Kinetics of Chlorination of Aniline by Dichloramine-T in Aqueous Acetic Acid Medium

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Chlorination of aniline by dichloramine-T in 1:1 aqueous acetic acid medium, in the presence and absence of acetate ions is first order in [oxidant], nearly first order in [aniline], inverse fractional order in $[H^+]$ and fractional order in added [acetate ion] at constant ionic strength. Effects of added reaction products and variations in ionic strength and solvent composition of the reaction medium have also been investigated. Mechanisms consistent with the observed results are discussed and the related rate laws deduced.

The present investigation is a part of our mechanistic studies with positive halogens in general and N,N-dihalosulphonamides in particular¹⁻⁴. We report herein the kinetics of chlorination of aniline by N,N-dichloro-*p*-toluenesulphonamide (dichloramine-T, DCT) in 1:1 (v/v) water-acetic acid medium under varying conditions.

Materials and Methods

N,N-Dichloro-*p*-toluenesulphonamide (dichloramine-T or DCT) was prepared in the laboratory and its purity checked by elemental analyses, spectral data (IR and PMR) and iodometric estimation of active halogen present in it. Stock solution (~ 0.1 mol dm⁻³) of DCT was prepared in purified dry acetic acid and standardised by iodometric method.

Aniline was redistilled before use. All other reagents used were of AR grade. The ionic strength of the medium was kept at 0.2 or 0.4 mol dm⁻³ by adding concentrated aqueous solution of sodium acetate or sodium perchlorate.

Kinetic measurements

The kinetic studies were carried out in 50% (v/v) aqueous acetic acid under pseudo-first order conditions ([aniline] > > [CAT]; 5-10 times). The reactions were initiated by quick addition of a measured quantity of DCT solution in acetic acid, thermally equilibrated at a desired temperature, to a mixture containing known amounts of aniline, sodium acetate (and sodium perchlorate), HCIO₄, acetic acid and water [to maintain 50% (v/v) solvent composition], pre-equilibrated at the same temperature. The progress of the reaction was monitored for nearly two half-lives by iodometric method. The pseudofirst order rate constants computed by the method of least squares were reproducible within $\pm 4\%$.

Stoichiometry

The stoichiometry of DCT-aniline reaction was determined by equilibrating (at 303 K) reaction mixtures containing slight excess of DCT and different [HClO₄] in solvent mixtures of different compositions, both in the presence and absence of sodium acetate. Analysis of reaction mixtures showed that two moles of aniline reacted with one mole of DCT in accordance with Eq. (1).

$$2C_6H_5NH_2 + RNCl_2 \rightarrow 2C_6H_4CINH_2 + RNH_2$$
... (1)

where $R = CH_3C_6H_4SO_2$.

Results

Plots of log [DCT] versus time were linear for two half-lives (Fig. 1). Pseudo-first order rate constants (k_{obs}) remained unaffected by changes in [DCT]₀, both in the presence and absence of NaOAc (Table 1), establishing first order dependence in $[DCT]_0$. Rate increased with increase in [aniline] with almost first order dependence in [aniline] both in the presence and absence of NaOAc. Plot of k_{obs} versus [aniline] was linear without any intercept. Variation in $[H^+]$ by adding HClO₄ decreased the rate of oxidation both in the presence of NaOAc and in the absence (twenty-fold variation in HClO₄ changed pH by 0.5 unit only) (Table 2). Plot of log k_{obs} versus log $[H^+]$ showed inverse fractional order dependence in [H⁺] both in the absence and presence of NaOAc. Increase in ionic strength of the medium by adding NaClO₄ solution had negligible effect. Further the rate increased with increase in [NaOAc] at constant ionic strength. Plot of k_{obs} versus [NaOAc] was linear with a finite intercept, indicating participation of acetate ion in the reaction (Fig. 2). Addition of the reaction product, p-toluenesulphonamide had no ef-



Fig. 1—Plot of log[DCT] versus time $(10^{3}[S]_{0} = 5.0 \text{ mol } dm^{-3}, medium: 1:1 (v/v) water-acetic acid temp: 303 K. <math>10^{4}[DCT]_{0} (mol \ dm^{-3}) = (a) 2.0, (b) 5.0 (c) 7.5, (d) 10.0 and (e) 20 at \mu = 0.2 mol \ dm^{-3} (NaOAc) and (f) 2.0, (g) 5.0, (h) 10.0 and (i) 20 at \mu = 0.4 \ mol \ dm^{-3} (NaClO_{4}))$

