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Oxidation of triethylene glycol by N-chlorosaccharin in cetyltrimethylammonium bromide catalyzed system: A kinetics and mechanistic study

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ABSTRACT

The kinetics and mechanistic study of cetyltrimethylammonium bromide catalyzed oxidation of triethylene glycol [2,2'-ethylene diqxybis(ethanol)] by N-chlorosaccharin in aqueous acetic acid medium in presence of perchloric acid have been investigated at 303-323K temperature range. The reaction has first order dependence on N-chlorosaccharin concentration. The reaction rate follows first order kinetics with respect to [triethylene 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 products (saccharin) retards the reaction rate. Activation parameters are calculated from the Arrhenious plot. A suitable mechanism has been proposed in consistence with the kinetic data.

KEYWORDS

Kinetics;
Oxidation;
Triethylene glycol;
N-chlorosaccharin;
Micelle catalyzed system;
Cetyltrimethyl ammonium bromide.

INTRODUCTION

Triethylene glycol (TEG) is a colourless, odourless, non-volatile, and hygroscopic liquid. It is characterized by two hydroxyl groups along with two ether linkages, which contribute to its high water solubility, hygroscopicity, solvent properties and reactivity with many organic compounds. Triethylene glycol finds use as a vinyl plasticizer, as an intermediate in the manufacture of polyester resins and polyols, and as a solvent in many miscellaneous applications. Triethylene glycol (TEG) is derived as a co-product in the manufacture of ethylene glycol from ethylene oxide, and from “on-purpose” TEG production using diethylene glycol. The main uses for TEG depend upon its hygroscopic properties. Air conditioning systems use TEG as dehumidifiers and, when volatilized, as an air disinfectant for bacteria and virus control. Glycols, having high boiling point and affinity for water, are employed as liquid desiccant for the dehydration of natural gas. The oxidation of polyethylene glycols, different alcohols and diols by other oxidant has been carried out by various workers[1-11] but no one has ever used TEG.

The N-chlorosaccharin (NCSA) is a versatile oxidant[12-16]. In continuation of our work[17,18], $C_{16}TAB$ catalyzed oxidation of TEG by N-chlorosaccharin has been carried out. The oxidation of TEG by acidic N-chlorosaccharin is an extremely slow reaction. The reaction has found to be catalyzed by a cationic surfactant cetyltrymethylammonium bromide ($C_{16}TAB$).

EXPERIMENTAL

Triethylene glycol (E Merck) was used. N-chloro saccharin was prepared by reported procedure[13]. Double 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 of AR grade and double distilled water was used for preparation of solutions.

Reactants were mixed in the order: requisite volume of TEG, perchloric acid, $C_{16}TAB$, and water or other reagent solution, where necessary. A separately thermostatted solution of N-chlorosaccharin was added to commence the reaction. The 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

TEG (350mg/250ml water), perchloric acid (0.1M/100ml), $C_{16}TAB$ (12mg/100ml) and NCSA (10g/100ml) were mixed for product analysis. After the reaction time of over 48 hours, 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-DNP was added to it and then the reaction mixture was left overnight at refrigerator 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 TEG to be a [2,2'-oxibis (1-hydroxy)hexanal]. The aldehyde was conformed by IR spectra which shows bands at $3440 cm^{-1}$ and $1724 cm^{-1}$for OH stretching and C=O stretching respectively and a band at $2722 cm^{-1}$ 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[19-22]. Stoichiometry was determined by using varying ratios of the oxidant to TEG were thermostatted at 25°C for 48 hours incubation, and residual NCSA was determined iodometrycally 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 TEG) was calculated. TEG and N-chlorosaccharin react in 1:1 stoichiometry, as follows:

$$\begin{aligned}&\mathbf{OHCH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2OH+}\\&\mathbf{C_6H_4COSO_2NCl\rightarrow OHCH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}}\\&\mathbf{O\text{-}CH_2\text{-}CHO + C_6H_4COSO_2NH + H^+ + Cl^-}\end{aligned} \qquad (1)$$

RESULTS AND DISCUSSION

Order with respect to [N-chlorosaccharin]

In a typical kinetic run, for the reaction ([NCSA] $0.007 mol\ dm^{-3}$, $[H^+]$ $0.05 mol\ dm^{-3}$ and [TEG] $0.08 mol\ dm^{-3}$), a plot of log (a-x) versus time (Figure 1) gave a straight line, which indicates that reaction under the chosen conditions follows pseudo first order kinetics. The order with respect to NCSA is unity. The mean pseudo first-order rate constant, k_0 was found to be $(0.11 \pm 0.1) \times 10^{-5}\ s^{-1}$.

