



Mechanism of the oxidative cleavage of diethylene glycol by bromate in acid medium

Biswajit Pal

Department of Chemistry, St. Paul's C. M. College, 33/1 Raja Rammohan Roy Sarani, Kolkata, India

ABSTRACT

The oxidative cleavage of diethylene glycol by bromate ion has been studied in hydrochloric acid medium in the temperature range 298-313 K. The rate of the reaction is dependent on the first power of the concentration of diethylene glycol and bromate ion. The reaction rate increases with increase in H^+ concentration in the range (0.1 - 1.0) mol dm^{-3} and reaction is first order with respect to $[H^+]$. The reaction has been shown to occur with the formation of an unstable bromate ester which decomposes to the reaction product in one step two-electron transfer process. Formaldehyde has been identified as the oxidation product of diethylene glycol. The activation parameters of the oxidative cleavage of diethylene glycol have been evaluated.

Keywords: Oxidative cleavage; Diethylene glycol (DEG); Potassium bromate; Kinetics and mechanism.

INTRODUCTION

Diethylene glycol (DEG), is an important organic compound, used in the synthesis of 1,4-dioxane, morpholine, polyester resins, polyurethanes and plasticizers [1]. DEG is used as humectants for printing ink and glue [2] and the component in brake fluid, lubricants, wallpaper strippers, antifog solutions and heating/cooking fuel [1]. It is also widely used as solvent for resins, nitrocellulose, dyes, oils and other organic compounds. Owing to its (DEG) vast applications, it is essential to investigate the kinetics of its oxidation reaction in different experimental conditions. The kinetic studies on the oxidation of ethylene glycol by different oxidizing agents are well documented [3-5]. However, the literature reports [6-8] involving the oxidations of dihydroxy ethers are scanty and the mechanisms of redox reactions are yet to be understood.

Bromate, an oxyanion, is known to be an excellent oxidizing agent having $E_0 = 1.52$ volts at 298 K in an acid medium [9]. Bromate has been widely used as an oxidant in the oxidation of large number of organic and inorganic compounds in acid medium and after the reaction itself reduced to bromide and molecular bromine. The bromate ion oxidation of metal ions has been investigated in presence of different inorganic reductants [10, 11]. The bromate ion oxidation of some organic compounds such as α -hydroxy acids [12], α , β -unsaturated compounds [13], aryl alcohols [14], thiourea [15], methylene violet [16], aromatic aldehyde [17] were investigated in acid medium. Despite of the rich chemistry of both the oxidant and the reductant molecules, the electron transfer reaction between BrO_3^- and DEG has not received attention. Moreover, DEG contains an ether linkage between two ethylene glycol moieties. Thus it would be quite interesting to investigate the oxidative cleavage of DEG. The present communication deals with the kinetics and mechanism of the oxidation of diethylene glycol by bromate ion in acid medium under different experimental conditions.

EXPERIMENTAL SECTION

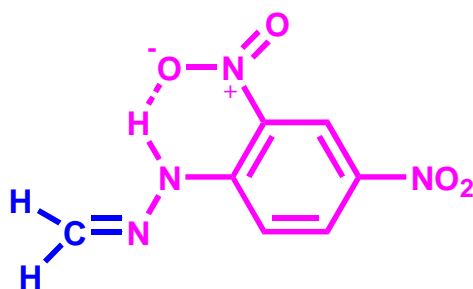
Potassium bromate (BDH), sodium perchlorate (BDH), mercuric acetate (E. Merck), sodium thiosulphate (S.D. fine Chem. Ltd.), copper sulphate (S.D. fine Chem. Ltd.) were used as received. All other inorganic compounds were of the highest purity available. Diethylene glycol (Fluka) was used as supplied without further purification. All solutions were prepared in double distilled water. The prepared potassium bromated solution was standardized against sodium thiosulphate solution which was previously standardized against copper sulphate solution. Sodium perchlorate was used to maintain the constant ionic strength during the reaction. In order to avoid any undesirable photochemical reaction the reaction vessels were rapped with black paper.

