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Kinetics of Nuclear Bromination of Aromatic Amines by N-Bromosuccinimide

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Kinetics of bromination of aniline, N-methylaniline, N,N-dimethylaniline, *p*-toluidine, *p*-chloroaniline and *p*-bromoaniline by NBS in pure acetic acid and acetic acid-water mixture (75 : 25, % v/v) under conditions of acidity (0·05*M* to 1*M* of $HClO_4$ or H_2SO_4) are reported for the first time. $Hg(OAc)_2$ has been used to fix the liberated Br^- and thus the bromination by Br_2 has been eliminated. The reactions are first order with respect to NBS and amine. The reaction has an inverse acid dependence for the amines studied. The reaction between the dipole of NBS and aromatic ring is envisaged.

RECENTLY we have communicated[1] the results on the kinetics of nuclear chlorination of aromatic amines by N-chlorosuccinimide under varying conditions. Though the nuclear bromination of aromatic amines by N-bromosuccinimide (NBS) is generally instantaneous, a careful study has shown that it is possible to study the kinetics of NBS halogenation under acidic conditions, where there is effective protonation leading to overall reduced reactivity. Hence, kinetics of bromination of aromatic amines by NBS has been studied systematically for the first time under conditions of acidity (0·05*M* to 1*M* $HClO_4$ and H_2SO_4) and in the presence of mercuric acetate to have a clear reaction not complicated by any competing bromination by free bromine. NBS is known to function either through molecular bromine or through the positive halogen end. The functioning of NBS through molecular bromine has been totally suppressed, by the use of $Hg(CH_3COO)_2$ which fixes the Br^- as unionized $HgBr_2$ or more likely as $HgBr_4^{2-}$. The role of mercuric acetate is essentially that of combining with the Br^- formed during the course of the reaction[2].

Materials and Methods

All the amines were of AR grade and were redistilled or recrystallized before use. Acetic acid was purified by standard procedure. All other chemicals used were of AR grade. NBS was estimated by standard iodometric method.

Results and Discussion

Reactivity of aniline, N-methylaniline and N,N-dimethylaniline in glacial acetic acid and aq. acetic acid — The reactions in pure acetic acid are first order in the amine and first order in NBS. The products are *p*-bromo derivatives in each case. The first order nature of the process with respect to substrate (S) is confirmed by varying the concentration of the substrate (Table 1). $k_1/[S]$ values are constant. The order of reactivity is: N-methylaniline>N,N-dimethylaniline>aniline.

TABLE 1 — DEPENDENCE OF RATE CONSTANT ON SUBSTRATE IN PURE ACETIC ACID AND AQ. ACETIC ACID

[$Hg(OAc)_2$ = 0·005*M*; NBS = 0·0005*M*; $HClO_4$ = 0·05*M*; temp. = 35°]

Compound	$10^2[S]$ *M*	$10^2\ k_1$ min^{-1}	k_2 litre $mole^{-1}$ min^{-1}
	100% ACETIC ACID		
Aniline	0·53	0·13	0·24
	1·07	0·29	0·27
	1·54	0·409	0·26
N-Methyl-aniline	0·53	0·23	0·43
	1·03	0·45	0·44
	1·55	0·66	0·42
N,N-Dimethyl-aniline	0·50	0·14	0·28
	1·02	0·28	0·27
	1·50	0·40	0·27
	HOAc-WATER (75 : 25, % v/v)		
Aniline	0·13	0·048	36·5
	0·28	0·115	41·4
	0·52	0·208	39·5
N-Methyl-aniline	0·12	0·267	221·0
	0·28	0·639	226·0
	0·48	1·08	222·7
N,N-Dimethyl-aniline	0·13	0·20	150·7
	0·26	0·40	148·9
	0·52	0·79	151·3

The reactions in aqueous acetic acid (75 : 25, v/v) are first order each in amine and NBS. Rate constants at varying concentrations of substrate are recorded in Table 1.

The reactions are accelerated substantially in aqueous acetic acid. Rate constants at varying percentages of HOAc are recorded in Table 2.

The products are the corresponding tribromo derivatives. Such tribromo derivatives have been isolated earlier[3]. The order of reactivity is: N-methylaniline>N,N-dimethylaniline>aniline.

Effect of acidity — The effect of acidity has also been studied by varying the concentration of $HClO_4$ in each case and dependence on H_0 is found to be unity. The inverse dependence has been rationalized on the basis of the free bases being the reactive species. Such reasoning has also been advanced by Bell[4]. The reaction has also been studied in sulphuric acid (0·05*M*). The reactions are generally much faster in H_2SO_4 as compared to $HClO_4$ (Table 3).

The order of reactivity N-methylaniline>N,N-dimethylaniline>aniline has also been observed in alkylation reactions. In the competition of polar and steric effects associated with the methyl group present on the nitrogen, it is the polar influence that dominates in the secondary amine where as the steric effect in N,N-dimethylaniline lowers its reactivity vis-à-vis that of N-methylaniline[5].

Variation of solvent composition for these amines also proves that the reactions are accelerated in acetic acid containing increased percentage of water. In addition to the dielectric constant effect, it appears that H_2O is able to polarize the NBS much more effectively leading to higher reactivity in aqueous medium.

Reactivity of p-substituted anilines in non-aqueous and partially aqueous medium — The reactions are first order in the substrate and NBS in both the solvent systems. k_1 values at varying [S] and k_2 values are given in Table 4.

