Kinetics of Oxidation of Diethylamine by *N*-Chlorobenzotriazoles

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Kinetics of the oxidation of diethylamine with 1-chlorobenzotriazole, 1-chloro-4-nitrobenzotriazole, and 1,4,5,6,7-pentachlorobenzotriazole in aqueous acetic acid, in the presence of perchloric acid, has been studied. The oxidation is a second-order reaction uncatalyzed by acid. The rates and the activation parameters of the oxidation by the three chloramines do not differ significantly and the chloramines oxidize by a common mechanism.

Diethylamine (DEA) is an important aliphatic amine used in the manufacture of pharmaceuticals such as procaine (a local anaesthetic), dye stuff, corrosion inhibitors, *etc.* Chloramines, used as disinfectants and antiseptics, contain one or more chlorine atoms attached to nitrogen covalently and behave both as oxidizing and chlorinating agents. The organic chloramines resemble hypochlorite in their oxidative behaviour and are more stable than hypochlorite.

There is no information available on the oxidation of DEA by chloramines and here we report on the kinetics of oxidation by *N*-chlorobenzotriazoles. DEA was oxidized with bromamine-B by *Ananda et al.* [1]. Although reports on the kinetics and mechanism of oxidation of a variety of substrates by 1-chlorobenzotriazole are numerous [2, 3], this is the first to compare the reactivities of some substituted 1-chlorobenzotriazoles.

The oxidation conducted in the presence of fixed large excess of perchloric acid in aqueous acetic acid under pseudo-first-order conditions of [DEA] $\gg$ [chloramines] affords linear plots of log{[chloramines]} *vs.* time. The linearity of these plots (Fig. 1) together with the constancy of the slope at varying [chloramines]$_0$ indicate a first-order dependence of the reaction rate on [chlorobenzotriazoles]. The pseudo-first-order rate constants (k') obtained at 313 K are listed in Table 1. Due to the poor solubility of pentachlorobenzotriazole the kinetic measurements of the oxidation with this chloramine were carried out in 70 % acetic acid. The reaction is first-order with respect to DEA and the order with respect to the amine was obtained under
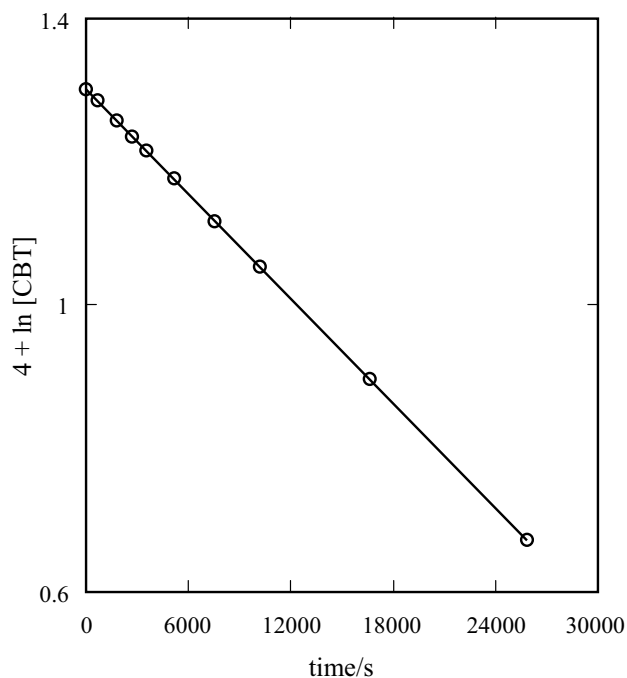

Fig. 1. Pseudo-first-order plot ([PCBT]$_0$ = 2.00 × 10^{-3} mol dm^{-3}, [DEA]$_0$ = 3.00 × 10^{-2} mol dm^{-3}, [HClO$_4$] = 0.10 mol dm^{-3}, 70 % aqueous acetic acid, T = 313 K).

the condition: [DEA]$_0 \gg$ [chloramines] by determining the pseudo-first-order rate constants at different [DEA]$_0$. The pseudo-first-order rate constants increase with increasing concentration of DEA and plots of k' *vs.* [DEA]$_0$ are straight lines passing through the ori-