Procedure and rate measurements:

The oxidation reaction was studied under pseudo-first order conditions, in which diethylene glycol was present in large excess to that of the bromate ion. The reaction mixture was thermally equilibrated at the desired temperature in a well circulated water bath. The reaction was carried out by withdrawing calculated amount of the reaction mixture at regular intervals of time and quenched with excess KI soln. Measured amount of mercuric acetate was added to the reaction mixture to prevent bromine molecule liberated from KBrO_3 during oxidation reaction and also removed bromide ion by forming complex [13]. It is to be mentioned that mercuric acetate is inert towards oxidation of diethylene glycol. Finally, the progress of the reaction will be followed by measuring the unconsumed bromate iodometrically using starch indicator. The pseudo-first order rate constants (k_{obs}) were computed from the linear plots of $\log [\text{BrO}_3^-]$ versus 'time' ($R^2 \geq 0.98$). The rate constants (k_{obs}) were reproducible within $\pm 5\%$.

Product analysis:

The reaction mixture containing diethylene glycol ($20 \times 10^{-2} \text{ mol dm}^{-3}$), potassium bromate ($2 \times 10^{-3} \text{ mol dm}^{-3}$), hydrochloric acid (0.5 mol dm^{-3}) and mercuric acetate ($2 \times 10^{-2} \text{ mol dm}^{-3}$) was set aside in a closed container for 2 h to ensure the completion of the reaction and then distilled. A small portion of the distillate was treated with 5 ml of 12 N H_2SO_4 and a pinch of solid chromotropic acid. The mixture was then warmed on a water bath at $\sim 60^\circ\text{C}$ for 5 min. A pink violet color [18, 19] developed, indicating the presence of formaldehyde, obtained from the reaction between diethylene glycol and bromate ion in acid medium. Another portion of the distillate was mixed with 2,4-dinitrophenyl hydrazine solution in 4N H_2SO_4 when a yellow 2,4-dinitrophenyl hydrazone derivative of the reaction product was precipitated. The precipitate was filtered, washed thoroughly, purified and then analyzed (m.p. $\approx 167\text{-}169^\circ\text{C}$ [20, 21]; Found C = 40.06, H = 2.82, N = 25.7 % reqd for $\text{C}_7\text{H}_6\text{N}_4\text{O}_4$, C = 40.0, H = 2.85, N = 26.6 %). The above observations indicate the presence of 2,4-dinitrophenyl hydrazone derivatives of formaldehyde (Scheme 1) which confirms the generation of formaldehyde as the reaction product.



Scheme 1: 2,4-DNP derivative of the oxidation product of diethylene glycol

RESULTS AND DISCUSSION

The oxidation of diethylene glycol was studied at varying concentrations of potassium bromate [$(0.5 - 5.0) \times 10^{-3} \text{ mol dm}^{-3}$] keeping $[\text{DEG}]$, $[\text{H}^+]$ and temperature constant at $10 \times 10^{-2} \text{ mol dm}^{-3}$, 0.5 mol dm^{-3} and 303 K , respectively. The pseudo-first order rate constant (k_{obs}) was found to be independent of the initial concentration of bromate (Table 1), indicating that the rate is of first order with respect to BrO_3^- . The empirical rate law at constant $[\text{H}^+]$ and excess of DEG concentration is

$$-d[\text{BrO}_3^-] / dt = k_{\text{obs}} [\text{BrO}_3^-] \quad (1)$$

Table 1: Effect of $[\text{BrO}_3^-]$, $[\text{H}^+]$ and $[\text{Cl}^-]$ on the pseudo-first order rate constant (k_{obs}) of the oxidation of DEG at 303 K

$10^3 [\text{BrO}_3^-]$ (mol dm^{-3})	$10^2 [\text{DEG}]$ (mol dm^{-3})	$[\text{H}^+]$ (mol dm^{-3})	$[\text{Cl}^-]$ (mol dm^{-3})	$10^4 k_{\text{obs}}$ (s^{-1})
0.5	10.0	0.5	0.5	18.7
2.0	10.0	0.5	0.5	18.3
4.0	10.0	0.5	0.5	18.5
5.0	10.0	0.5	0.5	18.2
2.0	5.0	0.1	0.8	1.71
2.0	5.0	0.2	0.8	4.12
2.0	5.0	0.4	0.8	7.03
2.0	5.0	0.6	0.8	12.1
2.0	5.0	0.8	0.8	14.8
2.0	5.0	0.1	0.2	1.75
2.0	5.0	0.1	0.3	1.68
2.0	5.0	0.1	0.4	1.69
2.0	5.0	0.1	0.6	1.77

