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Kinetics and mechanism of oxidation of diethyleneglycol by N-chlorosaccharin in cetyltrimethylammonium bromide catalyzed system

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ABSTRACT

The kinetics and mechanism of Cetyltrimethylammonium bromide catalyzed oxidation of Diethylene glycol [2,2'-oxydiethanol] by N-chlorosaccharin in aqueous acetic acid medium in presence of perchloric acid have been investigated at 318-338K temperature range. The reaction has first order dependence on N-chlorosaccharin concentration. The reaction rate follows fractional order kinetics with respect to[Diethylene glycol] with excess concentration of other reactants. The micelle effect due to Cetyltrimethylammonium bromide- a cationic surfactant has been studied. The change in ionic strength shows negligible salt effect. The dielectric effect is found to be positive. Addition of one of the product saccharin retards the reaction rate. Activation parameters are calculated from the Arrhenious plot. A possible mechanism consistent with the experimental results has been proposed.

KEYWORDS

Diethylene glycol;
N-chlorosaccharin;
Kinetics;
Mechanism;
Micelle system.

INTRODUCTION

Diethylene glycol (DEG) is used in the plastic industry as a raw material for polyester resins and polyurethanes. DEG is used as drying agent for natural and industrial gases, and as a humectant for cork and paper. Diethylene glycol is an ingredient of lubricants, hydraulic oils, emulsifiers, and textile treatments, and is used as a plasticizer. Oxidation of DEG by different oxidant has been carried out by various workers[1-11] but no one has ever used N-chlorosaccharin as an oxidant. The N-chlorosaccharin($C_6H_4COSO_2NCl$) abbreviated, as NCSA is a versatile oxidant[12-16]. The oxidation of DEG by acidic N-chlorosaccharin is an extremely slow reaction. The reaction has found to be catalyzed by a cationic surfactant cetyltrimethylammonium bromide(C_{16}TAB). Therefore, C_{16}TAB catalyzed oxidation of DEG by N-chlorosaccharin has been undertaken.

EXPERIMENTAL

Diethylene glycol (E Merck) was used. N-chlorosaccharin was prepared by reported procedure[13]. Doubly distilled water and purified acetic acid

were used for preparation of NCSA solution and standard solution of NCSA was prepared afresh. Sodium perchlorate (Merck) was used to keep the ionic strength constant. The other chemicals were used of analytical reagent grade and double distilled water was used for preparation of solutions.

Reactants were mixed in the order: requisite volume of DEG, perchloric acid, C_{16}TAB, and water or other reagent solution, where necessary. Separately thermo stated solution of N-chlorosaccharin was added to commence the reaction. Residual amount of NCSA was determined iodometrically by using standard sodium thiosulphate solution, and potassium iodide-starch as an indicator. In all the experiments, the reactions were followed up to two half lives. A constant ionic strength of the reaction mixture was maintained by adding required amount of sodium perchlorate solution.

The product analysis and stoichiometry

DEG (300mg/250ml water), perchloric acid (0.1M/100ml), C_{16}TAB (10mg /100ml) and NCSA(10g/100ml) were mixed for product analysis. After the reaction time over 48 hour, the organic components were separated from the mixture into ether; the ethereal extract was dried and concentrated using rotatory evaporator, under low pressure. Using benzene, ethyl acetate mixture 8:2(v/v) as an eluent, preliminary studies were carried out by thin layer chromatography. A distinct single spot was obtained. A solution of 2, 4-dinitropheny lhydrazine was added to it and then the reaction mixture was left overnight at refrigerated temperature (5°C). The solution was centrifuged and brown-orange residue is obtained. This formation of hydrazine derivative adequately confirmed the oxidation