Table 1–Effect of Varying $[DCT]_0$, $[Aniline]_0$, Ionic Strength, Solvent Composition, and Addition of Reaction Product on Rate of Chlorination of Aniline by Dichloramine-T (DCT) in 1:1 (v/v) Aqueous Acetic Acid at 303 K

$10^{4}[DCT]_{0}$.	10^{3} [Aniline] ₀ (mol dm ⁻³)	$10^4 k_{ m obs} ({ m s}^{-1})$ at	$t \mu (mol dm^{-3})$
(morum)	(morum)	0.4 (NaClO ₄)	0.2 (NaOAc)
2.0	5.0	0.55	9.1
5.0	5.0	0.52	9.1
10.0	5.0	0.48	8.9
5.0	1.0	1. <u> </u>	1.9
5.0	2.0	0.25	3.8
			$(1.8^{b}, 5.6^{c})$
5.0	3.0	_	5.6
5.0	5.0	0.52	9.1
			$(4.8^{\rm b}, 15.0^{\rm c})$
5.0	7.0	0.78	13.9
	0,0		$(7.4^{b}, 21.3^{c})$
5.0	10.0	1.10	19.5
5.0	5.0	0.60 ^{a1}	25.6 ^{d1}
5.0	5.0	0.52 ^{a2}	15.6 ^{d2}
5.0	5.0	0.49 ^{a3}	6.0 ^{d3}
5.0	5.0	$\alpha = \eta + \alpha + \frac{1}{2} \alpha + \alpha + \beta$	8.9e1
5.0	5.0	$mp \log \overline{u} > n = r$	8.6 ^{e2}
5.0	5.0	versis <mark>T</mark> CH ₁ CO	8.5 ^{e3}

^a μ (mol dm⁻³)=(1) 0.2, (2) 0.4, (3) 0.5

b.c Values at 293 and 313 K respectively

^d HOAc (%, v/v) = (1) 30, (2) 40, (3) 60.

^c In the presence of PTS, 10^{3} [PTS] (mol dm⁻³)=(1) 2.0, (2) 5.0, (3) 10.0

Table 2–Effect of Variation in [H⁺] (by the Addition of HClO₄) or [NaOAc] on Rate of Chlorination of Aniline by Dichloramine-T in 1:1 (v/v) Water-Acetic Acid Medium at 303 K (10⁴(DCT) = 10³(Aniline) = 5.0 mol dm⁻³)

$(10^{4}[DCT]_{0} = 10^{3}[Aniline]_{0} = 5.0 \text{ m}$	nol	dm_
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$[HClO_4]$		pH at μ (m	nol dm ^{-3})	(mol dm ^{-,3})		
		0.4 (NaClO ₄)	0.2 (NaOAc ^a)	0.4 (NaClO ₄)	0.2 (NaOAc ^a)	
	0.0	1.14	2.71	0.52	9.1	
	0.005	NOTHER RUN	2.67	tale loss annos n	8.4	
	0.01	0.99	2.60	0.40	8.2	
	0.02	0.70	2.52	0.31	6.8	
	0.05	0.49	2.42	0.29	1 diw 5.91 m 585	values. Incre
	0.10	"F(2.18	udicate - partieup	e streng i.4 .4 also ii	
	10[NaOAc]					
	to trois off in	1.86	2.05	0.16	3.9 000	
	OSL nc0.1terce	mis dti 2.14 mi 90	2.40	0.30	6.4	
	d1 9(2.0) bou	ot vils. 2.50	2.71	0.66	9.1	
	3.0 / 0.50	2.74	2.84	0.95	13.6	
s F(H ⁺) are nate (Fig. 2).	While varying [H	ClO ₄]				

S refers to substrate)

fect on the rate. But the increase in HOAc content of the solvent medium decreased the rate (Table 1). Activation parameters were calculated by studying the reaction at 293, 303 and 313 K (Table 3).