The influence of variation of the diethylene glycol concentration was studied in the temperature range (298 – 313 K) but keeping $[\text{BrO}_3^-]$ and $[\text{H}^+]$ constant at $2 \times 10^{-3} \text{ mol dm}^{-3}$ and 0.5 mol dm^{-3} , respectively. The pseudo-first order rate constant increases with increase in DEG concentration (Table 2). At each temperature, the plot of k_{obs} versus $[\text{DEG}]$ gave straight line passing through origin (Fig. 1). The quotients $k_{\text{obs}} / [\text{DEG}]$ are presented in Table 2, indicating that the order with respect to $[\text{DEG}]$ is unity. Thus at constant $[\text{H}^+]$, the reaction follows the rate law,

$$-\text{d}[\text{BrO}_3^-] / \text{dt} = k_2 [\text{DEG}] [\text{BrO}_3^-] \quad (2)$$

where, $k_2 (= k_{\text{obs}} / [\text{DEG}])$ is the second order rate constant.

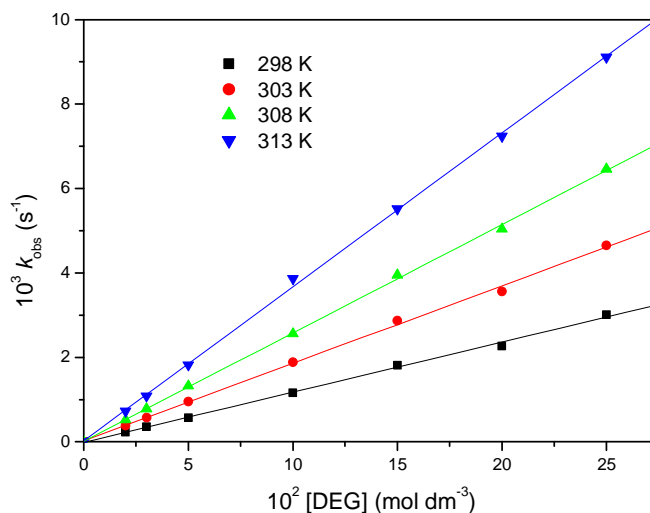


Fig. 1 Variation of pseudo-first order rate constant with DEG concentration. Plots of k_{obs} versus $[\text{DEG}]$ at four different temperatures $[\text{BrO}_3^-] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{H}^+] = 0.5 \text{ mol dm}^{-3}$

The effect of variation of hydrogen ion on the pseudo-first order rate constant was studied at different $[\text{H}^+]$ (0.1 – 1.0 mol dm^{-3}) but at constant ionic strength (0.85 mol dm^{-3}), BrO_3^- and DEG concentrations. The reaction rate increased with the increase in $[\text{H}^+]$ (Table 1). The plot of k_{obs} against $[\text{H}^+]$ was linear passing through the origin (Fig. 2). This indicates that the dependence of rate on $[\text{H}^+]$ is unity. In this acidity range, the rate equation is suggested as,

$$-\text{d}[\text{BrO}_3^-] / \text{dt} = k_3 [\text{DEG}] [\text{BrO}_3^-] [\text{H}^+] \quad (3)$$

where, $k_3 (= k_{\text{obs}} / [\text{DEG}] [\text{H}^+])$ is the third order rate constant.

Table 2: Effect of variation of [DEG] on the pseudo-first order rate constant (k_{obs}) in the temperature range 298-313 K. $[\text{BrO}_3^-] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{H}^+] = 0.5 \text{ mol dm}^{-3}$. Figures in the parentheses represent the values of $k_2 (=k_{\text{obs}} / [\text{DEG}])$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).

