

## Kinetics and mechanism of cetyltrimethylammonium bromide catalyzed oxidation of diethylene glycol by chloramine-T in acidic medium

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(Received 15 October 2002, revised 18 February 2003)

**Abstract:** The kinetics and mechanism of the C<sub>16</sub>TAB catalyzed oxidation of diethylene glycol (2,2'-oxydiethanol) by chloramine-T in acidic medium has been studied. The reaction has a first-order dependence on chloramine-T. With excess concentrations of other reactants, the reaction rate follows fractional order kinetics with respect to [diethylene glycol]. The micellar effect due to cetyltrimethylammonium bromide, a cationic surfactant, has been studied. The reaction is catalyzed by chloride ions as well. The small salt effect and increase in the reaction rate with increasing dielectric constant suggest the involvement of neutral molecules in the rate determining step. Addition of *p*-toluenesulfonamide retards the reaction rate. On the basis of product analysis, a pertinent mechanism is proposed.

**Keywords:** diethylene glycol, chloramine-T, micellar catalysis.

### INTRODUCTION

Polyethylene glycols (PEG) are frequently used as solvents and lubricants. Polyethylene glycol mixed with honey and pollen extract has been used for treating test lesions in milking cows and for preventing peritoneal adhesions by promoting non-adherent healing. The oxidation of PEG by different oxidants has been studied by various workers<sup>1</sup> but chloramine-T (*p*-Me-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>NCINa·1.5 H<sub>2</sub>O) as an oxidant has not been investigated. Chloramine-T, abbreviated as CAT, is a versatile oxidant.<sup>2</sup> The oxidation of diethylene glycol (DEG) by acidic chloramine-T is an extremely slow reaction. The reaction has been found to be catalysed by the cationic surfactant C<sub>16</sub>TAB (cetyltrimethylammonium bromide). Therefore, the C<sub>16</sub>TAB catalyzed oxidation of DEG by chloramine-T has been studied in this work.

### EXPERIMENTAL

The chemicals used were of Analar grade and double distilled water was used throughout to prepare the solutions.

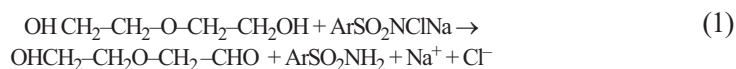
*Kinetic procedure*

The reagent solutions were mixed in the order: required volumes of DEG, perchloric acid, C<sub>16</sub>TAB, plus water or other reagents, where necessary. A separately thermostatted solution of chloramine-T was added to commence the reaction. Residual chloramine-T was determined iodometrically using standard sodium thiosulfate as titrant and potassium iodide-starch as an indicator. In all the experiments, the reactions were followed for up to two half lives. A constant ionic strength of the reaction mixture was maintained by adding the required amount of sodium sulphate solution.

*Stoichiometry and product analysis*

DEG (300 mg / 250 ml water), perchloric acid (0.1 M / 100 ml), C<sub>16</sub>TAB (10 mg in 100 ml) and CAT (7 g / 150 ml) were mixed for the product analysis. After the required reaction time (over 48 h), the organic components were extracted from the mixture into ether. The ethereal extract was shaken with a saturated solution of sodium bicarbonate. The ether extract was dried and concentrated using a rotary evaporator, under low pressure. Preliminary studies were carried out by thin layer chromatography, using a benzene: ethyl acetate mixture (8:2) as the eluent. A distinct single spot was obtained. A solution of 2,4-dinitrophenylhydrazine was added to it and the reaction mixture was left overnight in a refrigerator (5 °C). The solution was centrifuged and a brown-orange residue was obtained. The formation of the hydrazine derivative adequately confirmed the oxidation product of DEG to be a butanal. The fact that only one hydroxyl group was attacked and other remained intact is supported by the stoichiometry of the reaction. A literature survey showed that similar types of oxidation products were reported by Sharma *et al.*<sup>3,4</sup> in the oxidation of 1,3-propanediol and butanediol by peroxodiphosphate. Studies on the further characterization of the reaction products are in progress.