Order with respect to [TEG]

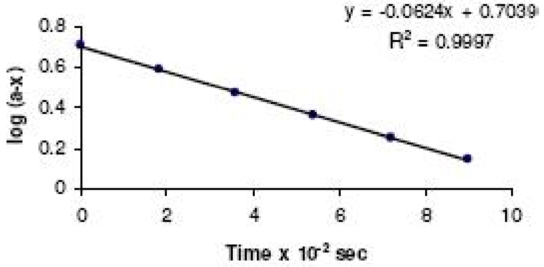

Figure 1 : The effect of N-Chlorosaccharin addition

On varying TEG concentration from 0.04 to 0.24mol dm^{-3}, there is an increase in rate of reaction. The plot of log k versus log [TEG] (Figure 2) gave a straight line with slop equal to 1.04 (R^2=0.99), suggesting that order with respect to TEG is first. A double reciprocal plot between k^{-1} versus $[TEG]^{-1}$ (Figure 3) has been found to be a straight line with positive intercept at y-axis. This kinetic evidence of complex formation between the substrate and the oxidant, further support the first order dependence.

Effect of variation of $[H^+]$

On varying perchloric acid in concentration from 0.0125 by 0.2000mol dm^{-3} there is a decrease in reaction rate. The plot of log k versus log $[H^+]$ (Figure 4) gave a straight line with positive intercept 0.54(R^2= 0.96), suggesting that acid plays a complex role in the reaction system. The retardation by $[H^+]$ may be mainly attributed to the conversion of the more reactive neutral species of TEG to less reactive protonated form.

Dependence of rate on $[C_{16}TAB]$

The addition of $C_{16}TAB$ in the reaction system catalyzed the reaction. The reported critical miceller concentration of $C_{16}TAB$ is 9.2×10^{-4} at 25°C. The reaction rate increase with the increase in concentration of $C_{16}TAB$ from 2.0×10^{-3} to 10.0×10^{-3}mol dm^{-3}. 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 miceller systems is their ability to affect the rates of chemical reactions. The reaction rate can either be accelerated or retarded, 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 miceller catalysis[23]. Micelles are formed due to assembling of amphiphilic molecules of surfactant in above a certain concentration called as critical miceller concentration[24,25]. Miceller catalysis of reaction in aqueous solutions is usually explained on the basis of a distribution of reactants between water and the miceller '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[26,27]. 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 TEG and the micelle.

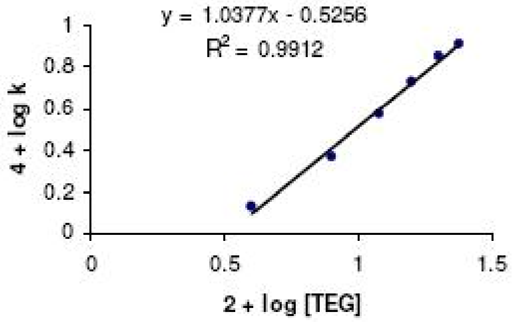

Figure 2 : The order with respect to [TEG]

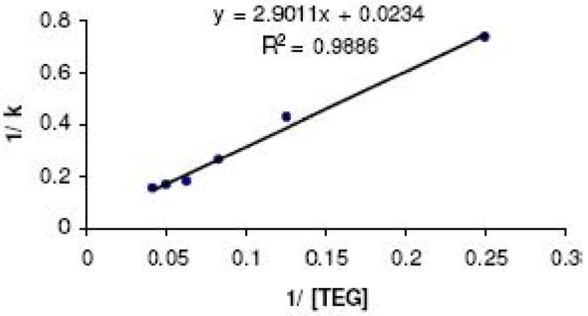

Figure 3 : The double reciprocal plot of k^{-1} and $[TEG]^{-1}$.