10^2 [DEG] (mol dm^{-3})	$10^3 k_{\text{obs}}$ (s^{-1})			
	298 K	303 K	308 K	313 K
2	0.23 (0.011)	0.38 (0.019)	0.52 (0.026)	0.73 (0.036)
3	0.35 (0.012)	0.57 (0.019)	0.78 (0.026)	1.09 (0.036)
5	0.57 (0.011)	0.95 (0.019)	1.32 (0.026)	1.82 (0.036)
10	1.16 (0.012)	1.89 (0.018)	2.56 (0.025)	3.87 (0.038)
15	1.81 (0.012)	2.87 (0.019)	3.95 (0.026)	5.52 (0.037)
20	2.27 (0.011)	3.56 (0.018)	5.04 (0.025)	7.24 (0.036)
25	3.01 (0.012)	4.65 (0.018)	6.46 (0.025)	9.11 (0.036)

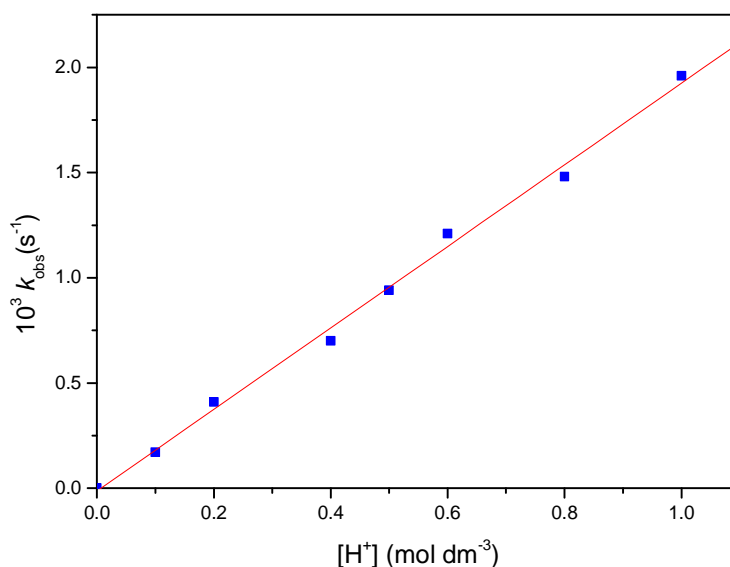


Fig. 2 Variation of reaction rate with H^+ concentration. Plots of k_{obs} versus $[\text{H}^+]$ at 303 K $[\text{BrO}_3^-] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{DEG}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$

The reaction was studied at different chloride concentration (0.2 – 0.8) mol dm^{-3} varied by the addition of NaCl but at constant $[\text{BrO}_3^-]$, [DEG], $[\text{H}^+]$ and temperature. The value of pseudo-first order rate constant was found to be independent of NaCl concentration (Table 1).

In the present investigation, the intervention of free radicals was tested by the addition of acrylonitrile in the concentration range 5-20 % (v/v) to the reaction mixture containing $[\text{BrO}_3^-]$, [DEG] and $[\text{H}^+]$ of $2 \times 10^{-3} \text{ mol dm}^{-3}$, $5 \times 10^{-2} \text{ mol dm}^{-3}$ and 0.5 mol dm^{-3} , respectively. No haziness or suspension was detected. This indicates that the reaction proceeds with a one-step two electron transfer process with no reducing intermediates like free radicals [19].

The oxidation of DEG by bromate was studied over a temperature range of 298-313 K. The values of k_3 were calculated at different temperatures. The values of enthalpy of activation (ΔH^\ddagger) and entropy of activation (ΔS^\ddagger) were calculated from the plot of $\log(k_3/T)$ versus $1/T$ (Fig. 3) using the theory of absolute reaction rate (eqn. 4).

$$k_3 = (RT/Nh) \exp(-\Delta H^\ddagger / RT) \exp(\Delta S^\ddagger / R) \quad (4)$$

The value of enthalpy of activation and entropy of activation for this oxidation reaction were calculated to be $56 \pm 3 \text{ kJ mol}^{-1}$ and $-87 \pm 8 \text{ JK}^{-1} \text{ mol}^{-1}$, respectively.

