



KINETICS OF OXIDATION OF CYCLOHEXANOL BY N-CHLORONICOTINAMIDE IN AQUEOUS ACETIC ACID MEDIUM

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ABSTRACT

Kinetics of oxidation of Cyclohexanol by N-Chloronicotinamide(NCN) in 50% V/V aqueous acetic acid mixture has been investigated in the presence of HClO₄ and NaCl. The observed rate of oxidation is first-order with respect to oxidant(NCN) and fractional-order with respect to cyclohexanol. A decrease in dielectric constant of the medium increases the rate. Addition of nicotinamide (NA), the reduction product of NCN, has a retarding effect on the rate of oxidation. Arrhenius and activation parameters are calculated.

Kinetics of bromination¹ and oxidation^{2,3} of saturated organic compounds by N-bromosuccinimide (NBS) have been received considerable attention. Kinetics and mechanism of oxidation of amino acids by NCN has been reported in aqueous acetic acid medium,⁴ we report herein the result of similar studies on the oxidation of cyclohexanol with NCN in aqueous acetic acid medium.

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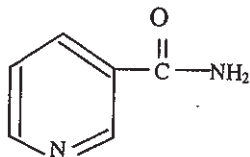
Materials and Methods

One litre of glacial acetic acid (A.R., Qualigen) was taken in a two litre round bottom flask and 25 g. of solid chromium-tri-oxide was added.

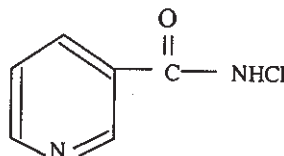
The flask was refluxed with a water condenser for about six hours. It was then cooled and distilled. Pure acetic acid was collected at 117-1180°C and stored in brown bottles.

Preparation of NCN⁵

NCN a new, mild, stable, effective and inexpensive oxidant for organic substrates. NCN was prepared by passing a slow stream of chlorine into solution of nicotinamide (15 g in 30 ml 3N HCl) at room temperature for 30 minutes. NCN formed as a white precipitate was filtered and the process of passing chlorine into the filtrate and filtering off the precipitate was repeated till no more precipitate was obtained. It was filtered, washed with ether and recrystallised from ethanol m.p. 221-223°C, yield 75%. The standard stock solution of NCN was prepared by dissolving the required quantity of it in water and standardized by titrating against standard sodium thiosulphate solution iodometrically. This NCN solution was found to be invariant in its strength over a period of three months.



Nicotinamide(NA)



N-Chloronicotinamide(NCN)

The cyclohexanol (A.R) was used as such without further purification. Perchloric acid(A.R) was used as source of [H⁺] ions. Sodium chloride (Merck) was used as source of [Cl⁻] ions. Conductivity water used throughout the study.

The reaction was carried out under pseudo first-order condition ([cyclohexanol] > [NCN]). The reaction was followed by potentiometrically by setting up a cell consisting of a redox electrode (platinum wire was dipped in reaction mixture) and reference electrode (saturated calomel electrode). The emf of the cell was measured periodically using a Equip-Tronics (EQ-DGD) potentiometer, while the reaction mixture was stirred continuously when the reaction was followed by potentiometrically.

Stoichiometry and Product Analysis

The reaction mixture containing varying proportion of NCN and cyclohexanol (3:1) were kept at room temperature for 24 hours. Estimation of unreacted NCN showed that one mole of cyclohexanol consumed one mole of NCN. The overall stoichiometry of the oxidation reaction may be represented as



A mixture of cyclohexanol and NCN (3:1 ratio) was prepared in acetic acid-water mixture (1:1). The mixture was allowed to stand for 1 hour in the dark to ensure the completion of the reaction. The solution was then treated with an excess (200ml) of a saturated solution of 2,4-dinitrophenylhydrazine in (2 mol dm⁻³) HCl and set aside for 10 hours. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off dried recrystallised in ethanol. The product was found to have identical melting point with an authentic sample of DNP of cyclohexanone.

Results and Discussion

Under the condition $[\text{NCN}] \ll [\text{cyclohexanol}]$ the plot of $\log(E_t - E_\infty)$ (where E_t is the emf of the cell at time 't' and E_∞ the corresponding value at the completion of reaction) vs time is linear, indicating first-order dependence of the rate on $[\text{NCN}]$. The pseudo first-order rate constant decreases with increase in initial concentration of the oxidant (Table 1).

Increase in $[\text{cyclohexanol}]$ has a slight positive effect on the rate of $[\text{cyclohexanol}]$ (Table 1). A plot of $\log k_{\text{obs}}$ vs $\log [\text{cyclohexanol}]$ is linear with slope 0.5 ($r = 0.975$)

The effect of $[\text{H}^+]$ is investigated by varying $[\text{HClO}_4]$ at constant $[\text{Cl}^-]$ ion. The effect of $[\text{Cl}^-]$ is investigated by varying $[\text{NaCl}]$ at constant $[\text{H}^+]$ ion. The effect of $[\text{H}^+]$ and $[\text{Cl}^-]$ have no effect on reaction rate.

