Mechanism of Oxidation of Ascorbic Acid by N-Chlorobenzamide

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The oxidation of ascorbic acid by N-chlorobenzamide (NCB) in 30% methanol follows first and zero order dependences in NCB and ascorbic acid respectively. The order in hydrochloric acid is ~2 being unity in both H+ and Cl- ion concentrations. Ionic strength and solvent effects are negligible. A mechanism involving the formation of free chlorine from the interaction of NCB and hydrochloric acid is proposed in the rate determining step. The activation energy of the oxidation process is 18.4 ± 0.2 kcal mole^{-1}.

THE use of N-chlorobenzamide (NCB) as a volumetric reagent for the oxidimetric determination of several inorganic and organic substances, in acidic medium is described by Singh et al.[1]. No work has been reported so far on the mechanism of NCB oxidative action on organic substrates. Possibility of oxidation of ascorbic acid (AH_2) by NCB is mentioned in literature but no details are given. In the present paper the kinetics of oxidation of ascorbic acid by NCB in acid medium are reported and a suitable mechanism has been proposed.

Materials and Methods

Standard solutions of NCB (m.p. 116°)[2,3] were always prepared fresh in methanol (AR, BDH) and stored in dark bottles. Aq. solution of ascorbic acid (GR, S. Merck) was also prepared fresh. Conductivity water was used throughout the course of investigation. All other reagents used were of AR grade. Reactions were carried out in 150 ml gena glass flasks coated black from outside to avoid any photochemical decomposition.

Kinetic measurements — The progress of reaction was followed by estimating ascorbic acid at definite time intervals against the standardized ceric sulphate using variamine blue as indicator[4]. It was ascertained that no reaction took place between Ce(III) and NCB in such media.

For determining the stoichiometry, the reaction mixtures containing known excess of ascorbic acid over NCB were kept at 40° for 4 hr in the presence of $0.2M$ HCl. The amount of ascorbic acid remaining unreacted revealed that equivalent amounts of reagents were consumed giving dehydroascorbic acid and benzamide as the products (Eq. 1).

$$C_6H_8O_6 + C_6H_5CONHCl = C_6H_6O_6 + C_6H_5CONH_2 + HCl \quad \ldots(1)$$
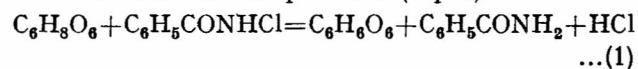
Results

The kinetics of oxidation of ascorbic acid by excess NCB was studied at several initial concentrations of the reactants (Table 1). The plots of [ascorbic acid] versus time were always linear (Fig. 1) thereby indicating the pseudo zero order rate constants (k_0)

TABLE 1 — EFFECT OF VARYING [REACTANTS] AT 30° IN 30% METHANOL

Exp. No.	$[AH_2]$ $M \times 10^4$	$[NCB]$ $M \times 10^3$	$[HCl]$ $M \times 10^2$	$k_0 \times 10^8$ moles litre^{-1} sec^{-1}
1	6	10	10	11.2
2	8	10	10	11.2
3	10	10	10	10.8
4	14	10	10	11.5
5	20	10	10	11.6
6	10	6	10	6.56
7	10	8	10	8.89
8	10	14	10	16.0
9	10	20	10	23.0
10*	10	10	6	6.40
11*	10	10	8	9.79
12*	10	10	10	14.1
13*	10	10	14	24.0
14*	10	10	20	47.0

*In the presence of $1.2M$ NaClO$_4$.

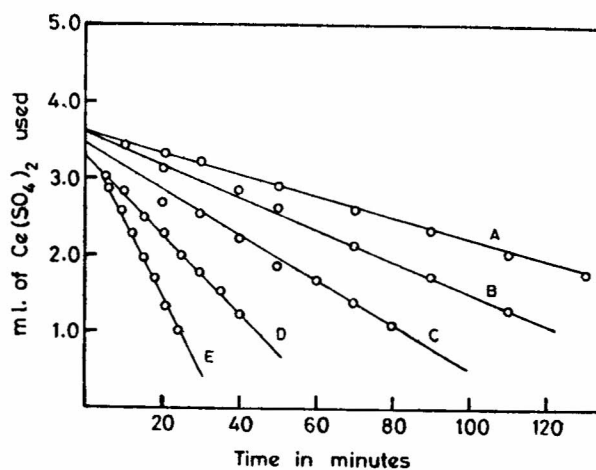Fig. 1 — Zero order rate plots in ascorbic acid at 30° {$[AH_2] = 10^{-3}M$, [HCl] $= 0.1M$, [MeOH] = 30%, and [NCB] = 6.0, 8.0, 10, 14 and $20 \times 10^{-3}M$ for A, B, C, D and E plots respectively]

TABLE 2 — EFFECT OF ADDED $NaClO_4$ AND NaCl AT 30°

{[NCB] = 0·01M, [AH_2] = 10⁻³M, [HCl] = 0·1M, [MeOH] = 30%}

[$NaClO_4$] M	$k_0 \times 10^8$ moles litre⁻¹ sec⁻¹	[NaCl] M	$k_0 \times 10^8$ moles litre⁻¹ sec⁻¹	[Cl⁻]* M	$k_0 \times 10^8$ moles litre⁻¹ sec⁻¹
None added	10·8	None added	10·8	0·1	14·1
0·2	10·9	0·1	18·0	0·2	24·8
0·4	11·3	0·2	24·6	0·3	33·9
0·6	11·7	0·3	31·3	0·4	47·1
0·8	13·3	0·4	40·6	0·5	56·5
1·2	14·1	0·6	55·6	—	—

