

Kinetics of Oxidation of Hydrazine & Hydroxylamine by N-Chlorobenzamide

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The rates of oxidation of hydrazine and hydroxylamine by N-chlorobenzamide (NCB) have been measured in hydrochloric acid media. The reactions follow identical kinetics, being first order each in [NCB], $[H^+]$ and $[Cl^-]$ and show independent nature to the reducing substrates. Added salt and solvent effects are negligible. Molecular chlorine obtained from the reaction of NCB and HCl has been found to be the effective oxidant.

OXIDATION of hydrazine¹ and hydroxylamine² by a variety of oxidants in aqueous solutions has been studied. In general, hydrazine is quantitatively converted into nitrogen but other products such as ammonia and hydrazoic acid have also been reported.

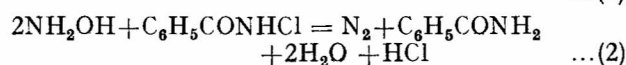
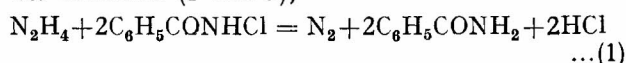
It was interesting that the oxidation of hydroxylamine by ferricyanide³ showed a variable stoichiometry depending upon the relative concentrations of the reactants. Both hydrazine and hydroxylamine were quantitatively estimated in strong acidic solutions by N-chlorobenzamide⁴. In this paper the results of the kinetics of oxidation of hydrazine and hydroxylamine by N-chlorobenzamide (NCB) are recorded and a suitable mechanism is proposed.

Materials and Methods

Standard solutions of NCB (m.p. 115°), prepared by the methods described earlier^{5,6}, were freshly prepared in methanol (AR, BDH) and stored in dark bottles. Solutions of hydrazine sulphate and hydroxylamine hydrochloride (both AR, BDH samples) were prepared in doubly redistilled water. All other reagents used were of AR grade. Kinetics were followed by estimating NCB iodometrically using starch as indicator.

Stoichiometry—The reactions were obtained at several concentrations of the reactants using known

excess of NCB at 40°. The results conformed to the reactions (1 and 2),



and are in accord with the results of Singh and coworkers⁴ who have experimentally obtained nitrogen and benzamide as the end-products of the reaction.

Results

Effects of varying [NCB] and [substrates]—The kinetics were studied at several initial concentrations of the reactants at 40° and 45° (Table 1). The log [NCB] versus time plots were linear and the pseudo-first order rate constants (k_1) in NCB were, therefore, calculated from the slopes of these plots. A more than three-fold variation in the [substrates] had no effect on k_1 values, suggesting an independent nature of the rate in the reducing substrates. A slight increase in rate constants for the oxidation of hydroxylamine is due to the increase in $[Cl^-]$ as a result of the increase in $[NH_2OH.HCl]$. In the case of hydrazine sulphate, the values of rate constants were independent of the [reductant].

TABLE 1 — EFFECT OF VARYING [REACTANTS] ON THE REACTION RATE

[NCB] $M \times 10^3$	$[N_2H_4.H_2SO_4]$ $M \times 10^2$	{[Methanol] = 20%; [HCl] = 0.20M}					
		$k_1 \times 10^5 \text{ sec}^{-1}$ at		$[NH_2OH.HCl]$ $M \times 10^2$	$k_1 \times 10^5 \text{ sec}^{-1}$ at		
		40°	45°		40°	45°	
2.0	1.2	9.8	14.9	2.4	11.3	17.8	
2.0	1.6	9.9	14.9	3.2	12.0	19.1	
2.0	2.0	9.8	15.3	4.0	12.8	19.5	
2.0	2.8	9.9	15.5	5.6	13.0	21.1	
2.0	4.0	10.9	—	8.0	13.9	22.7	
1.2	2.0	9.9	14.8	4.0	11.9	19.5	
1.6	2.0	10.0	15.3	4.0	12.1	20.8	
2.8	2.0	10.1	16.5	4.0	12.7	21.9	
4.0	2.0	10.5	17.7	4.0	13.0	22.7	

Effects of varying $[Cl^-]$ and $[H^+]$ —The rates of oxidation of hydrazine and hydroxylamine were strongly catalysed by HCl. In order to find out the extent of halogen acid catalysis, the effects of H^+ and Cl^- ions were investigated independently. The respective orders of the reactions were obtained from the logarithmic plots (Fig. 1). It was observed that the order in $[H^+]$ is unity while that in $[Cl^-]$ is between 0.85 and 1 for the oxidation of hydrazine and hydroxylamine by NCB. The reactions, therefore, follow a second order dependence in HCl within the permissible limits of error.

Effect of varying ionic strength—A five-fold increase in ionic strength ($\mu = 0.2$ to $1.0M$) by adding $NaClO_4$ increased the rates slightly. The values of rate constants varied from 9.8 to 13.0 and 11.3 to 14.6 for hydrazine and hydroxylamine respectively at 40° .

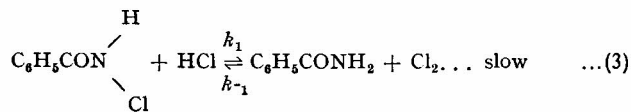
Effect of varying solvent composition—The effect of solvent was negligible. A variation in methanol concentration from 10 to 40% at 40° changed the rate constants from 9.2 to 10.3 and 11.5 to 12.9 for the oxidation of hydrazine and hydroxylamine respectively.

