right] \dots (10)$$

Scheme 1. Formation of charged species, radicals and chemical stabilisation of ^{80m}Br, ^{80}Br and ^{82}Br species in DBM - N,N-DMA mixtures.

Thus Scheme 1 shows that the charged species of both kinds are produced during nuclear activation of DBM or DBM - N,N-DMA targets and they may be preferentially electrodeposited on the electrodes. Hot bromine atoms after being slowed down to thermal energy range may become stabilised exclusively by diffusion controlled reactions. In the course of time, the excited intermediate (eqn. 10, Scheme 1) undergoes dissociation into a DBM and a N,N-DMA molecule.

As to the absence of cathodic deposition from the mixture one can reasonably infer that the electron picking-up process in the system is quite efficient enough to transform all the cationic bromines into anionic ones. Electrons from internal conversion and Auger charging (eqn.2, Scheme 1) in a condensed system of a molecular liquid like DBM or DBM -N,N-DMA mixtures, may be considered to be in a quasi free state [19] distinct from trapped or solvated electrons. Attachment of these electrons [20] to neutral radiobromine species (eqns. 6-8, Scheme 1) or multiply positively charged fragments (eqns. 3-5, Scheme 1) of high electron affinity is facilitated in the new chemical environment created by the addition of N,N-DMA to DBM. Hence, it is possible that all the positively charged radiobromines are neutralised and transmuted into anionic ones rendering the cathode surface free from cationic deposition as observed in the case under study.

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