Table 1. Effect of varying [NCN] and cyclohexanol on the rate of reaction

[HClO₄] = 0.2 mol dm⁻³ [NaCl] = 0.8 mol dm⁻³
Solvent = CH₃COOH-H₂O (1:1) Temp = 313 K

[NCN] × 10 ³ mol dm ⁻³	Cyclohexanol × 10 ² mol dm ⁻³	k _{obs} × 10 ⁵ s ⁻¹
1.0	2.0	7.00
2.0	2.0	6.82
3.0	2.0	6.00
4.0	2.0	6.50
2.0	1.0	5.39
2.0	2.0	6.82
2.0	3.0	7.55
2.0	4.0	9.17

An increase in the rate constant is noticed on decreasing the dielectric constant of the medium. Plot of log k_{obs} vs 1/D (r = 0.944), where D is the dielectric constant of the medium, gives straight line with positive slope, indicating the fact that the reaction is an ion-dipole type. It was found that rate of the reaction decreases on increasing nicotinamide[NA]. Thus nicotinamide has a retarding effect on the rate of oxidation. Addition of salts like Na₂SO₄ to the reaction medium has no effect on the rate.

The oxidation of cyclohexanol was studied at different temperatures (313-328K), the Arrhenius and the activation parameters were evaluated

(Table 2). Arrhenius plot of log k_{obs} vs 1/T is linear (r = 0.979). The energy of activation (E_a), enthalpy of activation (ΔH[#]), entropy of activation (ΔS[#]), free energy of activation (ΔG[#]) and pre-exponential factor (A) were found to be 76.25 kJ/mol, 73.98 kJ/mol, -34.93 J/K/mol, 81.91 kJ/mol and 4.20 × 10⁸ s⁻¹ at 313 K respectively.

Table 2. Effect of temperature on the rate of reaction

$[\text{NCN}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{cyclohexanol}] = 2 \times 10^{-2} \text{ mol dm}^{-3}$
 $[\text{NaCl}] = 0.8 \text{ mol dm}^{-3}$ $[\text{HClO}_4] = 0.2 \text{ mol dm}^{-3}$
 Solvent = $\text{CH}_3\text{COOH-H}_2\text{O}$ (1:1)

Temp K	$k_{\text{obs}} \times 10^5 \text{ s}^{-1}$
313	6.82
318	11.05
323	15.43
328	23.49

Mechanism

Based on the above observation the following mechanism may be proposed for the oxidation by cyclohexanol by NCN.



HOCl^+ is formed in the first step by the hydrolysis of NCN .⁸ HOCl^+ may be the effective oxidizing species in the present investigation. This may act as the active oxidant attacking the alcohol in the slow step. The proposed rate equations.

$$\text{Rate} = k_2 [\text{cyclohexanol}] [\text{HOCl}^+] \text{ ----- (3)}$$

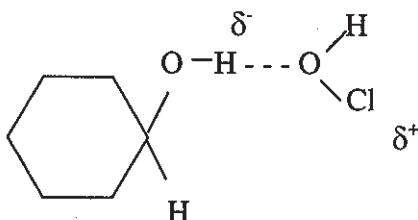
Applying steady state approximation to the active oxidizing species

$$[\text{HOCl}^+] = \frac{k_1 [\text{NCN}]}{k_{-1} [\text{NA}] + k_2 [\text{cyclohexanol}]}$$

Substituting the value for $[\text{HOCl}^+]$ in equation (3)

$$\text{Rate} = \frac{k_2 k_1 [\text{cyclohexanol}] [\text{NCN}]}{k_{-1} [\text{NA}] + k_2 [\text{cyclohexanol}]}$$

This rate-law predicts the first-order dependence on [NCN] and fractional order dependence on [cyclohexanol], the decrease in rate with increase in [nicotinamide]. The addition of $[H^+]$ and $[Cl^-]$ ions have no effect on the rate determining step. The effect of dielectric constant indicates of the fact that the reaction is an ion-dipole type. The negative ΔS^\ddagger value may be explained as due to the formation of ionic transition state with extensive charge separation resulting from the transfer of either two electrons or hydride ion in the rate-determining step^{6,7} as shown below.



Conclusion

The oxidation of cyclohexanol with NCN was found to be first-order with respect to [NCN] and fractional-order with respect [cyclohexanol]. The addition of $[NaCl]$ and $[HClO_4]$ concentration had no effect on the rate of the reaction. The rate increases with increasing percentage of acetic acid in the reaction medium. The product of oxidation was identified as cyclohexanone. The Arrhenius and activation parameters were calculated. A probable mechanism for oxidation of cyclohexanol by NCN was proposed and rate law explaining all observed experimental facts was deduced.

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