

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 ($\sim 0.1 \text{ mol dm}^{-3}$) of DCT was prepared in purified dry acetic acid and standardised by iodometric method.

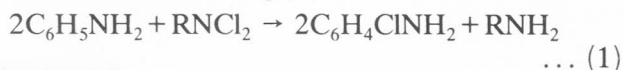
Aniline was redistilled before use. All other reagents used were of AR grade. The ionic strength of the medium was kept at 0.2 or 0.4 mol dm^{-3} by adding concentrated aqueous solution of sodium acetate or sodium perchlorate.

Kinetic measurements

The kinetic studies were carried out in 50% (v/v) aqueous acetic acid under pseudo-first order conditions ($[\text{aniline}] \gg [\text{CAT}]$; 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), HClO_4 , 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 pseudo-first 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 $[\text{HClO}_4]$ 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).



where $\text{R} = \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$.

Results

Plots of $\log [\text{DCT}]$ versus time were linear for two half-lives (Fig. 1). Pseudo-first order rate constants (k_{obs}) remained unaffected by changes in $[\text{DCT}]_0$, both in the presence and absence of NaOAc (Table 1), establishing first order dependence in $[\text{DCT}]_0$. 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 HClO_4 decreased the rate of oxidation both in the presence of NaOAc and in the absence (twenty-fold variation in HClO_4 changed pH by 0.5 unit only) (Table 2). Plot of $\log k_{\text{obs}}$ 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 NaClO_4 solution had negligible effect. Further the rate increased with increase in $[\text{NaOAc}]$ at constant ionic strength. Plot of k_{obs} versus $[\text{NaOAc}]$ 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-

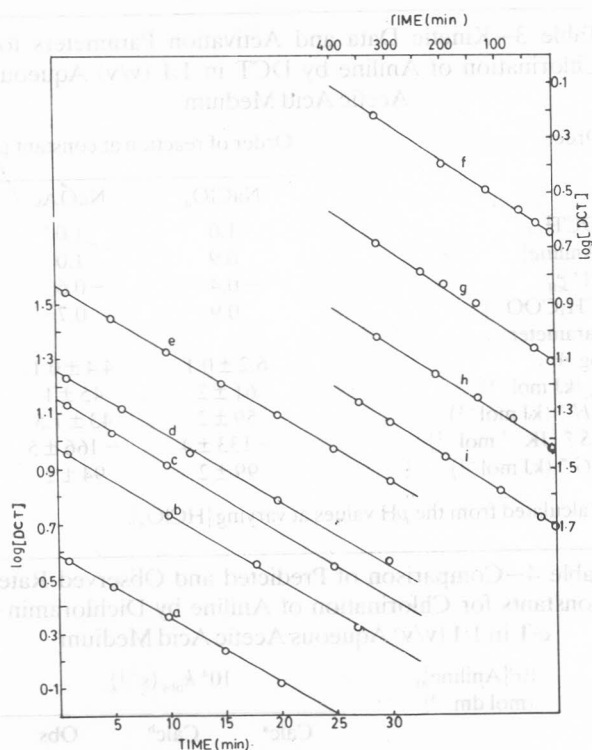


Fig. 1—Plot of $\log[DCT]$ versus time ($10^3[S]_0 = 5.0 \text{ mol dm}^{-3}$, medium: 1:1 (v/v) water-acetic acid temp: 303 K. $10^4[DCT]_0$ (mol dm^{-3}) = (a) 2.0, (b) 5.0 (c) 7.5, (d) 10.0 and (e) 20 at $\mu = 0.2 \text{ mol dm}^{-3}$ (NaOAc) and (f) 2.0, (g) 5.0, (h) 10.0 and (i) 20 at $\mu = 0.4 \text{ mol dm}^{-3}$ (NaClO₄))

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

$10^4[DCT]_0$ (mol dm^{-3})	$10^3[Aniline]_0$ (mol dm^{-3})	$10^4 k_{\text{obs}}$ (s^{-1}) at μ (mol dm^{-3})	
		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	—	1.9
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 ^b , 15.0 ^c)
5.0	7.0	0.78	13.9
			(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	—	8.9 ^{e1}
5.0	5.0	—	8.6 ^{e2}
5.0	5.0	—	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.

^e 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

($10^4[DCT]_0 = 10^3[Aniline]_0 = 5.0 \text{ mol dm}^{-3}$)

$[HClO_4]$ (mol dm^{-3})	pH at μ (mol dm^{-3})		$10^4 k_{\text{obs}}$ at μ (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	—	2.67	—	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	5.9
0.10	—	2.18	—	4.4
$10[NaOAc]$				
0.5	1.86	2.05	0.16	3.9
1.0	2.14	2.40	0.30	6.4
2.0	2.50	2.71	0.66	9.1
3.0	2.74	2.84	0.95	13.6

^aWhile varying $[HClO_4]$

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

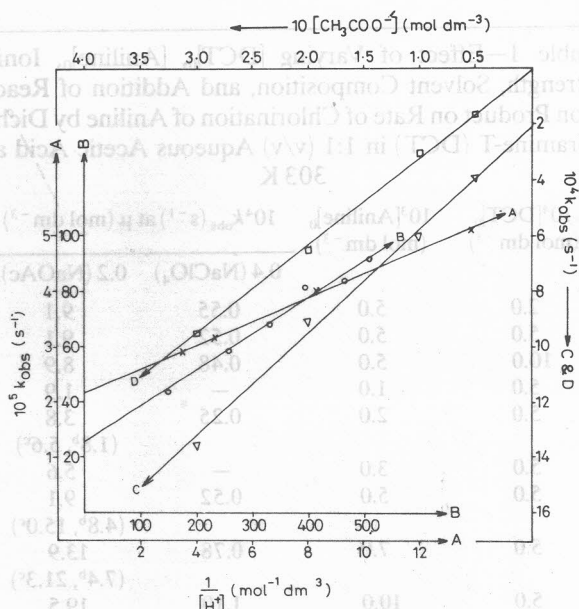
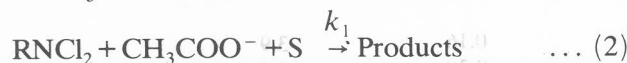