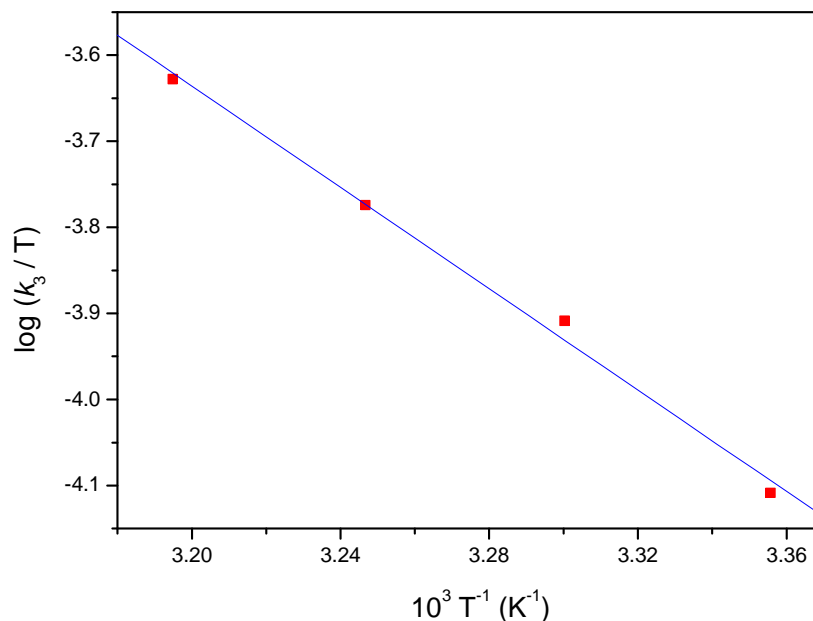
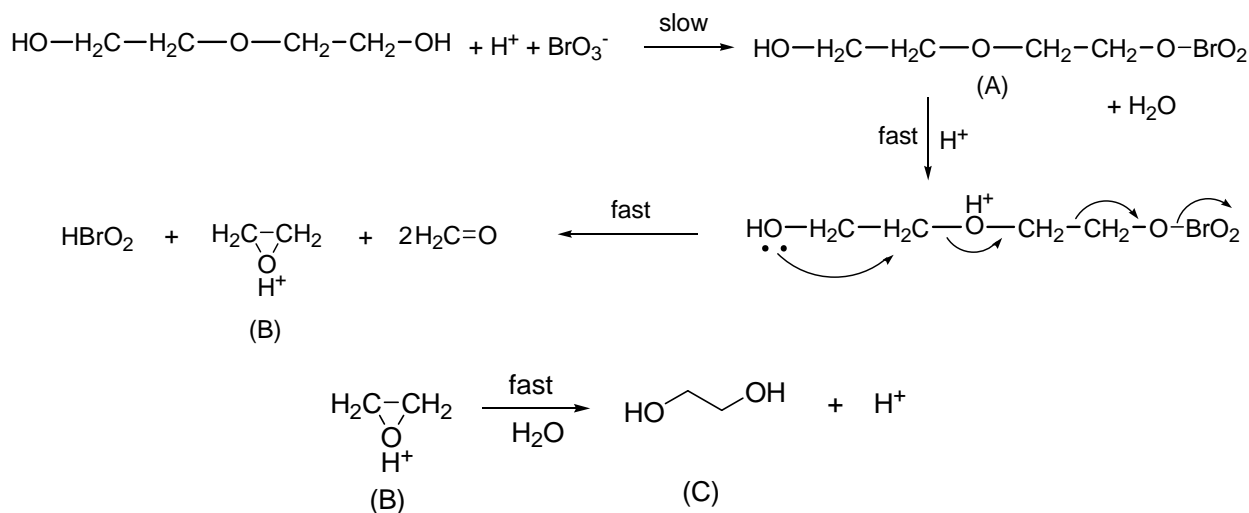


Fig. 3 Influence of temperature on the second-order rate constant. Plot of $\log(k_3/T)$ versus $1/T$