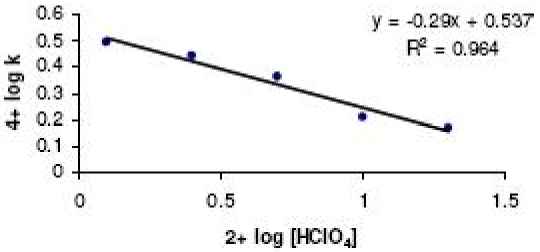

Figure 4 : The Effect of perchloric acid addition

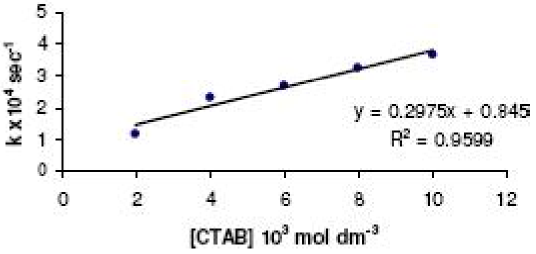

Figure 5 : The micelle effect

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 is further supported by observing the effect of change in dielectric constant of the reaction medium. The effect of dielectric constant in reaction medium was studied by adding acetic acid (35-60%) in the reaction medium at constant concentrations of other reactants. The rate of reaction increases by increasing the proportion of acetic acid in the solvent medium; this validates the involvement of neutral species in the rate-determining step. Addition of saccharin (one) of the reaction (products), from 0.5×10^{-3} to 2.5×10^{-3}mol dm^{-3} at constant NCSA and TEG concentration, decreases the rate of reaction. This conforms that HOCl is the main oxidizing species. The retardation of reaction rate on the addition of saccharin suggests a pre-equilibrium step that 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= 0.97) 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 TEG and HOCl.

Effect of temperature

The reaction was studied at different temperatures. The rate constants at 308, 313, 318, 323 and 328K were found to be 1.61×10^4sec^{-1}, 2.35×10^4sec^{-1}, 3.11 $\times10^4$sec^{-1}, 4.81×10^4sec^{-1}, and 6.08×10^4 sec^{-1} respectively. From the linear Arrhenius plot of log k vs 1/T (Figure 7) activation parameters for overall reaction were evaluated Ea= 60.22 KJ mol^{-1} ΔH*= 57.62 KJ mol $^{-1}$, ΔG*=5.95 KJ mol^{-1}, ΔS*= -122.46JKmol^{-1} respectively.

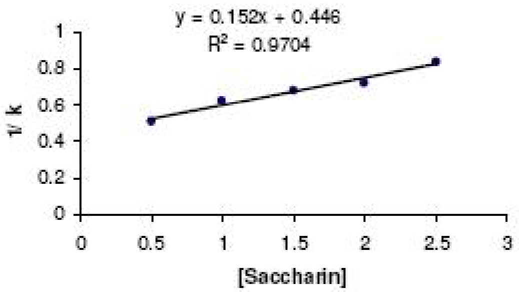

Figure 6 : The effect of saccharin addition on the rate of reaction

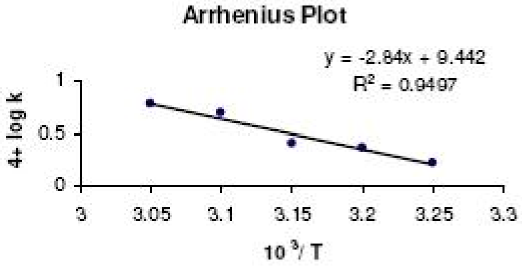

Figure 7: The Arrhenius plot

Mechanism

From the various relevant literatures[28-32] the different probable steps involved in NCSA system may be summarized as follows:

$$\text{NCSA} + H_2O \rightarrow \text{HOCl} + \text{Saccharin} \quad (2)$$

$$\text{HOCl} + H^+ \rightarrow H_2O^+Cl \quad (3)$$

$$\text{NCSA} + H^+ \rightarrow \text{NCSAH}^+ \quad (4)$$

$$\text{NCSAH}^+ + H_2O \rightarrow H_2O^+Cl + \text{Saccharin} \quad (5)$$

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

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

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

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

The small salt effect, the increase in reaction rate on increasing the dielectric constant and the linear reciprocal plot between k^{-1} versus $[TEG]^{-1}$ with positive