The stoichiometry was determined by incubating various ratios of the oxidant to DEG at 25 °C for 48 h and determining the residual CAT iodometrically using standard sodium thiosulfate as the titrant and potassium iodide-starch as the indicator. The mole ratio (number of moles of the oxidant consumed per mole of oxidized DEG) was calculated. DEG and chloramine-T react in 1:1 stoichiometry, as follows:



## RESULTS AND DISCUSSION

*Reaction order with respect to chloramine-T*

In a typical kinetic run, for the uncatalyzed reaction ([CAT] = 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 0.05 mol dm<sup>-3</sup> and [DEG] = 0.08 mol dm<sup>-3</sup>), a plot of log (a-x) versus time gave a straight line, which indicates that the reaction under the chosen conditions follows pseudo first-order kinetics. The order with respect to [oxidant] is unity (Table I). The mean pseudo first-order rate constant, k<sub>0</sub>' was found to be (7.16 ± 0.2) × 10<sup>-4</sup> s<sup>-1</sup>. A slight fall in rate constants with increasing [chloramine-] may be explained on the basis of some deactivation caused by traces of inactive sodium chlorate formed in a side reaction as shown in Eq. (2).<sup>5</sup>

*Reaction order with respect to DEG*

On varying the DEG concentration from 2.0 × 10<sup>-2</sup> to 20.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>, an increase in the reaction rate was observed. The plot of log k<sub>0</sub>' versus log [DEG] gave a straight line with a slope equal to 0.46 (R<sup>2</sup> = 0.99), suggesting that order with respect to substrate is fractional. A double reciprocal plot of 1/k versus 1/[DEG] was found to be a straight line with a positive intercept at the y axis. This kinetic evidence of complex forma-

tion between the substrate and the oxidant further supports the fractional order dependence.

TABLE I. Reaction order with respect to chloramine-T

[CAT]/10 <sup>-3</sup> mol dm <sup>-3</sup>	k <sub>0</sub> /10 <sup>-3</sup> s <sup>-1</sup> *
1.0	8.34
2.0	5.18
3.0	3.42
4.0	2.38
6.0	1.22
8.0	0.70

\*Mean of duplicate experiments.

*Effect of variation of pH*

On varying the sulphuric acid concentration from 0.10 to 0.40 mol dm<sup>-3</sup>, an increase in the reaction rate (Table II) was observed. The plot of log k<sub>0</sub>' versus [H<sup>+</sup>] gave a straight line with a slope of 0.20 (R<sup>2</sup> = 0.99), suggesting that the acid plays a complex role in the reaction system. The cause of the increase in the reaction rate with increasing acid concentration may be attributed to the following equilibria<sup>6</sup>:



It is evident from the above reactions that an increase in the acid concentration results in the formation of more HOCl, consequently the reaction rate increases.

TABLE II. Effect of variation in the hydrogen ion concentration

[H <sub>2</sub> SO <sub>4</sub> ]/mol dm <sup>-3</sup>	k <sub>0</sub> /10 <sup>-4</sup> s <sup>-1</sup> *
1.25	1.82
2.50	2.08
5.00	2.35
10.0	2.53
20.0	3.29
40.0	3.42

\*Mean of duplicate experiments.

*Dependence of the rate on [C<sub>16</sub>TAB]*

The addition of C<sub>16</sub>TAB in the reaction system catalyses the reaction. The reported critical micellar concentration (cmc) of C<sub>16</sub>TAB is  $9.2 \times 10^{-4} \text{ mol dm}^{-3}$  at 25 °C. The reaction rate increases with increasing detergent concentration from  $2.0 \times 10^{-3}$  to  $8.0 \times 10^{-3} \text{ mol dm}^{-3}$  (Table III). The plot of  $k_0'$  versus [C<sub>16</sub>TAB] gives a straight line (Fig. 1). Surfactants tend to form micelles due to the assembling of amphiphilic molecules of surfactant in water above a certain concentration (critical micellar concentration, abbr: cmc).<sup>7</sup> The micelles may provide a favourable orientation of the reactants by polarity gradients. Ionic micelles stabilise polarised transition states within the aggregates and therefore enhance a reaction. In the present case, a hydrophobic interaction is most likely to be operative due to the relatively large hydrocarbon chains of the substrate. 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 (in terms of moles per unit time per liter of the entire solution) increases accordingly. Another likely reason seems to be electrostatic attraction between the polar DEG molecule and the micelle.

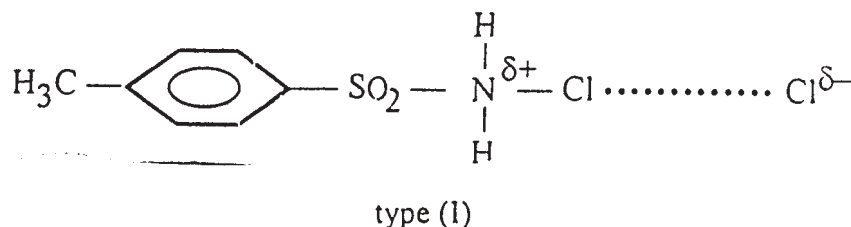
TABLE III. C<sub>16</sub>TAB catalyzed reaction

[C <sub>16</sub> TAB]/10 <sup>-3</sup> mol dm <sup>-3</sup>	$k_0'/10^{-3} \text{ s}^{-1*}$
0	0.09
2.0	1.02
3.0	1.84
4.0	2.78
4.8	3.29
5.2	3.58
6.0	4.36

\*Mean of duplicate runs.