*In the presence of 1·2M $NaClO_4$.

in ascorbic acid (Table 1). An increase in [NCB] increased the rate (k_0) proportionately and the average value of k_0[NCB] was found to be $11 \cdot 1 \pm 0 \cdot 4 \times 10^{-6}$ sec⁻¹ at 30° in 0·1M HCl. The order in hydrochloric acid was calculated from the slope of the linear plot of log k_0 versus log [HCl] and it was found to be 1·75.
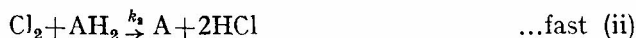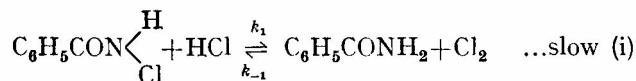
Effect of added salts — The effect of adding neutral salts, viz. $NaClO_4$ and NaCl, was investigated. The results show that the oxidation of ascorbic acid by NCB has specific chloride ion effect. A large variation in [$NaClO_4$] (μ=0·1 to 1·3) increased the rate only slightly while addition of NaCl strongly catalysed the reaction (Table 2). Further, the effect of Cl⁻ at constant ionic strength (in the presence of 1·2M $NaClO_4$) was also investigated and the order in [Cl⁻] was calculated to be 0·8 from the slope of the linear plots of log k_0 versus log [Cl⁻]. As the reactions were investigated in methanolic solutions, the effect of methanol on the rate of oxidation was also studied. A variation in [methanol] from 20 to 50% changed the rate constant from 10·2 to 11·3.

Effect of temperature — The effect of temperature was quite marked. The values of rate constants (k_0) were obtained as 7·50, 10·8, 19·4, 32·4 and $51 \cdot 7 \times 10^{-8}$ moles litre⁻¹ sec⁻¹ at 25°, 30°, 35°, 40° and 45° respectively. The activation energy ($\Delta E\ddagger$) of the oxidation of ascorbic acid by NCB was found to be $18 \cdot 4 \pm 0 \cdot 2$ kcal mole⁻¹.

Discussion

Kinetics of the oxidation of ascorbic acid by hydrogen peroxide[5], Os(VIII)[6], hexacyanoferrate(III)[7], hexachloroplatinate[8], peroxydisulphate[9] and Ag(I)[10] have been reported. Some metal ion and metal chelate catalysed oxidations[11] of ascorbic acid have also been examined. In general, these oxidations show a negative influence of hydrogen ions. However, the oxidation of ascorbic acid by NCB is strongly catalysed by HCl and the order is found to be ~2 (1·75). H⁺ and Cl⁻ ions independently catalyse the rate of oxidation and the order in [Cl⁻] calculated separately is nearly unity (0·8). The order in hydrogen ions is, therefore, unity by difference. Apart from the above, the oxidation of ascorbic acid by NCB follows zero and first order dependences in ascorbic acid and NCB respectively.

This clearly reveals that ascorbic acid is involved in the fast step (ii) while the oxidant and acid constitute the slow reaction [step (i)].

$$C_6H_5CON\begin{matrix}H\\\\Cl\end{matrix} + HCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_6H_5CONH_2 + Cl_2 \quad ...slow \text{ (i)}$$

$$Cl_2 + AH_2 \overset{k_2}{\rightarrow} A + 2HCl \quad ...fast \text{ (ii)}$$

During the Orton rearrangement of N-haloacetanilides, such specific halogen acid catalysis has been reported by Hughes and Ingold[12]. The postulated mechanism involves the production of free chlorine as suggested in step (i) above.

Taking $k_2 \times [AH_2] \gg k_{-1}$ [benzamide] as a suitable approximation and [HCl]$\propto$[H⁺][Cl⁻], the rate-law Eq. (2) is obtained.

$$-\frac{d}{dt}[AH_2] = k[NCB][H^+][Cl^-] \quad ...(2)$$

The rate-law Eq. (2) satisfies the experimental observation that the oxidation of ascorbic acid involves zero and first order dependences in ascorbic acid and NCB respectively, and the order with respect to both H⁺ and Cl⁻ ions is unity or two in HCl. Under the conditions it is not possible to distinguish kinetically between the participation of undissociated HCl on one hand and of H⁺ and Cl⁻ ions on the other hand. Since the acid is almost completely dissociated, the result is consistent with the assumption that undissociated HCl molecules are the effective catalysts for the oxidation of ascorbic acid by NCBr Similar conclusions have been drawn to account for the halogen acid catalysis during the rearrangemenof N-chloroacetanilides[13]. The catalysis ofhydro bromic acid in the decomposition of hydrogen peroxide has also been explained[14] on the basis of rate-determining reaction between H_2O_2 and HBr.

Hughes and Ingold[12] have suggested the possibility of a rate-determining reaction between Cl⁻ ion and the protonated N-haloamide. Such a possibility is less likely for the oxidation of ascorbic acid because this would involve negative ionic strength and dielectric constant effects. The observed kinetic data show an insignificant effect of ionic strength ([$NaClO_4$] from 0 to 1·2M) and dielectric constant ([methanol] from 20 to 50%) and thus indicate the involvement of a neutral molecule in the rate-determining step. The high energy of activation (18·4 kcal mole⁻¹) also does not favour a reaction between the oppositely charged ions.

A slight decrease in experimental value of the order in Cl⁻ ion (0·8) can be explained on the basis of the fact that at high [Cl⁻], thermal decomposition of NCB becomes significant thus resulting in a decrease in the rate of oxidation of ascorbic acid.

Acknowledgement

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