Effect of varying temperature—Studies were carried out at 30° , 35° , 40° , 45° and 50° and the values of the rate constants obtained correspond to $\Delta E^\ddagger = 19.1$ and 19.1 kcal mole $^{-1}$; k^* (where $k^* = k_1/[H^+]$; $[Cl^-] = 24.5 \times 10^{-4}$ and 26.6×10^{-4} litre 2 mole $^{-2}$ sec $^{-1}$; $A = 4.86 \times 10^{10}$ and 5.06×10^{10} litre 2 mole $^{-2}$ sec $^{-1}$; and $\Delta S^\ddagger = -10.7$ and -10.6 e.u. for the oxidation of hydrazine and hydroxylamine respectively.

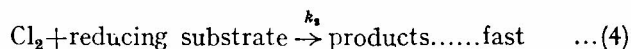
Discussion

The oxidation of hydroxylamine and hydrazine by NCB shows first and zero order dependences on NCB and reducing substrate respectively. A second order dependence in HCl was observed, being unity in both H^+ and Cl^- ions. It is well known that N-haloamides⁷ in the presence of halogen acids

give rise to free chlorine, and thus show specific halogen acid catalysis. Bell⁸ reviewed many acid-base catalysed reactions and observed that the specific halogen acid catalysis is always consistent with the assumption that undissociated halogen acid serves as the effective catalyst. Direct dependence in NCB further suggests that the rate determining reaction should involve interaction between NCB and HCl (Eq. 3).



The chlorine formed reacts with hydrazine or hydroxylamine in a fast step (Eq. 4) to give the products



A similar mechanism for the oxidation of ascorbic acid by NCB was proposed earlier on a similar basis⁶.

Step (4) in the above mechanism may consist of more than one step for the oxidation of hydrazine where a four-electron transfer is involved as shown in Eqs. (5) and (6).



The formation of N_2H_2 as an intermediate during the oxidation of hydrazine with two-electron transfer oxidants is well documented^{1,9}.

The above mechanism leads to the following rate law:

$$-\frac{d[NCB]}{dt} = k_1[NCB][HCl] \quad \dots(7)$$

where $k_2 \times [\text{reducing substrates}] \gg k_{-1} [\text{benzamide}]$ has been taken as a suitable approximation.

The rate Eq. (7) indicates a first order dependence each in NCB, H^+ and Cl^- and an independent nature in reducing substrates. This is in complete agreement with the experimental results and the values of specific rate constants (k_s) for the rate equation,

$$-\frac{d[NCB]}{dt} = k_s[NCB] \quad \dots(8)$$

were obtained as $(2.45 \pm 0.26) \times 10^{-3}$ and $(2.66 \pm 0.12) \times 10^{-3}$ litre 2 mole $^{-2}$ sec $^{-1}$ at 40° for the oxidation of hydrazine and hydroxylamine respectively.

Hughes and Ingold⁷ during the study of Orton-rearrangement of N-haloacetanilides suggested that the rate determining reaction takes place between Cl^- ion and the protonated N-haloamide. Such a possibility, however, would involve an interaction between the two oppositely charged ions and thus would give rise to a primary negative salt and a positive solvent effect. The oxidation of hydrazine and hydroxylamine by NCB showed negligible salt and solvent effects and thus are not in favour of a reaction involving two oppositely charged ions. The fairly high energies of activation and small negative entropy value also support the involvement of neutral molecules as has been proposed in step (3).

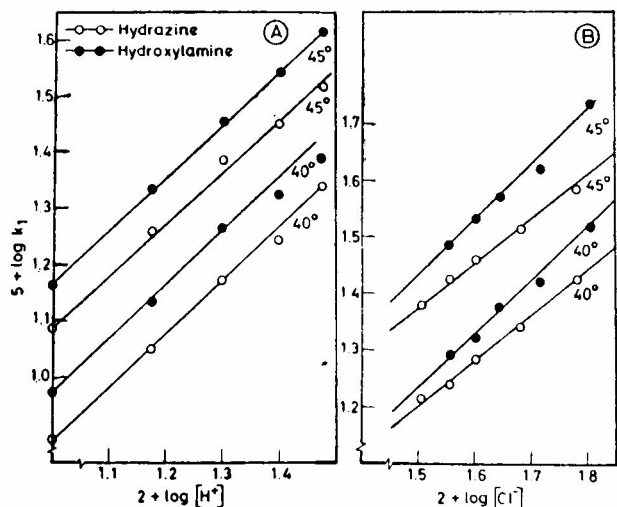


Fig. 1 — Plots of $\log k_1$ versus $\log [H^+]$ (A) and k_1 versus $[Cl^-]$ (B) at 40° and 45° {(A): $[Hydrazine] = 1/2 [hydroxylamine] = 0.02M$; $[Cl^-] = 0.30M$ ($NaCl$); $[NCB] = 2.0 \times 10^{-3}M$; $[methanol] = 20\%$; and $\mu = 0.6M$ ($NaClO_4$); (B): $[hydroxylamine] = 0.02M$; $[NCB] = 2.0 \times 10^{-3}M$; $[HCl] = 0.2M$; $[methanol] = 20\%$; $\mu = 0.6M$ ($NaClO_4$)}

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