*Effect of variation of the [Cl<sup>-</sup>]*

The role of chloride ion in the kinetics and mechanism of the oxidation reaction by CAT is very crucial. The plot of  $\log k_0'$  versus  $\log [\text{Cl}^-]$  is a straight line with a slope of 0.19 ( $R^2 = 0.98$ ). The cause of the acceleration in the reaction rate is the generation of molecular chlorine/HOCl due to the interaction between a chloride ion and a chloronium ion produced by the hydrolysis of a N–Cl bond, in polar medium. Alternatively, the added chloride ion may co-ordinate with the protonated oxidant to give rise to species of the type (I).



*Effect of variation of the ionic strength, dielectric constant and addition of p-toluene-sulphonamide (PTS)*

With the employed reactant concentrations  $[\text{H}^+] 0.05 \text{ mol dm}^{-3}$ ,  $[\text{C}_{16}\text{TAB}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{CAT}] 4.0 \times 10^{-3} \text{ mol dm}^{-3}$ , the initial ionic strength of the reaction mixture was 0.058. There is no substantial change in the reaction rate on varying the ionic strength from 0.056 to 0.118 by the addition of neutral sodium perchlorate, this absence of a significant salt effect suggests the participation of neutral species in the rate determining step, *i.e.*, the substrate molecule and HOCl. This assumption obtained further support from the effect of change in the dielectric constant of the reaction medium. The increase in reaction rate with increasing dielectric constant further validates the involvement of neutral molecules in the rate determining step. The addition of PTS, one of the reaction products, from  $1.0 \times 10^{-3}$  to  $8.0 \times 10^{-3} \text{ mol dm}^{-3}$  at constant CAT and DEG concentration, decreases the reaction rate. This supports the hypothesis that HOCl is the main oxidizing species:



*Mechanism*

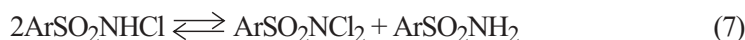
Chloramine-T is a strong electrolyte<sup>6</sup> and in aqueous solution it behaves as follows:



The anion  $\text{ArSO}_2\text{NCl}^-$  is protonated in acidic solutions to give *N*-chlorotoluene-*p*-sulphonamide



This  $\text{ArSO}_2\text{NHCl}$  undergoes disproportionation or hydrolysis according to following reactions:



In weakly acidic media (pH 6–7),  $\text{ArSO}_2\text{NHCl}$  is the prominent reacting species of CAT while at higher acid concentrations (pH < 2.8)  $\text{ArSO}_2\text{NHCl}$  is further protonated according to Eq. 10.



Thus, the possible oxidizing species in acidic solutions of CAT are  $\text{ArSO}_2\text{NH}_2\text{Cl}^+$ ,  $\text{ArSO}_2\text{NHCl}$ ,  $\text{ArSO}_2\text{NCl}_2$  (dichloramine-T) and  $\text{HOCl}$ . In the present studies, it was found that the reaction rate is retarded on addition of PTS. This is indicative of the fact that either  $\text{ArSO}_2\text{NCl}_2$  and/or  $\text{HOCl}$  could be the main oxidizing species. To account for the experimental observations, the following mechanism was envisaged. The linear double reciprocal plot with intercept on y-axis of  $k^{-1}$  vs.  $[\text{DEG}]^{-1}$  suggests the formation of a complex between the substrate and the oxidant. Thus, it is proposed that the slowest and the rate determining step is



The small salt effect, increase in reaction rate on increasing the dielectric constant and straight line double reciprocal plots between  $1/k$  versus  $1/[\text{DEG}]$  with positive intercept at y axis, support Eq. (11) as being the rate determining step. The thus formed complex decomposes quickly into the products, Eq. (12).

#### *Mechanism in the presence of chloride ions*

With increasing concentration of chloride ions, the reaction rate increases. The order with respect to chloride ions is fractional. The increase in the rate in the presence of chloride ions may be attributed to the following reactions:



Thus, the  $\text{HOCl}$  generated in Eq. 15 commences oxidizing the substrate simultaneously in a parallel reaction to that shown in Eqs. 11 and 12.

