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N-Chloropyrazinamide Oxidation of Aliphatic Primary Alcohols: A Kinetic Study

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Abstract: Kinetics of oxidation of some aliphatic primary alcohols *viz*., methanol, ethanol, propan-1-ol, butan-1-ol and pentan-1-ol by N-chloropyrazinamide (NCPZA) has been studied in aqueous acetic acid medium. The reaction shows first order dependence with respect to [NCPZA] and [H$^+$]. The order with respect to [alcohol] is zero. Addition of chloride ion concentration has no significant effect on the reaction rate. The rate of oxidation increases with decreases in dielectric constant of the medium. The variation of ionic strength and addition of the reduction product, pyrazinamide have also been studied. Arrhenius and thermodynamic activation parameters have been evaluated. A suitable mechanism consistent with the observed kinetics has been proposed.

Keywords: kinetics, oxidation, mechanism, aliphatic alcohols, N-chloropyrazinamide.

INTRODUCTION

Kinetic study provides useful information about the mechanism and rate of chemical reaction, which helps to run a chemical reaction successfully by a way of selecting optimum condition as to get maximum yield. It also helps us to study the factors which influence the rate of reaction such as temperature, pressure, substrate concentration, oxidant concentration, composition of reaction mixture and catalyst. The reaction kinetics plays a very important role in the investigation of the reaction mechanism. Aliphatic alcohols are used as hard surface treatment disinfectants, sanitizers, a sterilant, virucides, fungicides and mildewcides. Kinetics of oxidation of alcohols by various oxidizing reagents has been well documented[1-19]. The kinetics of oxidation of some aliphatic primary alcohols by a newly synthesized oxidant, N-chloropyrazinamide (NCPZA) has not been reported so far and hence need for the present investigation.

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EXPERIMENTAL

All chemicals were used of AnalaR grade. Conductivity water was used throughout the study. All the alcohols were used after their distillation by proper method and purity checked by their boiling point. The solution of perchloric acid was prepared by known volume of acid in water and standardized by sodium hydroxide using phenolphthalein indicator. Sodium chloride solution was used as a source of [Cl⁻].
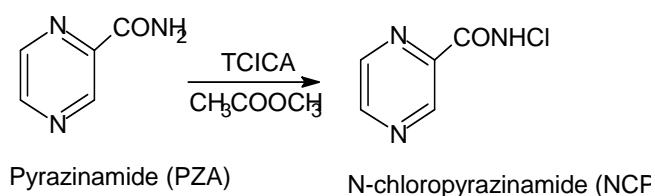

Pyrazinamide (PZA)   N-chloropyrazinamide (NCF

Fig. 1. Reaction for the synthesis of N-chloropyrazinamide

N-chloropyrazinamide[20] was prepared by chlorinating pyrazinamide using trichloroisocyanuric acid (Fig. 1). NCPZA solution was prepared by dissolving the known amount of NCPZA solid in water and standardized by iodometrically using starch indicator.

KINETIC MEASUREMENTS

The reaction was carried out under pseudo-first order conditions [alcohol] >> [NCPZA] in aqueous acetic acid medium containing perchloric acid. The reactions were followed potentiometrically by measuring the potentials of the reaction mixture at regular time intervals. The pseudo-first order rate constant was computed from the linear plots of log $(E_t – E.$) versus time where E_t is the potential at time 't' and E.   is the potential at infinity time.

Product analysis

A mixture of propan-1-ol (0.03 M), NCPZA (0.02 M), perchloric acid (0.30 M) and sodium chloride (0.30 M) was made up to 50 ml in 80% acetic acid-20% water mixture (v/v). The mixture was kept in thermostat for 4 h and the residual mixture was then extracted with diethyl ether and washed with water. The ether layer was separated and dried over anhydrous sodium sulphate. The product was confirmed to be propon-1-al.