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Table 1. Rate Constants of the Oxidation of Diethylamine by Chlorobenzotriazoles (0.10 M-HClO$_4$, 50 % Aqueous Acetic Acid, T = 313 K)

| [Chloramine]$_0 \cdot 10^3$ | [DEA]$_0 \cdot 10^2$ | CBT | | NCBT | | PCBT* | |
| | | $k' \cdot 10^5$ | $k_2 \cdot 10^3$ | $k' \cdot 10^5$ | $k_2 \cdot 10^3$ | $k' \cdot 10^5$ | $k_2 \cdot 10^3$ |
mol dm^{-3}	mol dm^{-3}	s^{-1}	dm^3 mol^{-1} s^{-1}	s^{-1}	dm^3 mol^{-1} s^{-1}	s^{-1}	dm^3 mol^{-1} s^{-1}
1.00	3.00	5.2		6.1		5.6	
2.00	3.00	5.2	1.7	6.0	2.0	5.6	1.9
3.00	3.00	5.2		6.0		5.6	
4.00	3.00	5.2		6.0		5.6	
2.00	1.50	2.6	1.7	3.0	2.0	2.8	1.9
2.00	2.00	3.5	1.7	4.0	2.0	3.7	1.9
2.00	2.50			5.0	2.0		
2.00	4.00	7.0	1.7	8.0	2.0	7.4	1.9
2.00	5.00	8.7	1.7	10.0	2.0	9.5	1.9
2.00	5.50	9.6	1.7			10.4	1.9
2.00	6.00	10.4	1.7	12.1	2.0	11.3	1.9

*70 % aqueous acetic acid.

Table 2. Lack of Acid Catalysis ([CBT]$_0$ = 2.00 × 10^{-3} mol dm^{-3}, [DEA]$_0$ = 3.00 × 10^{-2} mol dm^{-3}, 50 % Aqueous Acetic Acid, T = 313 K)

[HClO$_4$]/(mol dm^{-3})	0.04	0.10	0.20	0.30	0.40	0.50
$k' \cdot 10^5$/s^{-1}	5.1	5.2	5.2	5.3	5.3	5.4

Table 3. Reaction Rate at Different Solvent Compositions ([CBT]$_0$ = 2.00 × 10^{-3} mol dm^{-3}, [DEA]$_0$ = 3.00 × 10^{-2} mol dm^{-3}, [HClO$_4$] = 0.10 mol dm^{-3}, T = 313 K)

HOAc-H$_2$O/%	40-60	50-50	60-40	70-30
$k' \cdot 10^5$/s^{-1}	5.5	5.2	4.5	4.8

Table 4. Activation Parameters

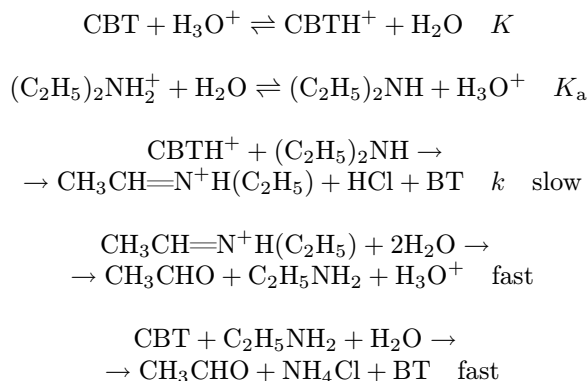| | E_a | ln{$A/$ (dm^3 mol^{-1} s^{-1})} | $\Delta H^{\#}$ | $\Delta S^{\#}$ |
	kJ mol^{-1}		kJ mol^{-1}	J K^{-1} mol^{-1}
CBT	85	26	82	35
NCBT	84	26	82	36
PCBT	86	27	84	30