Fig. 2—(i) Plot of k_{obs} versus $1/[\text{H}^+]$ at varying $[\text{HClO}_4]$ ($10^4[\text{DCT}]_0 = 10^3[\text{S}]_0 = 5.0 \text{ mol dm}^{-3}$, medium: 1:1 (v/v) water-acetic acid, temp: 303 K (A) $\mu = 0.4 \text{ mol dm}^{-3}$ with NaClO_4 , (B) $\mu = 0.2 \text{ mol dm}^{-3}$ with NaOAc)

(ii) Plot of k_{obs} versus $[\text{CH}_3\text{COO}^-]$ ($10^4[\text{DCT}]_0 = 10^3[\text{S}]_0 = 5.0 \text{ mol dm}^{-3}$, medium 1:1 (v/v) water-acetic acid, temp.: 303 K. (C) in the absence of NaClO_4 and (D) $\mu = 0.4 \text{ mol dm}^{-3}$ with NaClO_4)

CH_3COOCl . First order dependence in $[\text{DCT}]$, nearly first order dependence in $[\text{aniline}]$, fractional order in $[\text{acetate}]$ and inverse fractional order dependence in $[\text{H}^+]$ 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 $[\text{acetate}]$, and k_{obs} versus $1/[\text{H}^+]$ 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 $[\text{acetate}]$ at constant ionic strength also indicates participation of CH_3COO^- in the reaction.



and



(S refers to substrate)

Related rate laws are given by Eqs (4) and (5).

$$-\frac{d[\text{DCT}]}{dt} = k_1[\text{DCT}][\text{S}][\text{CH}_3\text{COO}^-] + k_2[\text{DCT}][\text{S}] \quad \dots (4)$$

Table 3—Kinetic Data and Activation Parameters for Chlorination of Aniline by DCT in 1:1 (v/v) Aqueous Acetic Acid Medium

Order	Order of reaction at constant μ	
	NaClO_4	NaOAc
$[\text{DCT}]$	1.0	1.0
$[\text{Aniline}]$	0.9	1.0
$[\text{H}^+]_{\text{eff}}^a$	-0.4	-0.6
$[\text{CH}_3\text{COO}^-]$	0.9	0.7
Parameter		
$\log A$	6.2 ± 0.1	4.4 ± 0.1
E_a (kJ mol $^{-1}$)	61 ± 2	45 ± 1
ΔH^\ddagger (kJ mol $^{-1}$)	59 ± 2	43 ± 1.5
ΔS^\ddagger (JK $^{-1}$ mol $^{-1}$)	-133 ± 4	-166 ± 5
ΔG^\ddagger (kJ mol $^{-1}$)	99 ± 2	94 ± 2

^aCalculated from the pH values at varying $[\text{HClO}_4]$.

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

$10^3[\text{Aniline}]_0$ (mol dm $^{-3}$)	$10^4 k_{\text{obs}}$ (s $^{-1}$)		
	Calc ^a	Calc ^b	Obs
1.0	1.9	1.9	1.9
2.0	3.8	3.9	3.8
3.0	5.8	5.8	5.6
5.0	9.6	9.8	9.1
7.0	13.4	13.6	13.9
10.0	19.2	19.5	19.3

Calculated from k_1 and k_2 values computed from the plot of

^a k_{obs} versus $[\text{CH}_3\text{COO}^-]$ (Eq. 5)

^b k_{obs} versus $1/[\text{H}^+]$ (Eq. 6)

and

$$k_{\text{obs}} = k_1[\text{S}][\text{CH}_3\text{COO}^-] + k_2[\text{S}] \quad \dots (5)$$

Substituting $[\text{CH}_3\text{COO}^-] = K_a[\text{CH}_3\text{COOH}]/[\text{H}^+]$ we get

$$k_{\text{obs}} = \left\{ \frac{K_a k_1 [\text{CH}_3\text{COOH}]}{[\text{H}^+]} + k_2 \right\} [\text{S}] \quad \dots (6)$$

Rate law (6) envisages that the plot of k_{obs} versus $[\text{S}]$ 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 $[\text{CH}_3\text{COO}^-]$ and k_{obs} versus $1/[\text{H}^+]$ 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 $[\text{S}]_0$. Predicted values compare very well with the experimental rate constants (Table 4).

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

$10^4[\text{DCT}]_0 = 10^3[\text{S}]_0 = 5.0 \text{ mol dm}^{-3}$; $\mu = 0.2 \text{ mol dm}^{-3}$ with NaOAc.

Aniline	$10^4 k_{\text{obs}}$ (s^{-1})	Aniline	$10^4 k_{\text{obs}}$ (s^{-1})
Unsubstituted	9.1	<i>m</i> -nitro	0.76
<i>p</i> -chloro	7.0	<i>o</i> -chloro	3.2
<i>p</i> -bromo	8.1	3,4-dichloro	4.0
<i>p</i> -iodo	8.9	N-methyl	18.0
<i>p</i> -methyl	10.1	N,N-dimethyl	6.0

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

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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