Stoichiometry

To determine the stoichiometry for the oxidation of alcohols with NCPZA, a mixture of NCPZA (0.04 M), methanol (0.02 M), perchloric acid (0.30 M) and sodium chloride   (0.30 M) was made up to 25 ml in 80% acetic acid - 20% water mixture. After keeping the reaction mixture for 24 h, the excess of NCPZA was determined iodometrically and it was found that the stoichiometry was 1:1. Similar stoichiometric experiments were carried out for all the alcohols and stoichiometry was found to be 1:1.

$$RCH_2OH + C_4H_3N_2CONHCl + HCl \longrightarrow RCHO + C_4H_3N_2CONH_2 + 2\ HCl$$
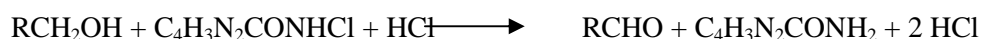
where   R = H; R' = H for methanol, R = CH_3; R' = H for ethanol,

R = CH_3CH_2; R' = H for propan-1-ol, R = $CH_3CH_2CH_2$; R' = H for butan-1-ol,

R = $CH_3 CH_2CH_2CH_2$; R' = H for pentan-1-ol.

RESULTS AND DISCUSSION

Effect of oxidant concentration: The oxidation is carried out with different initial concentrations of NCPZA and the results are given in Table 1. It is seen that the pseudo first-order rate constant remains the same with the increase in the initial concentration of the oxidant.

Table 1: Effect of variation of [NCPZA] for the oxidation of alcohols at 323 K

[Alcohol]　　= 3.0 x 10^{-2} M　　　　　　　[HClO$_4$]　　　　= 3.0 x 10^{-1} M
[NaCl]　　　= 3.0 x 10^{-1} M　　　　　　　Solvent (v/v)　= 80% CH$_3$COOH - 20% H$_2$O

[NCPZA] x 10^3 (M)	k_{obs} x 10^3 (s^{-1})				
	methanol	ethanol	propan-1-ol	butan-1-ol	pentan-1-ol
2.0	2.41	2.51	2.46	2.64	2.47
3.0	2.51	2.60	2.49	2.67	2.52
4.0	2.37	2.58	2.36	2.60	2.43
5.0	2.36	2.42	2.52	2.55	2.47
6.0	2.40	2.47	2.44	2.62	2.40

Effect of substrate concentration: In order to study the effect of [alcohol] on the rate of oxidation, the reactions are studied over a tenfold variation in [alcohol] at constant concentrations of all reactants at fixed temperature. The rate constants are found to be nearly the same for all the concentrations of alcohol exhibiting zero order kinetics with respect to [alcohol].

Effect of perchloric acid concentration: The effect of hydrogen ion concentration on the rate of oxidation is studied by varying [HClO$_4$] while keeping the concentration of other reactants constant (Table 2). The plots of log k_{obs} versus log [HClO$_4$] are linear with unit slope indicating first order dependence of [HClO$_4$] on the rate of oxidation.

Table 2: Effect of variation of [HClO$_4$] for the oxidation of alcohols by NCPZA at 323 K

[Alcohol]　　= 3.0 x 10^{-2} M　　　　　　　[NCPZA]　　　= 2.0 x 10^{-3} M
[NaCl]　　　= 3.0 x 10^{-1} M　　　　　　　Solvent (v/v)　= 80% CH$_3$COOH - 20% H$_2$O

[HClO$_4$] x 10 (M)	k_{obs} x 10^3 (s^{-1})				
	methanol	ethanol	propan-1-ol	butan-1-ol	pentan-1-ol
2.0	1.57	1.62	1.59	1.69	1.62
2.5	1.93	2.03	2.00	2.14	1.99
3.0	2.41	2.51	2.46	2.64	2.47
3.5	2.82	2.84	2.80	3.05	2.81
4.0	3.17	3.28	3.19	3.44	3.30

Effect of sodium chloride concentration: Addition of [Cl$^-$] ion in the form of sodium chloride has no significant effect on the rate, indicating that no free chlorine was formed.