gin. Also, the double logarithmic plots of k' vs. [DEA]$_0$ are linear with slope of unity. The second-order rate constants, calculated from the pseudo-first-order rate constants ($k' = k_2$[DEA]$_0$), remain constant at different [DEA]$_0$. The reaction is uncatalyzed by acid; the pseudo-first-order rate constant remains practically the same at different acidities of the medium (Table 2). Since the reaction medium is aqueous acetic acid, the kinetics of the oxidation could not be studied at low acidity ([H$^+$] $\ll$ [DEA]$_0$). The pH of 50 % and 70 % aqueous acetic acid are 1.27 ([H$^+$] = 0.054 mol dm^{-3}) and 0.71 ([H$^+$] = 0.195 mol dm^{-3}), respectively. The oxidation is not susceptible to the ionic strength of the medium indicating the involvement of at least one neutral molecule in the rate-determining step; addition of perchloric acid resulted in an increase of ionic strength of the medium from 0.04 mol dm^{-3} to 0.50 mol dm^{-3}. The reaction rate does not vary appreciably with the solvent polarity; by varying the content of acetic acid in the reaction mixture the solvent polarity was varied. The increase of acetic acid content from 40 % to 70 % decreases the relative permittivity of the medium from 49.6 to 27.9 (Table 3). The reaction rates at different temperatures (303—323 K) were determined and the activation parameters were calculated from the Arrhenius (ln{k_2} vs. $1/T$) and Eyring (ln{k_2/T} vs. $1/T$) plots (Table 4).

The oxidation is a second-order reaction uncatalyzed by acid. But the survey of literature reveals that the CBT oxidation is acid-catalyzed [2, 3]; in acidic medium the chloramine is protonated and the protonated haloamine acts as the oxidizing agent. DEA is a base (pK_a = 10.93) and in acidic solution exists as the conjugate acid. The free base is a better nucleophile than the conjugate acid and hence it is the probable reactive species. Similarly the protonated chloramine is a powerful electrophile and therefore it is the likely oxidizing species [2, 3]. The kinetic results point to the reaction of molecular diethylamine with the protonated chloramines as rate-limiting (Scheme 1). If the chloronium ion were to be the reactive species the oxidation should be inhibited by the reaction product – benzotriazoles (BT) [4]. This demands first-order and inverse first-order dependence of the reaction rate on [N-chlorobenzotriazoles] and [benzotriazoles], respectively [5], i.e. $-$d[CBT]/dt =
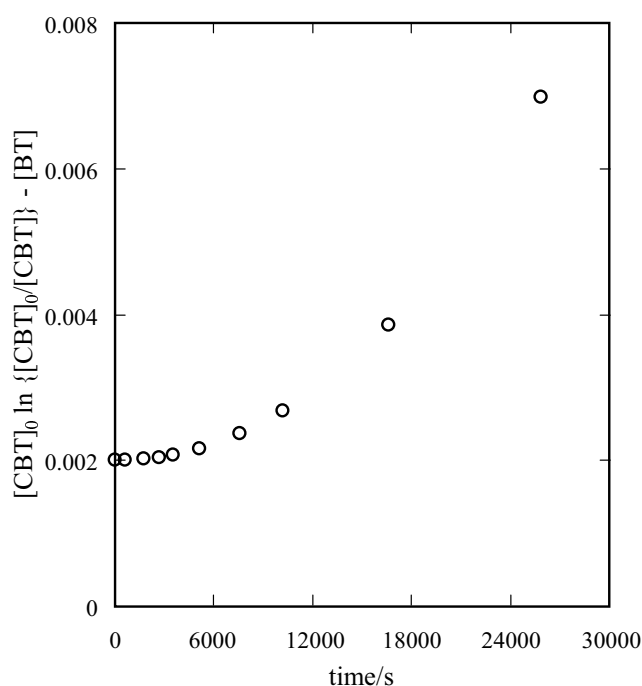
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$$CBT + H_3O^+ \rightleftharpoons CBTH^+ + H_2O \quad K$$

$$(C_2H_5)_2NH_2^+ + H_2O \rightleftharpoons (C_2H_5)_2NH + H_3O^+ \quad K_a$$

$$CBTH^+ + (C_2H_5)_2NH \rightarrow$$
$$\rightarrow CH_3CH{=}N^+H(C_2H_5) + HCl + BT \quad k \quad slow$$

$$CH_3CH{=}N^+H(C_2H_5) + 2H_2O \rightarrow$$
$$\rightarrow CH_3CHO + C_2H_5NH_2 + H_3O^+ \quad fast$$

$$CBT + C_2H_5NH_2 + H_2O \rightarrow$$
$$\rightarrow CH_3CHO + NH_4Cl + BT \quad fast$$

Scheme 1

Fig. 2. *N*-Chlorobenzotriazole first-order, benzotriazole inverse first-order plot (conditions as in Fig. 1).