Diethylene glycol is nearer to ethylene glycol in many respects but some of the physical properties such as boiling point, viscosity and specific gravity are higher in case of DEG as might be predicted from its higher molecular weight. Due to its structural dissimilarities the chemical properties are sufficiently different from those of ethylene glycol to make it more desirable materials in many applications. DEG is a straight-chain dihydric alcohol aliphatic compound terminated on both ends by a hydroxyl group. It is an ether-alcohol derivative. The ether part in DEG is not easily attacked by nucleophiles or bases. The ether moiety is relatively unreactive than the alcohol group present in DEG. Hydroxyl group in DEG exhibit both weak acid and weak base behavior and in presence of oxidizing agent it is converted to aldehyde or ketone.

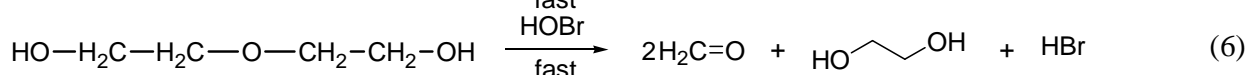
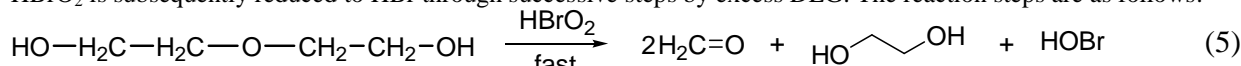


Scheme 2

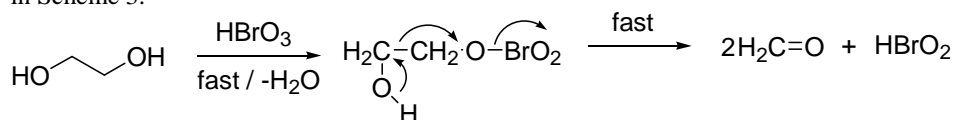
The rate of the reaction was found to be dependent on the first power of the concentrations of diethylene glycol and bromate. The reaction rate also increases with increase in hydrogen ion concentration and the order with respect to

$[H^+]$ is determined to be one. The experimental results are consistent with a mechanism involving a rate determining reaction between diethylene glycol, bromate and hydrogen ion. Sen Gupta et al. proposed [5] a reaction mechanism with the involvement of substrate, oxidant and H^+ ion in the rate determining step in the oxidation of mono-ols and vicinal-diols by bromate ion in acid media. Thus it may be plausible that diethylene glycol reacts with bromate and H^+ to give an unstable bromate ester (A) in the rate determining step. The involvement of a similar bromate ester has been reported in earlier investigations [5, 22]. The bromate ester (A) is then cleaved through neighboring group participation leading to the formation of formaldehyde and ethylene oxide (B) [23]. The ethylene oxide undergoes rapid hydrolysis to give ethylene glycol (C) [23].

$HBrO_2$ is subsequently reduced to HBr through successive steps by excess DEG. The reaction steps are as follows:

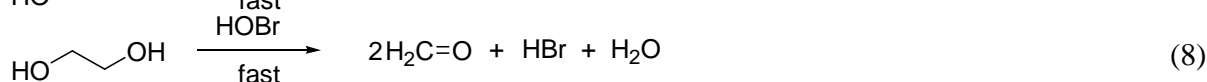
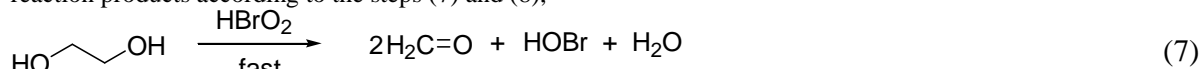


The intermediate diol, being highly reactive, undergoes oxidation with $HBrO_3$ to give aldehyde and $HBrO_2$ as shown in Scheme 3.