#### *Surfactant catalyzed mechanism*

The uncatalyzed reaction between the glycol under consideration and chloramine-T is extremely slow. The addition of  $\text{C}_{16}\text{TAB}$  accelerates the reaction substantially. The physical basis for micellar catalysis involves several contributing factors. First there is the effect of the micellar environment on the rate-controlling step in the reaction mechanism. The relative free energies of the reaction (s) and/or the transition state can be altered when the reaction occurs in the micellar phase instead of bulk water. This concept is reminiscent of enzymatic catalysis and many initial studies of rates in micellar systems focused on this possibility. A more important consideration is the interactive localization of the reacting species in the relatively small volume of the micelle compared to the bulk solution. This leads to a large increase in the effective concentration and the observed rate (in terms of moles per unit time per liter of the entire solution) increases accordingly. The following

mechanism is envisioned for the catalysis by C<sub>16</sub>TAB:

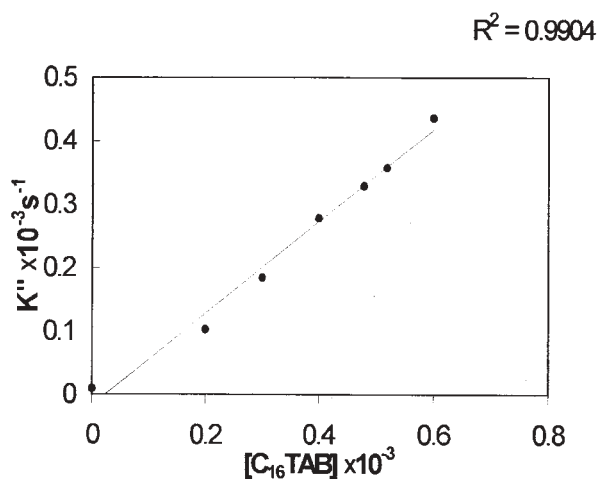
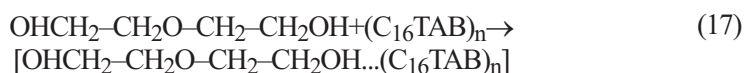


Fig. 1. [DEG] = 0.08 mol dm<sup>-3</sup>; [CAT] = 4.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; [chloramine-T] = 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; Temp: 45 °C.

*Rate laws*

The rate equation for the uncatalyzed reaction between DEG and CAT can be represented by the equation,

$$-d[\text{CAT}]/dt = k_0[\text{DEG}]^{1/2} [\text{CAT}] \quad (20)$$

When [CAT] is in excess, Eq. (21) reduces to

$$r = k'_0 [\text{DEG}]^{1/2} \quad (21)$$

where the rate constant for uncatalyzed reaction,  $k'_0 = k_0 [\text{CAT}]$ . The plot of reaction rate against  $\sqrt{[\text{DEG}]}$  gave a linear plot that validates Eq. (21). In the presence of the catalyst, the oxidation reaction proceeds through both uncatalyzed and catalyzed pathways. Therefore, the following represents the rate of depletion of CAT in presence of catalyst under excess [substrate] and acid concentrations:

$$-d[\text{CAT}]/dt = \{k'_0 + k'_c [\text{C}_{16}\text{TAB}]\}[\text{CAT}] \quad (22)$$

where  $k'_c = k_c[\text{CAT}]$

$$= k'' [\text{CAT}] \text{ where } k'' = \{k_0' + k_C' [\text{C}_{16}\text{TAB}]\} \quad (23)$$

If Eq. (23) is valid, a plot of the observed rate constant in presence of catalyst,  $k''$  versus  $[\text{C}_{16}\text{TAB}]$  should give a straight line (Fig. 1).

#### ИЗВОД

### КИНЕТИКА И МЕХАНИЗАМ ОКСИДАЦИЈЕ ДИЕТИЛЕН-ГЛИКОЛА СА ХЛОРАМИНОМ-Т КАТАЛИЗОВАНЕ ЦЕТИЛТРИМЕТИЛ-АМОНИЈУМ-БРОМИДОМ У КИСЕЛОЈ СРЕДИНИ

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Проучавана је оксидација диетилен-гликола(2,2'-оксидиетанол) хлорамином-Т која је катализована помоћу  $\text{C}_{16}\text{TAB}$  у киселој средини. Реакција је првог реда у односу на хлорамин-Т. У вишку концентрација других реактанта ред реакције у односу на диетилен-гликол је разломљен. Проучаван је и мицеларни ефекат цетилтриметил-амонијум-бромид, који је катјонска површински активна супстанца. Реакцију такође катализују и хлоридни јони. Мали сони ефекат и повећање брзине реакције повећањем диелектричне константе указује на учествовање неутралних молекула у спором ступњу реакције. Додавање *p*-толуенсулфонамида успорава реакцију. На основу резултата предложен је одговарајући механизам реакције.

(Примљено 15. октобра 2002, ревидирано 18. фебруара 2003)

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