

Kinetics and Mechanism of Oxidation of Hydroxylamine Hydrochloride by Chloramine-B in Perchloric Acid Medium[†]

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Manuscript received 24 September 1987, revised 29 February 1988, accepted 25 March 1988

The kinetics of oxidation of hydroxylamine hydrochloride (HH) by chloramine-B (CAB) in perchloric acid medium have been studied at 0°. The reaction shows a first order dependence each in [CAB] and [HH]. The reaction is catalysed by [H⁺] and [Cl⁻], and the order in both [H⁺] and [Cl⁻] is fractional. Addition of the reaction product, benzene sulphonamide and increase in ionic strength of the medium have negligible influence on the rate of reaction. The effect of changing the dielectric constant of the medium on the reaction rate has been studied. Thermodynamic parameters have been calculated and a mechanism consistent with the experimental results is proposed.

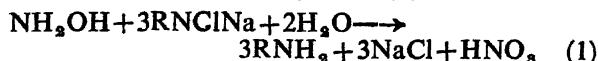
KINETICS of oxidation of substituted benzyl alcohols¹, dimethyl sulphoxide², unsaturated alcohols^{3,4}, 2-methylphenol⁵, and aniline⁶ by chloramine-B (CAB) have been reported. Kinetics of oxidation of hydroxylamine hydrochloride (HH) by CAB in hydrochloric acid medium have been reported⁷ recently, and the title investigation is a followup of our earlier work. The results show some interesting features which are different from those observed in chloramine-T⁸ (CAT) and bromamine-T⁹ (BAT) reactions.

Experimental

Hydroxylamine hydrochloride (S. Merck) was purified by recrystallisation and standardised by bromatometry. Chloramine-B was prepared by the reported method and its aqueous solution was standardised⁴ iodometrically. All other chemicals used were of analytical grade.

Kinetic measurements: A solution containing the requisite amount of substrate, acid, sodium perchlorate (to keep the ionic strength constant) and water (to keep the total volume constant throughout) was equilibrated at 0° and to it was rapidly added a measured amount of CAB solution pre-equilibrated at the same temperature. The progress of the reaction was followed by estimating the unconsumed CAB present in a measured aliquot of the reaction mixture withdrawn at regular intervals of time by iodometry.

The results of stoichiometric runs indicated that one mole of the substrate consumed three moles of CAB in accordance with equation (1),



where, R = C₆H₅SO₂. The reaction product, benzene sulphonamide was detected by tlc using

petroleum ether – chloroform – n-butanol (1 : 1 : 0.5, v/v) as the solvent system and iodine as the developing agent. The nitrate ion in solution was detected as usual.

Results and Discussion

The kinetics of oxidation of HH by CAB was investigated at several initial concentrations of the reactants. At constant [HClO₄] with [HH] in excess, the plots of log [CAB]_t against time are found to be linear indicating a first order dependence in [CAB]₀. The pseudo-first order rate constants in CAB at different initial concentrations are given in Table 1. The rate is first order in [HH] as is noticed by plotting log *k* against log [HH] (slope 0.99). The rate of reaction increases with increase in [HClO₄] (0.05–0.30 mol dm⁻³). The results are shown in Table 2. A plot of log *k* against log [HClO₄] is linear with a slope of 0.18. Addition of chloride ion as NaCl at constant [H⁺]

TABLE 1—EFFECT OF VARYING REACTANT CONCENTRATIONS ON RATE OF REACTION AT 0°

[CAB] ₀ × 10 ³ mol dm ⁻³	[HH] × 10 ³ mol dm ⁻³	<i>k</i> × 10 ⁴ s ⁻¹
3.0	5.0	6.14
4.0	5.0	6.45
5.0	5.0	6.45
6.0	5.0	6.09
7.0	5.0	6.37
5.0	2.5	3.27
5.0	7.5	9.87
5.0	10.0	11.11
5.0	12.5	19.19
5.0 ^a	5.0	6.47
5.0 ^b	5.0	6.33

^aIn presence of excess benzene sulphonamide. ^bAt ionic strength of 1.0 mol dm⁻³.