Effect of solvent composition: The influence of solvent dielectric constant on the rate of NCPZA oxidation of aliphatic alcohols has been carried out in various solvent mixtures of acetic acid and water. The rate of oxidation increases with increase in the acetic acid content of the solvent mixture (Table 3). Blank experiments performed show that acetic acid is not oxidized with NCPZA under the experimental conditions employed. The plots of log k_{obs} versus 1/D (D is the dielectric constant of the medium), gives straight line with positive slope.

Table 3: Effect of variation of solvent composition for the oxidation of aliphatic primary alcohols by NCPZA at 323 K

[Alcohol] $= 3.0 \times 10^{-2}$ M   [NCPZA] $= 2.0 \times 10^{-3}$ M
[HClO$_4$] $= 3.0 \times 10^{-1}$ M   [NaCl] $= 3.0 \times 10^{-1}$ M

CH$_3$COOH -H$_2$O % (v/v)	D	$k_{obs} \times 10^3$ (s^{-1})				
		methanol	ethanol	propan-1-ol	butan-1-ol	pentan-1-ol
65-35	28.63	0.31	0.29	0.18	0.23	0.37
70-30	25.45	0.48	0.47	0.35	0.41	0.59
75-25	22.27	1.11	1.04	0.82	0.89	1.29
80-20	19.09	2.41	2.51	2.46	2.64	2.47
85-15	15.91	6.42	6.62	6.88	6.88	6.23

where D is the dielectric constant of the medium

Effect of ionic strength: The ionic strength of the reaction medium is changed by the addition of sodium perchlorate and the influence of ionic strength on the reaction rate is studied. It is found that the ionic strength on the reaction medium has no significant effect with increase in [NaClO$_4$.H$_2$O].

Effect of pyrazinamide concentration: A variation in [pyrazinamide] has been employed with a view to find the reactive species of the oxidant. Increase in concentration of pyrazinamide has no significant effect on the rate of oxidation.

Polymerization test: The added acrylonitrile has no effect on the reaction rate, *i.e.* the reaction does not induce polymerization of acrylonitrile indicating the absence of free radical pathway.

Effect of temperature: The rates of oxidation of alcohols are determined at different temperature (Table 4) and the rates obey Arrhenius equation. E$_a$ is calculated from the slopes of the straight line obtained by plotting log k$_{obs}$ versus 1/T. The thermodynamic activation parameters are also calculated for all the alcohols (Table 5).

Table 4: Variation of rate with temperature for the oxidation of aliphatic primary alcohols by NCPZA

[Alcohol] $= 3.0 \times 10^{-2}$ M   [NCPZA] $= 2.0 \times 10^{-3}$ M
[HClO$_4$] $= 3.0 \times 10^{-1}$ M   [NaCl] $= 3.0 \times 10^{-1}$ M
Solvent (v/v) $= 80\%$ CH$_3$COOH - 20% H$_2$O

Temperature (K)	$k_{obs} \times 10^3$ (s^{-1})				
	methanol	ethanol	propan-1-ol	butan-1-ol	pentan-1-ol
313	1.42	1.50	1.33	1.30	1.41
318	1.91	1.95	2.05	1.77	1.73
323	2.41	2.51	2.46	2.64	2.47
328	3.31	3.57	3.43	3.35	3.39
333	4.62	4.49	4.59	4.35	4.45

Table 5: Arrhenius and thermodynamic activation parameters for the oxidation of aliphatic primary alcohols by NCPZA at 323 K

Alcohol	E_a kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ JK^{-1} mol^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}	log A
methanol	50.38	47.69	-64.29	68.46	9.55
ethanol	48.47	45.79	-66.70	67.33	9.26
propan-1-ol	51.89	49.21	-61.93	69.21	9.80
butan-1-ol	52.99	50.30	-60.44	69.83	9.96
pentan-1-ol	51.46	48.78	-62.73	69.05	9.19

The fairly high values of enthalpy of activation ($\Delta H^{\neq}$), free energy of activation ($\Delta G^{\neq}$) and energy of activation (E_a) indicate that the transition state is highly solvated. The negative values of the entropy of activation ($\Delta S^{\neq}$) suggest an extensive solvation of the transition state over the reactants[21].

