

Kinetics & Mechanism of Halogenation of Anilines, *p*-Toluidine & *p*-Nitroaniline by Chloramine-T

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The title reactions are first order each in the substrate and chloramine-T. It is established that the reactions do not proceed through the intermediate formation of hypochlorous acid. The solvent effects have been studied by carrying out the reaction in aq. DMF also. The results show that the reactions are essentially of dipole-dipole type. A mechanism involving direct halogen transfer from chloramine-T is postulated.

CHLORINATION of a variety of aromatic compounds, excepting aromatic amines, has been studied extensively by Soper and Smith¹, DelaMare *et al.*²⁻⁴. We report in this paper the kinetics of chlorination of some aromatic primary amines using chloramine-T in aq. acetic acid. To our knowledge this is a unique instance of halogenation by chloramine-T.

Materials and Methods

Chloramine-T used was of analar grade. Aniline was distilled and all other amines were recrystallized before use.

Standard iodometric method was employed for estimating chloramine-T. In all the cases the first order rate constants have been calculated from the initial percentages of the reaction to avoid competing disturbances, if any.

Results and Discussion

The reaction is second order, first order each in the substrate, and chloramine-T, in contrast to the earlier observation of zero order in substrate. The first order rate constant increases with increasing [substrate] (Table 1). Also k_1/S is constant, confirming that the reaction is first order in the substrate.

Dependence on H_0 is inverse in the case of aniline and other substrates which react by conjugative electron release, while there is direct dependence in the case of *p*-nitroaniline (Table 2). H_0 values for various percentages of aq. acetic acid have been taken from Wiberg⁶.

An increase in acetic acid and increase in DMF decrease the rate which points to the fact that it is a dipole-dipole reaction between chloramine-T and amines. The reactions are faster in aq. DMF as compared to those in aq. acetic acid (Tables 3 and 4) indicating that dipolar aprotic media of high dielectric constant cause an acceleration.

The data in Table 2 show that *p*-nitroaniline reacts slower than *p*-halogenoamines and *p*-toluidine. In all the cases the products are *ortho*-chloro isomers. In the case of aniline, the products are both *para*- and *ortho*-chloro isomers in equal ratio. This is

TABLE 1 — EFFECT OF VARYING [SUBSTRATE] IN THE CHLORINATION OF PRIMARY AROMATIC AMINES BY CHLORAMINE-T

{[Chloramine-T] = $4.5 \times 10^{-4} M$; [HClO₄] = $1.25 \times 10^{-2} M$;
solvent: 10% aq. HOAc; temp. = 35°}

[Substrate] $10^3 \times M$	$10^4 \times k_1$	$10^2 \times k_2$ (litre mole ⁻¹ sec ⁻¹)
ANILINE		
4.512	7.334	16.25 (8.125)
5.951	9.433	15.85 (7.925)
7.161	11.51	16.07 (8.035)
<i>p</i> -CHLOROANILINE		
4.39	6.25	14.23
4.626	6.624	14.32
5.488	7.868	14.33
<i>p</i> -BROMOANILINE		
2.848	5.553	19.5
5.218	9.73	18.65
7.297	13.13	18.00
<i>p</i> -IODOANILINE		
3.219	10.79	33.53
4.338	14.19	32.71
6.073	21.13	34.79
<i>p</i> -TOLUIDINE		
3.734	6.107	16.35
5.087	7.537	14.81
6.510	9.667	14.85
<i>p</i> -NITROANILINE		
3.817	0.9539	2.50
5.032	1.257	2.49
6.593	1.564	2.37

In the parentheses are rate constants for the *ortho*-isomer.

TABLE 2 — EFFECT OF ACIDITY ON THE REACTION RATE

{[Chloramine-T]= $4.5 \times 10^{-4}M$; [substrate]= $5 \times 10^{-3}M$;
solvent: 10% HOAc; temp.= 35° }

Aniline	$10^2 \times k_2$ (litre mole ⁻¹ sec ⁻¹) at			
	[H ⁺]= $0.625 \times 10^{-2}M$ (H ₀ =1.83)	[H ⁺]= $1.25 \times 10^{-2}M$ (H ₀ =1.74)	[H ⁺]= $2.5 \times 10^{-2}M$ (H ₀ =1.58)	[H ⁺]= $5 \times 10^{-2}M$ (H ₀ =1.26)
Unsubstituted]	28.56 (14.28)	16.25 (8.125)	9.97 (4.985)	6.34 (3.17)
<i>p</i> -Chloro	25.57	14.32	9.92	6.71
<i>p</i> -Bromo	31.96	18.65	11.87	9.40
<i>p</i> -Iodo	45.00	34.79	18.5	13.61
<i>p</i> -Methyl	24.9	14.85	10.43	5.14
<i>p</i> -Nitro	2.01	2.50	3.21	4.69

In the parentheses are rate constants for the *ortho*-isomer.

TABLE 3 — EFFECT OF VARYING COMPOSITION OF ACETIC ACID

{[Chloramine-T]= $4.5 \times 10^{-4}M$; [Substrate]= $5 \times 10^{-3}M$;
[HClO₄]= $1.25 \times 10^{-2}M$; temp.= 35° }

Aniline	$k_2 \times 10^2$ (litre mole ⁻¹ sec ⁻¹) at			
	10% HOAc	20% HOAc	30% HOAc	50% HOAc
Unsubstituted	16.25 (8.125)	11.28 (5.64)	8.567 (4.283)	5.643 (2.821)
<i>p</i> -Chloro	14.32	12.22	9.677	6.331
<i>p</i> -Bromo	18.65	14.53	12.27	8.153
<i>p</i> -Iodo	34.79	17.74	13.77	10.36
<i>p</i> -Methyl	14.85	9.897	7.415	5.971
<i>p</i> -Nitro	2.5	1.898	1.265	0.9974

In the parentheses are rate constants for the *ortho*-isomer.