[†]Presented at the 24th. Annual Convention of Chemists held at Kolhapur, 1987.

(0.2 mol dm⁻³) enhances the rate; Table 3 shows the results. A plot of log *k* against log [Cl⁻] gives a straight line with a slope of 0.21.

TABLE 2—EFFECT OF VARYING PERCHLORIC ACID ON RATE OF REACTION AT 0°

[CAB] = 5.0 × 10⁻³ mol dm⁻³, [HH] = 5.0 × 10⁻³ mol dm⁻³, μ = 0.5 mol dm⁻³

[HClO ₄] × 10 ³ mol dm ⁻³	<i>k</i> × 10 ⁴ s ⁻¹
5.0	5.06
10.0	5.56
15.0	6.21
20.0	6.45
25.0	7.16
30.0	7.60

TABLE 3—EFFECT OF VARYING [Cl⁻] ON RATE OF REACTION AT 0°

[CAB] = 5.0 × 10⁻³ mol dm⁻³, [HH] = 5.0 × 10⁻³ mol dm⁻³, [H⁺] = 2.0 × 10⁻¹ mol dm⁻³, μ = 0.5 mol dm⁻³

[Cl ⁻] × 10 ³ mol dm ⁻³	<i>k</i> × 10 ⁴ s ⁻¹
5.0	6.45
10.0	6.99
13.0	7.88
17.0	8.44
20.0	8.64

Addition of the reaction product, benzene sulphonamide to the reaction mixture had no effect on the rate. Increase in the ionic strength of the medium from 0.5 to 1.0 mol dm⁻³ had a negligible effect (Table 1). Dielectric constant of the medium has been varied by adding increasing proportions of ethanol to the reaction mixture. The rate of the reaction increases and a plot of log *k* vs 1/*D* (where *D* is the dielectric constant of the medium) is a straight line with a positive slope. The results are given in Table 4. The reaction has been studied at various temperatures (273–286.8 K). The energy of activation (*E*_a) was found to be 25.8 kJ mol⁻¹. The values of activation parameters are as follows: Δ*H*[‡] = 23.46 kJ mol⁻¹, Δ*S*[‡] = -219.54 JK⁻¹ mol⁻¹, Δ*G*[‡] = 85.00 kJ mol⁻¹, log *A* = 3.74.

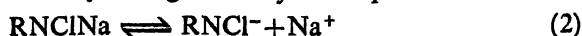
TABLE 4—EFFECT OF VARYING DIELECTRIC CONSTANT OF THE MEDIUM ON RATE OF REACTION AT 0°

[CAB] = 5.0 × 10⁻³ mol dm⁻³, [HH] = 5.0 × 10⁻³ mol dm⁻³, [HClO₄] = 0.2 mol dm⁻³, μ = 0.5 mol dm⁻³

EtOH %	<i>D</i>	<i>k</i> × 10 ⁴ s ⁻¹
0	87.0	6.45
10	81.0	6.78
20	74.0	7.30
30	67.9	7.91
40	61.5	8.86

Discussion

Chloramine-B like chloramine-T¹⁰, is a moderately strong electrolyte in aqueous solutions,



RNCl⁻ picks up a proton in the acid medium to give the conjugate acid RNHCl,



which in turn undergoes disproportionation to RNCl₂,



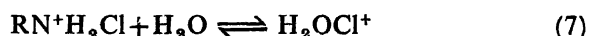
and hydrolyse to HOCl,



In strong acid solutions, RNHCl may give RN⁺H₂Cl,

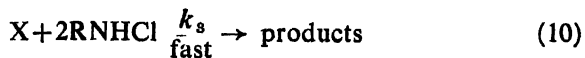
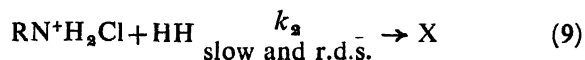


which in turn undergoes hydrolysis to give H₂OCl⁺,



Therefore, the probable oxidising species in the acid solutions of CAB are RNHCl and HOCl, and possibly RN⁺H₂Cl and H₂OCl⁺.