Product of the DEG to be a 2,2'-(1-hydroxy) butanal. The aldehyde was conformed by IR spectra which shows bands at 3340cm^{-1} and 1720cm^{-1}for OH stretching and C=O stretching respectively and a band at 2710cm^{-1} for aldehydic C-H stretching. The fact that only one hydroxyl group was attacked and other remained intact gets support from stoichiometry of the reaction as well. Literature survey shows that similar types of oxidative products were reported[17-20]. Stoichiometry was determined by using varying ratios of the oxidant to DEG were thermo stated at 25°C for 48h incubation, and residual NCSA was determined iodometrically using standard sodium thiosulphate as titrant and potassium iodide-starch as an indicator. The mole ratio (number of moles of the oxidant consumed per mole of DEG) was calculated. DEG and N-chlorosaccharin react in 1:1 stoichiometry, as follows:

$$OHCH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2OH + C_6H_4COSO_2NCl \rightarrow OHCH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CHO + C_6H_4COSO_2NCl + H^+ + Cl^- \quad (1)$$

RESULT AND DISCUSSION

Order with respect to [N-chlorosaccharin]

In a typical Kinetic run, for the reaction ([NCSA] 8.0×10^{-3}mol dm^{-3}, [H$^+$] 0.05mol dm^{-3} and[DEG] 0.08 mol dm^{-3}), a plot of log (a-x) versus time (Figure 1) gave a straight line, which indicates that reaction under the chosen condition follows pseudo first order kinetics. The order with respect to NCSA is unity. The mean pseudo first-order rate costant, k_0 found to $(0.17\pm 0.1)\times10^{-5}s^{-1}$

Order with respect to [DEG]

On varying DEG concentration from 4.0×10^{-3} to 20.0×10^{-3}mol dm^{-3} there is an increase in rate of reaction. The plots of log k versus log [DEG] (Figure 2) gave straight line with slop equal to 0.38 (R^2=0.99), suggesting that order with respect to DEG is fractional. Double reciprocal plot between k^{-1} versus [DEG] $^{-1}$ (Figure 3) has been found to be straight line with positive intercept at y-axis. This kinetic evidence of complex formation between the substrate and the oxidant, further support the fractional order dependence.

Effect of variation of [H$^+$]

On varying perchloric acid concentration from1.00×10^{-3} to 16.0×10^{-3}mol dm^{-3} there is an increase in reaction rate. The plots of log k versus log [H$^+$] (Figure 4) gave straight line with positive intercept 0.36

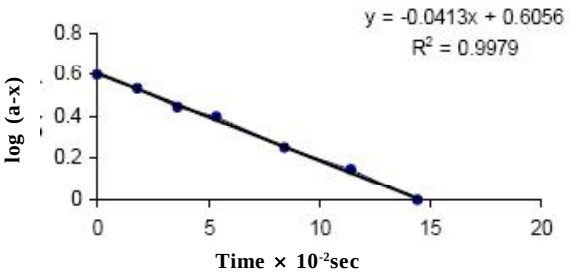

Figure 1

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(R^2= 0.94), suggesting that acid plays a complex role in the reaction system.

Dependence of rate on [C_{16}TAB]

The addition of C_{16}TAB in the reaction system catalyzed the reaction. The reported cmc of C_{16}TAB is 9.2×10^{-4} at 25°C. With the increase in concentration of C_{16}TAB from 2.0×10^{-3} to 12.0×10^{-3}mol dm^{-3}, the rate of reaction increases. The plot of k versus [C_{16}TAB] (Figure 5) gives a straight line. Surfactants are tending to form micelles. One of the important properties of micelle systems is their ability to affect the rates of chemical reactions. The reaction rate can either be accelerated or decelerated, depending on chemical system, the type and concentration of surfactant and other factors such as pH, ionic strength, etc. The effect of surfactants on reaction kinetics is called micelle catalysis[21]. Micelles are formed due to assembling of amphiphilic molecules of surfactant in above a certain concentration (critical micelle concentration called as cmc)[22,23] Micelle catalysis of reaction in aqueous solutions is usually explained on the basis of a distribution of reactants between water and the micelle 'pseudo phase'. The micelles may provide a favorable orientation of the reactants by polarity gradients. In present reaction hydrophobic interaction is most likely to be operative due to relative larger hydrocarbon chains of the substrate[24,25]. This interactive localization of the reacting species in the relatively small volume of the micelles compared to the bulk solution leads to a large increase in the effective concentration and as a result the observed rate increased accordingly. The other most probable reason seems to be electrostatic attraction between polar DEG and the micelle.