TABLE 4 — EFFECT OF VARYING COMPOSITION OF DMF

{[Substrate]= $5 \times 10^{-3}M$; [chloramine-T]= $3.5 \times 10^{-4}M$;
[HClO₄]= $5 \times 10^{-2}M$; temp.= 35° }

Substrate	$k_2 \times 10^2$ (litre mole ⁻¹ sec ⁻¹)	
	10% DMF	20% DMF
Aniline	29.51 (14.755)	4.03 (2.015)
<i>p</i> -Chloroaniline	19.49	3.35
<i>p</i> -Bromoaniline	27.58	5.09
<i>p</i> -Iodoaniline	41.51	5.59
<i>p</i> -Toluidine	21.40	3.76
<i>p</i> -Nitroaniline	16.58	3.55

In the parentheses are rate constants for the *ortho*-isomer.

also clear from the earlier investigations⁷. Hence to compare the reactivity of the unsubstituted derivative, the rate constant is divided by a statistical factor of 2 to give the partial rate with respect to *ortho*-isomer. This partial rate, when compared with the rates of other substrates, gives a clear picture of the reactivity which is in the following decreasing order: *p*-iodoaniline > *p*-bromoaniline > *p*-chloroaniline \sim *p*-toluidine > unsubstituted aniline (partial rate) > *p*-nitroaniline. The concept of partial rate factor has been invoked earlier in the study of hydrolysis of *gem*-dihalides⁸. The reactivity order establishes that chloramine-T reaction is different from the usual HOCl processes. The halogens functioning as electron sources in reactions

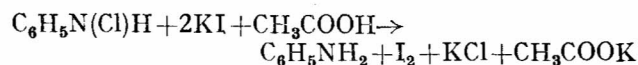
requiring electron accession are not unknown. In the oxidation of aromatic hydrocarbons⁹ it has been noted earlier that *p*-halogens react faster than the unsubstituted derivative due to the demand of electron accession at the reaction site by the resonance effect. At [HClO₄] < $2.5 \times 10^{-2}M$, the structure reactivity relationship is quite clear as seen from the linear plots of log k_2 versus σ . But at higher [HClO₄], because of direct dependence on the deactivated substrates and inverse dependence on the activated substrates, the log k_2 versus σ plot tends to become sigmoid. It appears that the inverse dependence may be due to the reactive species being the unprotonated amines whereas the direct dependence on acidity in case of *p*-nitroaniline shows that it is the protonated species that participate in the reaction. This is also corroborated by the fact that protonation of nitroanilines is rather difficult due to their very low basicity as reported earlier by Bell and Ramsden¹⁰.

HOCl is postulated as the intermediate in all the reactions with chloramine-T and steady state equations have been devised accepting this premise¹¹. It is not very clear whether it is the HOCl that reacts or it is chloramine-T that transfers the halogen directly to the substrate in substitution reactions. To confirm this, one can employ HCl and find whether there is an abnormal acceleration as HOCl and HCl react to give chlorine as observed by Soper and Smith¹ in their work on halogenation of aromatic substrates. It is pertinent to state that such addition of HCl does not cause any acceleration, or rather there is slight retardation. This seems to point out that probably HOCl is not formed at all in chloramine-T reactions. It could be the direct transfer of halogen from chloramine-T. Such direct interaction of halogens has been observed in the bromine oxidation of alcohols in acetic acid-acetate buffer¹². An independent run was done with aniline and HOCl to compare the rate with aniline and chloramine-T. The former is very fast proving that halogenation by HOCl and chloramine-T do not proceed by the same route.

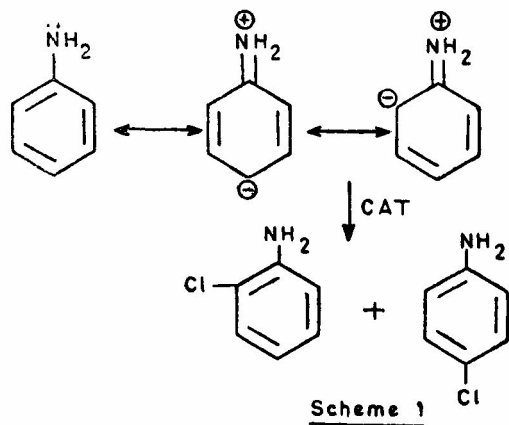
Further, the possibility of dichloramine-T¹³ being the species is ruled out as there is first order dependence with respect to the halogenating agent.

Mechanism — There are various pathways described for aromatic halogenation of amines. One of the pathways is by the formation of N-chloro intermediate¹⁴ which subsequently rearranges to *ortho*-halo and *para*-halo compound. The break down of N-chloro intermediate into nitrene and Cl⁻ was considered by Paul and Gerald¹⁵⁻¹⁶. It appears to us that Cl⁻ cannot be the attacking species on the aromatic ring, as the ring positions are charged negatively at *ortho*- and *para*-positions due to the inherent tendency of the amino group.

The N-halo intermediate is definitely not formed, as the N-halo compound should react with KI to liberate iodine.



Hence at a particular instant of time the iodine that is liberated is due to not only chloramine-T but



also due to N-halo compound that is formed. Hence iodometry cannot be used as a procedure for measuring the rates. Indeed, in the present study iodometry has been used to calculate the disappearance of chloramine-T at any instant. It, therefore, disproves any intermediate formation of N-halo compound.

The reaction sequence can be better represented as shown in Scheme 1.

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