Scheme 3

The unstable oxidant species viz., $HBrO_2$ and $HOBr$ may also react with intermediate ethylene glycol to produce the reaction products according to the steps (7) and (8),



An effort was made to isolate the intermediate diol (C) during the reaction but it was not successful as might be predicted that the intermediate compound immediately converted by the oxidant in acid medium yield the final oxidation product, formaldehyde. The oxidation product, $HCHO$ was identified by spot test and C, H, N analysis as mentioned in the product analysis section. This is to be mentioned that formaldehyde is stable and does not undergo further oxidation with the oxidant [24]. The proposed mechanism is supported by the value of the activation parameters. The moderately negative value of entropy of activation (ΔS^\ddagger) suggest that the transition state formed is considerably rigid, resulting in a reduction in the degrees of freedom of the molecule.

CONCLUSION

The present study shows that the bromate reacts with the DEG in presence of H^+ in the rate determining step with the formation of unstable bromate ester which subsequently decomposes to the reaction product in one step two-electron transfer process. The cleavage of carbon-carbon bond yields to the formation of formaldehyde as the oxidation product of diethylene glycol.

Acknowledgment

Thanks are due to University Grants Commission, New Delhi, India for financial support to Dr. B. Pal.

REFERENCES

- [1] LJ Schep; RJ Slaughter; WA Temple; DM Beasley, *Clin. Toxicol. (Phila)*, **2009**, 47, 525–35.
- [2] M O'Neil, The Merck Index, 14th ed. Whitehouse Station, NJ, Merck & Co, **2006**.
- [3] W Bai; Y Zhai; H Lu; W Song, *Indian J. Chem.*, **2008**, 47A, 1194-1198.
- [4] H Wang; Z Jusys; RJ Behm, *J. Electroanalytical Chem.*, **2006**, 595, 23-36.

-
- [5] KK Sen Gupta; SC Kumar; PK Sen; A Banerjee; H Chatterjee, *J. Chem. Research(S)*, **1991**, 118-119.
[6] J Shan; Y Li, *Eur. J. Chem.*, **2013**, 4, 203-206.
[7] B Pal; SN Basu; KK Sen Gupta, *Asian J. Chem.*, **2000**, 12, 176-184.
[8] J-H Shan; H-Y Wei; S-G Shen; H-W Sun, *Chin. J. Chem.*, **2003**, 21, 1470-1473.
[9] AI Vogel, Quantitative inorganic analysis, The EIMS and Longmans, Green and Co. Ltd., 3rd edn., p.89.
[10] GC Knight; RC Thompson, *Inorg. Chem.*, **1973**, 12, 63-66.
[11] JP Birk, *Inorg. Chem.*, **1978**, 17, 504-506.
[12] KK Sen Gupta; A Banerjee; H Chatterjee, *Tetrahedron*, **1992**, 48, 5323-5330.
[13] N Debnath; B Pal; KK Sen Gupta, *J. Indian Chem. Soc.*, **2002**, 79, 351-355.
[14] KK Sen Gupta; SC Kumar; PK Sen; A Banerjee, *Tetrahedron*, **1988**, 44, 2225-2231.
[15] RH Simoyi; IR Epstein; K Kustin, *J. Phys. Chem.*, **1994**, 98, 551-557.
[16] SB Jonnalagadda; MN Shezi, *J. Phys. Chem. A.*, **2009**, 113, 5540-5549.
[17] AK Jain; Meena; D Kumar, *Der Pharma Chemica*, **2014**, 6, 187-193.
[18] B Pal, *Int. J. Chem. Kinet.*, **2014**, 46, 31- 40.
[19] B Pal; KK Sen Gupta; PK Sen, *Transition Met. Chem.*, **2005**, 30, 593-600.
[20] B Pal; PK Sen; KK Sen Gupta, *J. Phys. Org. Chem.*, **2001**, 14, 284-294.
[21] KK Sen Gupta; B Pal; PK Sen, *Int. J. Chem. Kinet.*, **1999**, 31, 873-882.
[22] KK Sen Gupta; B Pal, *J. Indian Chem. Soc.*, **2014**, 91, 991-1004.
[23] IL Finar, Organic Chemistry: The Fundamental Principles, vol 1, 6th edn., ELBS, Longman, **1985**, 313.
[24] AK Bera; B Pal; KK Sen Gupta, *Int. J. Chem. Kinet.*, **2012** 44, 494-505.