MECHANISM

The most possible mechanism for the oxidation of aliphatic primary alcohols by N-chloropyrazinamide involves the protonation of NCPZA in the rate determining step followed by the interaction with alcohol to give the products. Under the experimental conditions, the possible oxidizing species are Cl_2, HOCl, H_2OCl^+, NCPZAH$^+$ and NCPZA itself in aqueous solution. Since there is no effect due to Cl$^-$, the possibility of involvement of Cl_2 is ruled out.

Since the rate increases with increase in [HClO$_4$], it is assumed that NCPZAH$^+$ is an effective oxidizing species in the present study and keeping the above data in consideration the following mechanism has been proposed for the oxidation of alcohols by NCPZA. The mechanism shown in this scheme leads to, under the condition that the formation constant K of the oxidant-substrate complex is large[22, 23].

$$\text{NCPZA} + \text{H}^+ \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad \text{NCPZAH}^+ \qquad \qquad \dots(1)$$

$$\text{NCPZAH}^+ + \text{S} \quad \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Complex} \quad (\text{fast}) \qquad \qquad \dots(2)$$

$$\text{Complex} \quad \xrightarrow{k_3} \text{Product} \quad (\text{slow}) \qquad \qquad \dots(3)$$

$$\text{rate} = k_3 \, [\text{Complex}] \qquad \qquad \dots(4)$$

Applying steady state approximation to complex,

$$\text{rate} = k_2 \, [\text{NCPZAH}^+] \, [\text{S}] - k_{-2} \, [\text{Complex}] - k_3 \, [\text{Complex}] = 0 \qquad \dots(5)$$

$$[\text{Complex}] = \frac{k_2 \, [\text{NCPZAH}^+] \, [\text{S}]}{k_{-2} + k_3} \qquad \qquad \dots(6)$$

$$\text{rate} = k_1 \, [\text{NCPZA}] \, [\text{H}^+] - k_{-1}[\text{NCPZAH}^+] - k_2 \, [\text{NCPZAH}^+] \, [\text{S}] = 0 \qquad \dots(7)$$

$$[\text{NCPZAH}^+] = \frac{k_1 \, [\text{NCPZA}] \, [\text{H}^+]}{k_{-1} + k_2 \, [\text{S}]} \qquad \qquad \dots(8)$$

Substituting equation (8) in (6),

$$[\text{Complex}] = \frac{k_2\ k_1}{k_{-2}+k_3} \times \frac{[\text{NCPZA}]\ [\text{H}^+]\ [\text{S}]}{k_{-1}+k_2\ [\text{S}]} \qquad \ldots (9)$$

Substituting equation (9) in (4),

$$\ldots (10)$$

$$\text{rate} = \frac{k_1\ k_2\ k_3}{k_{-2}+k_3} \times \frac{[\text{NCPZA}]\ [\text{H}^+]\ [\text{S}]}{k_{-1}+k_2\ [\text{S}]}$$

Assuming $k_{-1} \ll k_2\ [\text{S}]$, we get

$$\text{rate} = \frac{k_1\ k_2\ k_3}{k_{-2}+k_3} \times \frac{[\text{NCPZA}][\text{H}^+][\text{S}]}{k_2\ [\text{S}]} \qquad \ldots (11)$$

$$\text{rate} = \frac{k_1\ k_3}{k_{-2}+k_3} \times [\text{NCPZA}]\ [\text{H}^+] \qquad \ldots (12)$$

$$\text{rate} = k\ [\text{NCPZA}]\ [\text{H}^+] \qquad \ldots (13)$$

$$\text{where } k = \frac{k_1\ k_3}{k_{-2}+k_3}$$

$$S = \text{alcohol}$$

Equation (13) shows the first order dependence of [NCPZA] and [H$^+$] and zero order dependence of [alcohol].

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