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Formation of Charged Species in (n, γ) Activated 2-Bromopropionic Acid: An Atypical Case

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Synopsis. (n, γ) Activation of dibromomethane, tribromomethane, 1-bromonaphthalene, 2-bromophenol, and 2-bromopropionic acid has been studied in liquid phase by Charge Plate Technique. A (Ra–Be) neutron source of 300 mCi having an integral flux of 3.2×10^6 n cm^{-2} s^{-1} was used for the production of energetic bromine species. Both anionic and cationic charged species have been collected on charged plates for the targets used except in 2-bromopropionic acid where cathode activity was found nil. This result is unique and never observed before for pure liquid bromocompounds using charge plate collection experiments.

Experimental

We have studied the (n, γ) reaction in pure dibromomethane (DBM), tribromomethane (TBM), 1-bromonaphthalene (1-BN), 2-bromophenol (2-BP), and 2-bromopropionic acid (2-BPA) in liquid phase with the help of a 300 mCi (Ra–Be) neutron source having an integral flux of 3.2×10^6 n cm^{-2} s^{-1}.

Results and Discussion

It is observed that both positively and negatively charged species have been produced and collected on charged plates during the (n, γ) reaction in these bromo compounds except in 2-BPA where only anodic activities were observed and no positively charged species were collected on the cathode surface. This result is unique in the sense that complete absence of charged species on the cathode was never observed by previous workers for pure liquid bromo compounds using charge plate collection technique. Yields of positively and negatively charged species collecting on the Ag/AgBr electrodes under a constant electric field of 1050 volts D.C. during end −3 hours of 30 hours neutron activa-

Table 1. Formation of Charged Species in Some (n, γ) Activated Liquid Organic Bromo Compounds

Compounds under (n, γ) activation	Radio-nuclides	Yields on the electrodes (counts/min)		Reference
		Anode	Cathode	
Dibromomethane (DBM)	^{80}Br	8000	910	This work
	^{80m}Br	1600	170	
	^{82}Br	1000	110	
Tribromomethane (TBM)	^{80}Br	1750	1400	This work
	^{80m}Br	700	525	
	^{82}Br	600	470	
2-Bromopropionic acid (2-BPA)	^{80}Br	2300	—	This work
	^{80m}Br	775	—	
	^{82}Br	700	—	
1-Bromonaphthalene (1-BN)	^{80}Br	900	100	This work
	^{80m}Br	350	35	
	^{82}Br	392	56	
2-Bromophenol (2-BP)	^{80}Br	460	144	This work
	^{80m}Br	160	50	
	^{82}Br	180	68	
Bromobenzene (BB)	^{80}Br	5800	1000	Ref. 4
	^{80m}Br	1220	330	
	^{82}Br	1300	580	
Butyl bromide (*n*-BB)	^{80}Br	2900	480	Ref. 5
	^{80m}Br	760	120	
	^{82}Br	1120	490	
Ethyl bromide (EB)	^{80}Br	1328	841	Ref. 6
	^{80m}Br	900	170	
	^{82}Br	1080	575	
1,2-Dibromoethane (DBE)	^{80}Br	5976	777	Ref. 6
	^{80m}Br	3900	1115	
	^{82}Br	4200	5692	