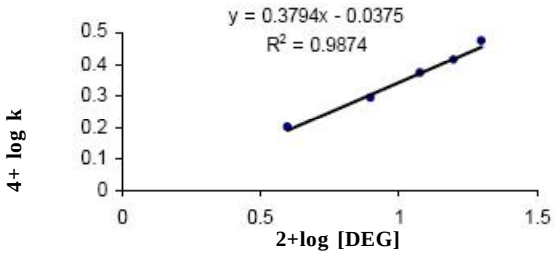

Figure 2

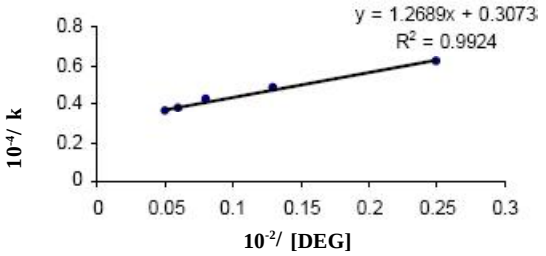

Figure 3

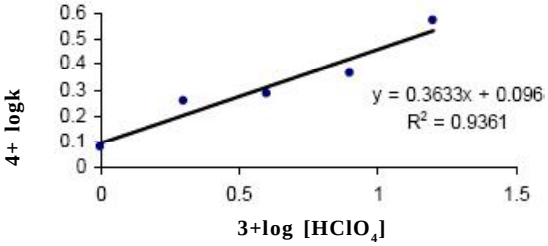

Figure 4

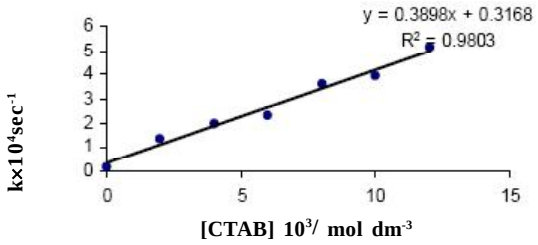

Figure 5

Effect of variation of ionic strength, dielectric constant and saccharin

With the employed reactant concentrations initial ionic strength of the reaction mixture was 0.064. The effect of ionic strength has been studied by varying the concentration of neutral sodium perchlorate from 6.4×10^{-2} to 12.4×10^{-2}mol dm^{-3}. It was found that there is no substantial change in the reaction rate on varying the ionic strength. The small salt effect suggests the participation of neutral species in rate determining step i.e. the substrate molecule and HOCl. This assumption further got support from effect of change in dielectric constant of the reaction medium. The effect of dielectric constant in reaction medium has been studied by adding acetic acid (40-60%) in the reaction medium at constant concentrations of other reactants. The rate of reaction increases by increasing the proportion of acetic acid in solvent medium; this validates the involvement of neutral species in the rate-determining step. At constant NCSA and DEG concentration addition of saccharin 0.5×10^{-3} to 2.5×10^{-3}mol dm^{-3} decreases the rate of reaction. This conforms that HOCl is the main oxi-