$k_{obs}[CBT]/[BT]$. The corresponding kinetic equation is $[CBT]_0 \ln\{[CBT]_0/[CBT]\} - [BT] = -k_{obs}t$ where $[BT] = [CBT]_0 - [CBT]$. Plots of $[CBT]_0 \ln\{[CBT]_0/[CBT]\} - [BT]$ *vs.* time are not linear indicating the absence of inhibition by benzotriazoles (Fig. 2). Also, if the reaction were to be inverse first-order in benzotriazoles, contrary to the experimental results, the kinetic run data should not fit in the pseudo-first-order plots and the pseudo-first-order rate constants calculated with [chlorobenzotriazoles]$_0$ and [chlorobenzotriazoles] at different reaction times using the integrated first-order rate equation should not remain constant (typical kinetic data not given). Recently, *Ananda et al.* [1] have reported on the kinetics of oxidation of DEA in acidic solution ([H$^+$] $\gg$ [DEA]), observed inhibition by H$^+$, shown the protonation of

the haloamine, evaluated the protonation constant of monobromoamine-B from the kinetic data, but failed to take into account the formation of the conjugate acid of DEA in acidic solution.

The rate law for the suggested mechanism is

$$-d[CBT]/dt = 2KK_ak[CBT][DEA]$$

with a pseudo-first-order rate constant of $k' = 2KK_ak[DEA]$.

The reaction order of the oxidation does not change with the substituents at the benzene ring of the chloramine. Also, the reactivity does not vary appreciably with the substituents in the chloramine. The activation parameters do not differ significantly, too. These results clearly show that the reactions of the chlorobenzotriazoles follow a common mechanism. This is in agreement with the report that the oxidation of fluoren-9-ols in aqueous acetic acid by CBT and NCBT follows a common mechanism [6]. Table 1 shows that the oxidation rates of NCBT and PCBT are slightly higher than that of CBT and this is due to the presence of electron-withdrawing groups in the substituted chlorobenzotriazoles.

EXPERIMENTAL

The chlorobenzotriazoles, *viz.* 1-chlorobenzotriazole (CBT), 1-chloro-4-nitrobenzotriazole (NCBT), and 1,4,5,6,7-pentachlorobenzotriazole (PCBT) were prepared and recrystallized using the standard methods; the purity was checked (99 %) by iodometric assay and melting point. Solutions of chlorobenzotriazoles in aqueous acetic acid were prepared and standardized iodometrically. Diethylamine (DEA) was distilled and dissolved in aqueous acetic acid. Aqueous solution of perchloric acid was used after standardization.

The reaction at fixed temperature, under the condition that [DEA]$_0$ and [HClO$_4$] $\gg$ [chloramines], was initiated by the addition of chlorobenzotriazoles to DEA and perchloric acid in aqueous acetic acid. The progress of the oxidation, at least up to two half-lives, was monitored by iodometric estimation of the chloramine at different reaction times. The pseudo-first-order rate constant, k', calculated by the method of least squares was reproducible within ± 5 %. Experiments show that under the reported conditions perchloric acid oxidizes neither DEA nor iodide ion.

At the product analysis chlorobenzotriazole (5 mmol) was added to 5 mmol of DEA, in the presence of 0.1 mol of perchloric acid. After the reaction was complete, the reaction solution was added to a saturated solution of 2,4-dinitrophenylhydrazine (50 cm^3) in 2 mol dm^{-3} hydrochloric acid. After stirring for 1 h in an ice bath, the precipitate was filtered in a glass crucible, washed with 2 mol dm^{-3} hydrochloric acid and dried in vacuum. Yield: 70 %.

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