TABLE 1: Order with respect to N-chlorosaccharin
[TEG] = 0.08 mole dm^{-3}; [HClO$_4$] = 0.05 mole dm^{-3}; [C$_{16}$TAB] = 0.004 mole dm^{-3}; Temperature =313K

[NCSA]/10^{-2}mol dm^{-3}	k /10^{-4} s^{-1} *
0.2	14.47
0.3	6.86
0.4	4.58
0.7	2.33
1.0	1.61
1.5	1.04

***Mean of duplicate experiments**

TABLE 2: Effect of Triethylene glycol concentration variation
[NCSA] = 0.007mole dm^{-3}; [HClO$_4$] = 0.05mole dm^{-3}; [C$_{16}$TAB] = 0.004mole dm^{-3}; Temperature= 313K

[TEG] /10^{-2}mol dm^{-3}	k/10^{-4} s^{-1}*
4.0	1.36
8.0	2.33
12.0	3.80
16.0	5.71
20.0	6.06
24.0	6.65

***Mean of duplicate experiments**

TABLE 3: Effect of hydrogen ion concentration variation
[TEG] = 0.08mole dm^{-3}; [NCSA] = 0.007mole dm^{-3}; [C$_{16}$TAB] = 0.004mole dm^{-3}; Temperature= 313 K

[HClO$_4$] / 10^{-2} mol dm^{-3}	k /10^{-4} s^{-1} *
1.25	3.09
2.50	2.76
5.00	2.30
10.50	1.66
20.00	1.45

***Mean of duplicate experiments**

TABLE 4: Effect of C$_{16}$TAB concentration variation
[TEG] = 0.08mole dm^{-1}; [NCSA] = 0.007mole dm^{-1}; [HClO$_4$] = 0.05mole dm^{-1}; Temperature= 313K

[C$_{16}$TAB] /10^{-3}mol dm^{-3}	k/10^{-4} s^{-1} *
0.0	0.011
2.0	1.20
4.0	2.30
6.0	2.70
8.0	3.25
10.0	3.70

***Mean of duplicate experiments**

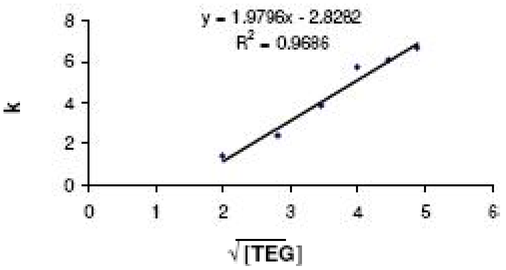

Figure 8 : The effect of [TEG] on rate of reaction

intercept on the y-axis (Figure 3), support the equation (6). The complex thus formed will be rapidly decomposed into the products, in equation (7).

C$_{16}$TAB catalyzed mechanism

The reaction between TEG 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:

$$\mathrm{nC_{16}TAB \rightarrow (C_{16}TAB\,)_n} \quad (8)$$

$$\mathrm{OHCH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2OH + (C_{16}TAB)_n \rightarrow [OHCH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2OH \ldots (C_{16}TAB)_n]} \quad (9)$$

$$\mathrm{[OHCH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2OH \ldots. (C_{16}TAB)_n] + HOCl \rightarrow X_1} \quad (10)$$

$$\mathrm{X_1 + H_2O \rightarrow OHCH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CHO + 2H_2O + HCl} \quad (11)$$

Rate law

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

$$\mathrm{-d\,[NCSA]\,/\,dt = k_0[TEG]^1[NCSA]} \quad (12)$$

When[NCSA] in excess above equation(12) reduces to

$$\mathrm{r = k'_0[TEG]^1} \quad (13)$$

Where the rate constant for catalyzed reaction, $k'_0 = k_0$ [NCSA]. The plot between k vs √ [TEG] (Figure 8) gave a linear plot that validates equation (13). In the 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 [TEG] and acid concentrations:

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

Here $k_c{'} = k_c$ [NCSA]

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

Equation (15) holds well, when a plot of observed rate constant in presence of catalyst, k versus [C$_{16}$TAB] is linear (Figure 5).

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