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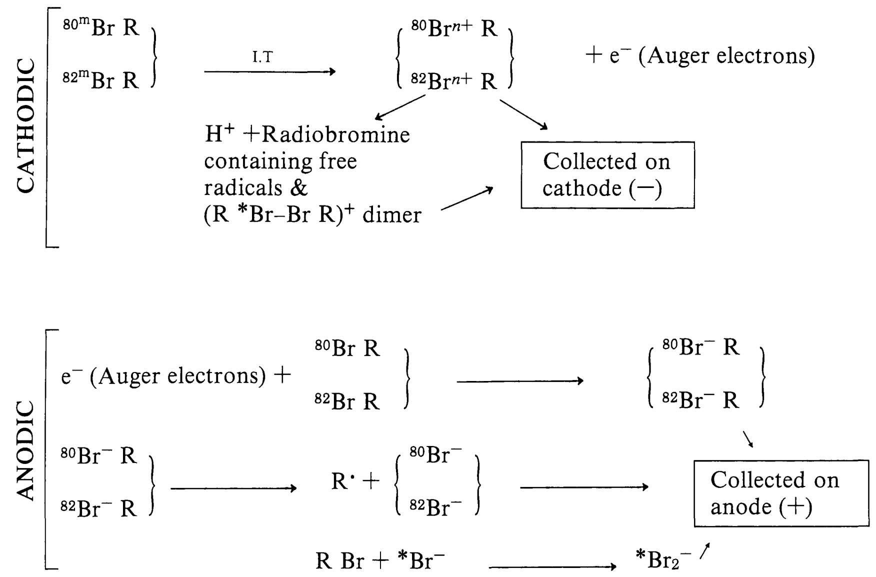

Scheme 1. Special production root for the formation of bromine charged species.

tion in these bromo compounds have been measured by an end-window type G.M. counter and summarized in Table 1.

We can take three possibilities into account here for the absence of cations from the cathode in the system: (a) no cationic species have been produced at all, (b) the electron picking-up process of the cationic bromines in this medium is so efficient and rapid that all the positively charged bromine species have been transmuted to anionic species and get deposited on anode, and (c) all cationic species have undergone some sort of interactions with the surroundings and resulted into a complete chemical stabilization.

As (n, γ) event and isomeric transition (I.T) followed by internal conversion process (I.C) are the clear evidences for the production of positively charged bromine species (Scheme 1), we can straightaway discard the first possibility.

Second possibility describes the transmutation of positively charged species into anionic ones either by sequential charge transfer:

$$\mathrm{R\ {*}Br}^{n+} \longrightarrow \mathrm{R\ {*}Br}^{1+} \longrightarrow \mathrm{R\ {*}Br}^{-}$$

Or from the localized radiation chemistry:

$$\mathrm{R\ {*}Br} + e^- \longrightarrow \mathrm{R\ {*}Br}^- \longrightarrow \mathrm{R} + {*}\mathrm{Br}^-$$

as proposed in the Auger Electron Reaction Hypothesis.[1] Lastly cationic stabilization may be facilitated in this medium. As the time for Auger charge build up to take place is shorter (10^{-15} s) than the molecular vibration period (10^{-14} to 10^{-12} s), 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 other surrounding ones and intermolecular charge redistribution which energetically hinders the molecule from undergoing a so called "Auger explosion" becomes important. We assume that these last two possibilities are operative for the disappearance of cationic bromines from the cathode.

We have not found any literature concerning the recoil work on liquid bromo carboxylic acid. There are reports on bromoacetic acid,[2] *m*- and *p*-bromobenzoic acid but these are solid phase studies.[3] Reportedly, a number of different reactions including the substitution of carboxyl group take place in these compounds. However, in the present case the role of carboxyl group is not so clear yet; it may have some marked effects on the deposition pattern as uniquely observed in the case of 2-BPA.

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References

1) P. R. Geissler and J. E. Willard, *J. Phys. Chem.*, **67**, 1675 (1963).

2) a) E. Glückauf and J. W. J. Fay, *J. Chem. Soc.*, **1936**, 390; b) J. W. J. Fay and F. A. Paneth, *ibid.*, **1936**, 384.

3) K. Sawlewicz and A. Halpern, *Radiochim. Acta*, **11**, 86 (1969).

4) C. Pandey and B. M. Shukla, *Radiochem. Radioanal. Lett.*, **52**, 1 (1982).

5) C. Pandey and B. M. Shukla, *Radiochem. Radioanal. Lett.*, **51**, 93 (1982).

6) A. Lal, *Indian. J. Phys.*, **41**, 39 (1967).