The observed kinetics for the oxidation of HH by CAB in HClO₄ medium can be accounted through Scheme 1.



Scheme 1

and rate law (11),

$$\frac{-d[\text{CAB}]}{dt} = \frac{k_2 K_1 [\text{CAB}][\text{HH}][\text{H}^+]}{1 + K_1[\text{H}^+]} \quad (11)$$

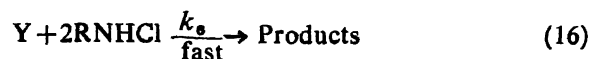
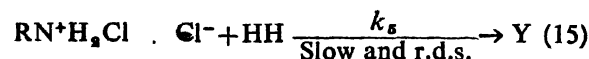
$$\text{or } k_{\text{obs}} = \frac{k_2 K_1 [\text{HH}][\text{H}^+]}{1 + K_1[\text{H}^+]} \quad (12)$$

$$\text{or } \frac{1}{k_{\text{obs}}} = \frac{1}{k_2 K_1 [\text{HH}][\text{H}^+]} + \frac{1}{k_2 [\text{HH}]} \quad (13)$$

At constant [HH], a plot of 1/*k*_{obs} vs 1/[H⁺] is linear with an intercept which is in agreement with the rate law (13). The observed non-influence of ionic strength of the medium and the product, benzene sulphonamide on the rate are in agreement with the proposed mechanistic scheme. The rate increases with the decrease in dielectric constant of the medium. The positive ethanol effect supports Scheme 1 where the rate-determining step involves a positive ion and a dipole¹¹.

Addition of chloride ion increases the rate and a fractional order dependence on [Cl⁻] is observed. Such behaviour has been noted in the Orton rearrangement¹² involving N-haloamides. Scheme 2

can be proposed for the experimental observations.



Scheme 2

Assuming steady state conditions for $\text{RN}^+\text{H}_2\text{Cl} \dots \text{Cl}^-$, the rate law (17),

$$\frac{-d[\text{CAB}]}{dt} = \frac{k_5 K_4 [\text{CAB}][\text{HH}][\text{H}^+][\text{Cl}^-]}{1 + K_4 [\text{H}^+][\text{Cl}^-]} \quad (17)$$

can be derived in agreement with the fractional order noted with respect to $[\text{Cl}^-]$. Equation (17) can be transformed into equation (18) for a double reciprocal plot of k' vs $[\text{Cl}^-]$.

$$\frac{1}{k'} = \frac{1}{k_5 K_4 [\text{HH}][\text{H}^+][\text{Cl}^-]} + \frac{1}{k_5 [\text{HH}]} \quad (18)$$

With constant $[\text{HH}]$ and $[\text{H}^+]$, a plot of $1/k'$ vs $1/[\text{Cl}^-]$ is found to be linear with an intercept, thus supporting the proposed mechanism.

In the case of oxidation of HH by CAT^6 in HClO_4 medium, Katgeri *et al.*⁹ observed that the reaction is first order in $[\text{CAT}]$ and $[\text{HH}]$ and inverse first order in $[\text{H}^+]$, and with BAT^9 , it was noticed that the reaction is first order each in $[\text{BAT}]$ and $[\text{HH}]$ at low $[\text{HH}]$, while it is zero order in

$[\text{HH}]$ at high $[\text{HH}]$. First order rate was observed in $[\text{H}^+]$. But with the CAB, the rate is found to be first order in $[\text{CAB}]$ and in $[\text{HH}]$. The rate is found to be fractional both in $[\text{H}^+]$ and $[\text{Cl}^-]$.

Acknowledgement

The authors are grateful to Prof. D. S. Mahadevappa and Dr. H. M. K. Naidu for helpful discussions. One of the authors (A.R.N.) thanks the University of Mysore, for the award of a Junior Research Fellowship.

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