It is clear that electron releasing groups are favouring the reaction whereas substituents like *p*-Cl and *p*-Br retard the process as they are essentially electron withdrawing groups ($-I$); though this effect is weak due to the contribution of resonance and inductive effects. The products in all the cases are the corresponding *o*-bromo derivatives.

The reactions are accelerated with increased percentage of water and the rate constants are given in Table 2.

Variation of acidity in 75-25% v/v HOAc-water shows that the reactions are retarded with the increase in $[H^+]$ (Table 3). The retardation is traced to protonation of the amine. The order with respect to H_0 is unity.

Mechanism — As $Hg(OAc)_2$ has been used with a view to fixing the Br^- as $HgBr_2$ or $HgBr_4^{2-}$, the halogenating agent is exclusively the NBS itself and it functions by direct halogen transfer. The reactions are straightforward C-halogenation processes either in aqueous acetic acid or in pure acetic acid, as the formation of N-bromo derivatives is unlikely as these are formed only at very low temperatures.

The reactions have been studied in the presence of NaOAc and there is large increase in the rate. This rules out either the hydrolysed species H_2OBr^+, HOBr or Br^+ as the brominating agents and it is not unlikely that the H^+ loss may occur in the rate-determining step depending upon the conditions in other halogenations as well.

TABLE 2 — EFFECT OF VARYING COMPOSITION OF THE SOLVENT ON REACTION RATE

[Substrate = 0·005*M*; NBS = 0·0005*M*; $Hg(OAc)_2$ = 0·005*M*; $HClO_4$ = 0·05*M*; temp.= 35°]

Amine	k_2 litre mole^{-1} min^{-1} in HOAc (%)			
	100	85	75	65
Aniline	0·26	14·4	39·5	84·3
N-Methyl-aniline	0·43	102·1	222·7	519·4
N,N-Dimethyl-aniline	0·27	50·7	151·3	229·5
p-Toluidine	0·42	3·02	10·5	21·3
p-Chloroaniline	0·14	1·07	2·97	6·05
p-Bromoaniline	0·13	1·10	2·90	6·19

TABLE 3 — ACIDITY DEPENDENCE OF RATE CONSTANT (k_2) IN THE BROMINATION OF AMINES BY NBS

[Solvent = HOAc-water 75 : 25 (% v/v); substrate = 0·005*M*; NBS = 0·0005*M*; $Hg(OAc)_2$ = 0·005*M*; temp.= 35°]

Amine	k_2 litre mole^{-1} min^{-1} in				
	H_2SO_4 (*M*)	$HClO_4$ (*M*)			
	0·05	0·05	0·1	0·5	1·0
Aniline	54·9	39·5	22·2	6·6	2·4
N-Methyl-aniline	463·00	222·7	139·4	32·6	11·2
N,N-Dimethyl-aniline	266·00	151·3	97·2	13·0	8·00
p-Toluidine	13·3	10·5	5·6	2·6	0·97
p-Chloroaniline	4·00	3·0	1·70	0·91	0·73
p-Bromoaniline	3·97	2·9	1·77	0·94	0·70

TABLE 4 — DEPENDENCE ON SUBSTRATE IN AMINE-NBS REACTIONS IN PURE ACETIC ACID AND AQ. ACETIC ACID

[NBS = 0·0005*M*; $Hg(OAc)_2$ = 0·005*M*; $HClO_4$ = 0·05*M*; temp.= 35°]

	10^2 [S] *M*	10^2 k_1 min^{-1}	k_2 litre mole^{-1} min^{-1}
	100% ACETIC ACID		
p-Toluidine	0·51	0·22	0·42
	1·02	0·40	0·39
	1·52	0·63	0·41
p-Chloroaniline	0·52	0·075	0·145
	1·01	0·15	0·147
	1·53	0·23	0·151
p-Bromoaniline	0·51	0·065	0·128
	1·01	0·14	0·139
	1·51	0·20	0·135
	AQ. ACETIC ACID (75 : 25, % v/v)		
p-Toluidine	0·13	1·36	10·43
	0·25	2·63	10·55
	0·52	5·48	10·52
p-Chloroaniline	0·27	0·74	2·8
	0·52	1·57	2·98
	1·02	3·3	3·2
p-Bromoaniline	0·26	0·85	3·2
	0·50	1·48	2·9
	1·00	3·33	3·3

We rule out the possibility of bromination through BrOAc, for the reason that the reaction rates should have been much faster with increased percentage of HOAc in a partially aqueous medium. It has been observed that the reactions are facile in acetic acid containing increased percentage of water. The results presented in this study indicate reaction of dipole of NBS and the aromatic ring.

References

1. RADHAKRISHNAMURTI, P. S. & SAHU, S. N., *Indian J. Chem.*, **14B** (1976), 898.
2. VENKATASUBRAMANIAN, N. & THIAGARAJAN, V., *Tetrahedron Lett.*, (1967), 3349.
3. KOSOLA POFF, G. M., *J. Am. chem. Soc.*, **75** (1953), 3596.
4. BELL, R. P. & RAMSDEN, E. N., *J. chem. Soc.*, (1953), 161.
5. RADHAKRISHNAMURTI, P. S. & PANDA, R. K., *Indian J. Chem.*, (1971), 1247.