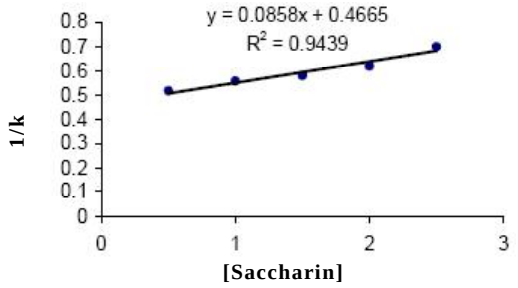

Figure 6

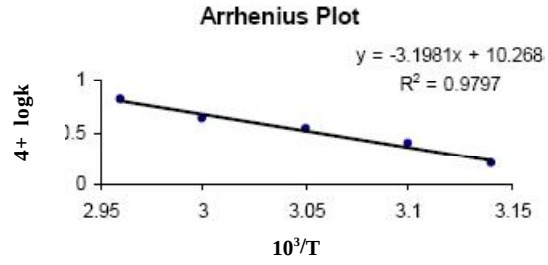

Figure 7

dizing species. The retardation of reaction rate on the addition of saccharin suggests a pre-equilibrium step involves a process in which saccharin is one of the products. If this equilibrium is involved in the oxidation process the retardation should be an inverse function of saccharin concentration, which is borne out by observation that the inverse of the rate constant gives a linear plot (R^2=0.94) against [saccharin](Figure 6). The addition of acrylonitrile to the reaction mixture had no effect, indicating the absence of free radical species during the reaction this observation further supports the participation of neutral species in rate determining step i.e. the substrate molecule and HOCl.

Effect of temperature

The reaction was studied at different temperatures. Rate constants at 318, 323,328, 333 and, 338K were found to be 1.70×10^4 sec^{-1}, 2.14×10^4 sec^{-1}, 3.41×10^4 sec^{-1}, 4.91×10^4 sec^{-1}, and 6.52×10^4 sec^{-1} respectively. From the linear Arrhenius plot of log k vs 1/T(Figure 7) activation parameters for overall reaction were evaluated Ea= 74.28KJ mol^{-1} ΔH^*= 71.60 KJ mol^{-1}, ΔG^* =99.35KJ mol^{-1}, ΔS^*= -85.92JK mol^{-1} respectively.

Mechanism

From the various relevant literatures[26-30] the different probable steps involved in NCSA system may be summarized as follows:

$$NCSA + H_2O \rightarrow HOCl + Saccharin \quad (2)$$
$$HOCl + H^+ \rightarrow H_2O^+Cl \quad (3)$$
$$NCSA + H^+ \rightarrow NCSAH^+ \quad (4)$$
$$NCSAH^+ + H_2O \rightarrow H_2O^+Cl + Saccharin \quad (5)$$

Therefore HOCl, H_2O^+Cl, $NCSAH^+$, are the possible oxidizing species in acidic medium.

The experimental observations indicate that for present case HOCl is the main oxidizing species, so following mechanism has been proposed. The linear double reciprocal plot of k^{-1} versus $[DEG]^{-1}$ with positive intercept at y-axis suggests the formation of complex between substrate and the oxidant. Thus, the slowest and the rate determining step proposed is-

$$OHCH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2OH + HOCl \xrightarrow{Slow} X_1 \quad (6)$$

$$X_1 + H_2O \xrightarrow{Fast} OHCH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CHO + 2H_2O + HCl \quad (7)$$

The small salt effect, increase in reaction rate on increasing the dielectric constant and linear reciprocal plots between k^{-1} versus$[DEG]^{-1}$ with positive intercept at y-axis (Figure 3), support the equation (6). The complex thus formed will be fast decomposed into the products, in equation (7).

C_{16}TAB catalyzed mechanism

The reaction between DEG and N-chlorosaccharin in acidic medium is very slow. Addition of C_{16}TAB catalyzed the reaction. The physical basis of micelle catalysis is the effect of the miceller environment on the rate-controlling step. The relative free energies of the reaction(s) and or the transition state can be altered when reaction takes place in the miceller system instead of bulk water. This concept is reminiscent of catalysis by an enzyme and many initial studies of rates in miceller system focused on this possibility. A more important consideration is the localization of the reacting species in the relatively small volume of the micelle compared to bulk solution.