Discussion Mechanism of chlorination

The probable reactive oxidant species in aqueous acetic acid medium are $RNCl_2$, $(RNCl_2H)^+$ and



Fig. 2–(i) Plot of k_{obs} versus $1/[H^+]$ at varying $[HClO_4]$ $(10^4[DCT]_0 = 10^3[S]_0 = 5.0 \text{ mol dm}^{-3}$, medium: 1:1 (v/v) wateracetic acid, temp: 303 K (A) $\mu = 0.4$ mol dm⁻³ with NaClO₄, (B) $\mu = 0.2 \text{ mol dm}^{-3}$ with NaOAc)

(ii) Plot of k_{obs} versus $[CH_3COO^-] (10^4[DCT]_0 = 10^3[S]_0 = 5.0 \text{ mol dm}^{-3}$, medium 1:1 (v/v) water-acetic acid, temp.: 303 K. (C) in the absence of NaClO₄ and (D) $\mu = 0.4 \text{ mol dm}^{-3}$ with NaClO₄)

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CH₃COOCl. First order dependence in [DCT], nearly first order dependence in [aniline], fractional order in [acetate] and inverse fractional order dependence in [H⁺] may be explained by a two-pathway mechanism, one via the formation of acyl hypochlorite intermediate (Eq. 2) and the other through the direct pathway (Eq. 3). This is supported by the fact that the plots of k_{obs} versus [acetate], and k_{obs} versus 1/[H⁺] are linear with finite intercepts (Fig. 2) and the corresponding reciprocal plots are nonlinear (figure not shown), attaining the limiting values. Increase in rate with increase in [acetate] at constant ionic strength also indicates participation of CH₃COO⁻ in the reaction.

$$\operatorname{RNCl}_2 + \operatorname{CH}_3 \operatorname{COO}^- + \operatorname{S} \xrightarrow{k_1} \operatorname{Products} \dots (2)$$

and

$$\operatorname{RNCl}_2 + \operatorname{S} \xrightarrow{k_2} \operatorname{Products} \dots (3)$$

(S refers to substrate) Related rate laws are given by Eqs (4) and (5).

$$-\frac{d[DCT]}{dt} = k_1[DCT][S][CH_3COO^-] + k_2[DCT][S]$$
...(4)

Table	3-Kir	netic	Data	and	Activ	vati	on	Param	ieters	for
Chlori	nation	of A	Aniline	by	DCT	in	1:1	(\mathbf{v}/\mathbf{v})	Aque	ous
			Acetic	Aci	d Mec	liur	n			

Order	Order of reaction at constant $\boldsymbol{\mu}$			
	NaClO ₄	NaÓAc		
[DCT] ·	1.0	1.0		
[Aniline]	0.9	1.0		
[H ⁺] ^a _{eff}	-0.4	-0.6		
[CH ₃ COO ⁻]	0.9	0.7		
Parameter				
log A	6.2 ± 0.1	4.4 ± 0.1		
$E_{\rm a}(\rm kJ\ mol^{-1})$	61 ± 2	45 ± 1		
ΔH^{\neq} (kJ mol ⁻¹)	59 ± 2	43 ± 1.5		
$\Delta S \neq (\mathbf{J}\mathbf{K}^{-1} \operatorname{mol}^{-1})$	-133 ± 4	-166 ± 5		
$\Delta G \neq (\text{kJ mol}^{-1})$	99 ± 2	94 ± 2		

^aCalculated from the pH values at varying [HClO₄].

Table 4—Comparison of Predicted and Observed Rate Constants for Chlorination of Aniline by Dichloramine-T in 1:1 (v/v) Aqueous Acetic Acid Medium

10^{3} [Aniline] ₀ (mol dm ⁻³)	18	$10^4 k_{\rm obs}({\rm s}^{-1})$	-747	
OE . 2	Calc ^a	Calc ^b	Obs	
1.0	1.9	1.9	1.9	
$10^{10} \text{ s}^{-1} = 0.2 \text{ mol dm}^{-1}$	3.8	TOC3.9 10 10	3.8	
emp: 303 K. 0.6 DCTL (mo	5.8	5.8 (V) I	5.6	
0.0 and (e) $200.2 \mu = 0.2$ mo	9.6	(5) 0.9.8 .0.5	9.1	
b) 10.0 and $(0.70 \text{ at } \mu = 0.4$	13.4	0.5 13.6 DAG	13.9	
10.0	19.2	19.5	19.3	

Calculated from k_1 and k_2 values computed from the plot of ${}^ak_{obs}$ versus [CH₃COO⁻](Eq. 5) ${}^bk_{obs}$ versus 1/[H⁺](Eq. 6)

and loom) if its Ho	[HCIO]	
$k_{\text{obs}} = k_1[S][CH_3COO$	$^{-}]+k_{2}[S]$	(5)

Substituting $[CH_3COO^-] = K_a[CH_3COOH]/[H^+]$ we get

$$k_{\rm obs} = \left\{ \frac{K_{\rm a} k_1 [\rm CH_3 \rm COOH]}{[\rm H^+]} + k_2 \right\} [\rm S] \qquad \dots (6)$$

Rate law (6) envisages that the plot of k_{obs} versus [S] should be linear with almost no intercept on the ordinate. This is actually found to be the case (figure not shown). Further, as already pointed out, plots of k_{obs} versus [CH₃COO⁻] and k_{obs} versus 1/[H⁺] are also linear with intercepts on the ordinate (Fig. 2). Values of the constants k_1 and k_2 have been calculated from the slopes and intercepts of the above plots respectively. These constants are used to predict the rate constants at varying [S]₀. Predicted values compare very well with the experimental rate constants (Table 4).