The following mechanism is proposed for the catalysis by C_{16}TAB:

$$nC_{16}TAB \rightarrow (C_{16}TAB)_n \quad (8)$$
$$OHCH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2OH + (C_{16}TAB)_n \rightarrow [OHCH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2OH\ldots(C_{16}TAB)_n] \quad (9)$$
$$[OHCH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2OH..(C_{16}TAB)_n] + HOCl \rightarrow X_1 \quad (10)$$
$$X_1 + H_2O \rightarrow OHCH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CHO + 2H_2O + HCl \quad (11)$$

SCHEME 1

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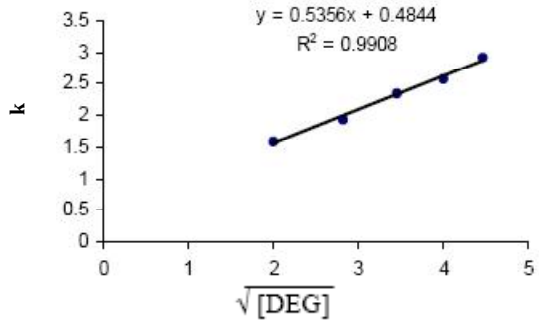

Figure 8

TABLE 1: Order with respect to N-chlorosaccharin. [DEG] =0.08mole dm^{-1};[$HClO_4$]=0.05mole dm^{-1}[C_{16}TAB]=0.004 mole dm^{-1}; Temperature 323K

[NCSA]/10^{-3}mol/dm^{-3}	k/10^{-4} s^{-1} *
2.0	9.51
3.0	5.09
4.0	4.15
8.0	2.07
12.0	1.17
16.0	0.83

*Mean of duplicate experiments

TABLE 2: Effect of d iethylene glycol concentration variation. [NCSA] =0.008mole dm^{-1}; [$HClO_4$]=0.05mole dm^{-1} ; [C_{16}TAB] =0.004mole dm^{-1}; Temperature 323K

[DEG] / 10^{-3} mol dm^{-3}	k / 10^{-4} s^{-1} *
4.0	1.61
8.0	2.07
12.0	2.37
16.0	2.65
20.0	2.92

*Mean of duplicate experiments

TABLE 3: Effect of hydrogen ion concentration variation. [DEG]=0.08mole dm^{-1} ; [NCSA]=0.008 mole dm^{-1}; [C_{16}TAB] = 0.004mole dm^{-1}; Temperature 323K

[$HClO_4$] / 10^{-3} mol dm^{-3}	k / 10^{-4} s^{-1} *
1.0	1.26
2.0	1.77
4.0	2.07
8.0	2.56
12.0	3.12
16.0	3.94

*Mean of duplicate experiments

TABLE 4: Effect of C_{16}TAB concentration variation. [DEG] =0.08mole dm^{-1}; [NCSA]=0.008mole dm^{-1}; [$HClO_4$]=0.05 mole dm^{-1}; Temperature 323K

[C_{16}TAB] / 10^{-3} mol dm^{-3}	k / 10^{-4} s^{-1} *
0.0	0.018
2.0	1.36
4.0	2.07
6.0	2.33
8.0	3.94
10.0	4.12
12.0	5.17

*Mean of duplicate experiments

Rate law

The rate equation for the catalyzed reaction between DEG and NCSA can be represented by the equation

$$-d[NCSA]/dt = k_0[DEG]^{1/2}[NCSA] \quad (12)$$

When [NCSA] in excess above equation 12 reduces to

$$r = k'_0[DEG]^{1/2} \quad (13)$$

Where the rate constant for catalyzed reaction, $k'_0=k_0$ [NCSA]. The plot between reaction rate and $\sqrt{[DEG]}$ (Figure 8) gave a linear plot that validates equation 13. In presence of the catalyst, the oxidation proceeds through catalyzed pathways. Therefore, the following represents the rate of depletion of NCSA in presence of catalyst under excess [DEG] and acid concentrations:

$$-d[NCSA]/dt = \{k_0' + k_c'[C_{16}TAB]\}[NCSA] \quad (14)$$

Here $k_c' = k_c$ [NCSA]

$$= k''[NCSA] \quad \text{Where } k'' = \{k_0' + k_c'[C_{16}TAB]\} \quad (15)$$

Equation 15 holds good, when a plot of observed rate constant in presence of catalyst, k versus [C_{16}TAB] is linear [Figure 5].

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