T	Table 5-Pseudo-first Order Rate Constants for Chlori-
	nation of Several Substituted Anilines by DCT in 1:1
	(v/v) Aqueous Acetic Acid at 303 K

 $10^{4}[DCT]_{0} = 10^{3}[S]_{0} = 5.0 \text{ mol dm}^{-3}; \mu = 0.2 \text{ mol dm}^{-3}$ with NaOAc. $10^4 k_{\rm obs}$ $10^4 k_{\rm obs}$ Aniline Aniline (s^{-1}) (s^{-1}) 0.76 Unsubstituted 9.1 *m*-nitro p-chloro 7.0 o-chloro 3.2 p-bromo 8.1 3.4-dichloro 4.0 p-iodo 8.9 N-methyl 18.0 *p*-methyl 10.1 N,N-dimethyl 6.0

mune (TCM) in aqueous acetic acid medium.

The reaction between aniline and DCT via N-chloro intermediate is supported by the observation that there is no reaction between DCT and acetanilide (containing an electron-withdrawing N-acetyl group) under identical conditions and the introduction of NO₂ group in benzene ring decreases the rate by about 20 times. Further the rate of chlorination of *o*-chloroaniline is about one-third that for aniline (Table 5). While the substituent at the *para*position decreases the rate by about 20%. Replacement of one of the hydrogens of - NH₂ group by methyl group increases the rate to almost double whereas replacement of both the hydrogen atoms

The second presence of TCM was followed pseutrain. The second in this medium followed pseudo-second order kinetics as seen from the linear plots of 1/titre versus time. But the observed rate constants decreased with increase in [TCM]₀. This may be due to the existence of many competing equilibria. The order in [substrate] was unity at [HCIO_1]=0.01 mol dm⁻² and became fractional at mation of more unreacive protonated form of substrate. The reaction rates were apparently independent of [H⁻¹] in the range studied which might be due to the cancellation of direct dependence on [H⁻¹] involved in the hydrolysis of TCM and inwerse dependence on [H⁻¹] for the protonation of unitine. The rates remained invariant by the addition of KC] and melamine.

In 90% aq. acetic acid in the presence of HCIO₂, the disappearance of TCM was followed up to 75% completion of the reaction. In this medium the reaction followed pseudo-first order kinetics, as seen from the linearity of the plots of log (titre) versus time. Here again the rate constants increased with increase in $[TCM]_0$. The rate of reaction is reaction of chance in [substants].

decreases the rate. Electron-releasing substituents (such as Me) at the *para-* and *meta-*positions generally increase the rates while electron-withdrawing substituents decrease the rate (Table 5).

Large negative entropies of activation and high positive free energy of activation (Table 3) suggest the role of bond breaking in attaining the activated state.

The observed negative dielectric effect is in conformity with the Amis' concept⁵ for dipolar molecule-dipolar molecule and dipolar molecule-negative ion interactions and the proposed mechanisms.

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tion of aromatic ammes. This prompt dertake the title investigation.

Materials and Methods

The reagents used were of AR (BDH) grade and were recrystallised or redistilled before use. Trichtoromelamine (Fluka), was used as such. The stock rolation of TCM was prepared in 100% acetic add in which it was highly stable and its concentration was determined fodometrically in acid medium in accordance with reaction [1].

$$C_{s}N_{s}H_{s}C_{s} + 61^{-} + 3H^{-} = C_{s}N_{s}H_{s} + 31^{-} + 3C^{-}$$

 $(1 \text{ CM}) = (1 \text{ CM})^{-}$

The kinetics were monitored by estimating the disappearance of [TCM] at various time intervals by standard iodometric procedure. Rate constants were reproducible within \pm ⁵⁰%. Self-decomposition of TCM was negligible under the conditions employed. The rate constants remained practically invariant in air or under O₂-free atmosphere. Only data at 35°C (\pm 0.1)°C in different aqueous acetic acid-perchloric acid media are presented here. The product obtained was *p*-chloroaniline under the provent sconditions.