International Journal of Research in Engineering and Science (IJRES)
ISSN (Online): 2320-9364, ISSN (Print): 2320-9356
www.ijres.org Volume 11 Issue 3 ǁ March 2023 ǁ PP. 464-468

Kinetic Study of Osmium Tetra Oxide Catalyzed Oxidative Degradation of Butane-2,3 Diol By N-Bromosaccharin

S.K. Singh[1],Deepti Pandey[1] Shashi Sonakiya[2*]
1.Govt. T.R.S. College (Centre for excellence) Rewa (M.P.) India.
2. Dept. of Chemistry, Awadhesh Pratap Singh University
Corresponding author: bajpaishashi19@gmail.com

Abstract: *The kinetics of oxidation of Butane-2,3-diol by N-bromosaccharin (NBSA)in presence of osmium tetra oxide has been studied. The reaction follows identical kinetic being first order in each, NBSA, osmium tetra oxide* (OsO_4) *and* OH^-*concentration while zero order kinetics with diol and saccharin. The reaction is* OsO_4*catalyzed. Various thermodynamic parameters have been computed. Stoichiometric study revealed 1:1 mole ratio. On the basis of thermodynamic parameters and stoichiometry a feasible mechanism has been proposed and rate law has been derived.*

Key Words: *Kinetics, N-bromosaccharin,osmium tetroxide, butane-2,3-diol, stoichiometry.*

Date of Submission: 10-03-2023 Date of acceptance: 23-03-2023

I. INTRODUCTION

The subject of chemical kinetics covers not only reaction rate but also covers a wide range of studies of the effects of the concentrations, temperature, catalyst etc. on reactions of various types. Mechanistic studies of reactions in solution have achieved commendable importance during the few decades. Oxidation reactions incorporating certain selective catalysis are of considerable academic and technological importance. N-bromosaccharin (NBSA) has been used as an oxidizing agent by several workers[1-5]. The kinetics of the oxidation of diol has been studied with a number of oxidizing agent[6-10]. Butane 2,3 diol is also reacted with metal ion[11].In the recent years, studies of oxidation of vicinal diols by N-halo oxidants under homogeneous and heterogeneous reaction conditions[12-20]have attracted considerable attention of the researchers. Literature survey reveals that osmium tetra oxideforms many coordination species with OH^-.The complexes $[OsO_4(OH).H_2O]^{2-}$ and $[OsO_4(OH)_2]^{2-}$most likely formed in alkaline solutions. The latter predominates at higher hydroxide ion concentrations, while the former is present at lower hydroxide ion concentrations[21-25].

II. MATERIALS AND METHODS

All the materials employed in this investigation were of analytical grade. The stock solution of synthesized NBSAwas prepared by dissolving its sample in 100% acetic acid (BDH). The solutions used were standardized iodometrically. De-mineralized distilled water was used for preparing the solution of hypo, butane-2,3-diol, osmium tetra oxide and other reagents.

The oxidation kinetic runs were performed under pseudo first-order condition. The experiments were carried out in a black coated stopper glass vessel to avoid any photochemical effect. A thermo-stated water bath was used to maintain the desired temperature within ± 0.1K. Requisite volumes of all reagents, except NBSA, were introduced into a reaction vessel and equilibrated at 303 K. A measured volume of NBSA, equilibrated separately at the same temperature, was rapidly poured into the reaction vessel. The progress of the reactions was monitored by periodically examining aliquots of the reaction mixture for unconsumed NBSAiodometricallyusing starch as the indicator. The stoichiometric results indicated 1 mole of diol consumes 1 mole NBSA as represented by the following empirical equation:

$$\text{R-CH(OH)CH(OH)R}_1 + \text{C}_6\text{H}_4\text{COSO}_2\text{NBr} \xrightarrow{\text{Os(VIII)}} \text{RCHO} + \text{R}_1\text{CHO} + \text{HBr} + \text{C}_6\text{H}_4\text{COSO}_2\text{NH}$$

Where R &R_1= CH_3

The end product from the oxidation of butane-2,3-diol was acetaldehyde and its presence confirm by existing conventional methods. These products were identified by the views of modes of reaction mechanism that formation of electron deficient species with double bond at transition state, rate of oxidation accelerates by any electron donating group[26-34].

III. RESULTS AND DISCUSSION

Oxidation of butane-2,3-diol by NBSA in presence of OsO_4 under the experimental condition had the following kinetic feature.

Order with respect to [oxidant] and [substrate]: When the butane-2,3-diol are in large excess, the plots of log (a-x) vs time **(Figure 1)** are found to be linear, indicating first-order dependence on NBSA. The pseudo first-order rate constants in NBSA calculated at different initial concentrations of the reactants are found to be independent of the substrate concentration. With an increase in vicinal diol concentration, the rate constants k_1 do not significantly alter in alkaline medium. Thus, it became clear that in diols, reaction follows zero order kinetics.[35,36]

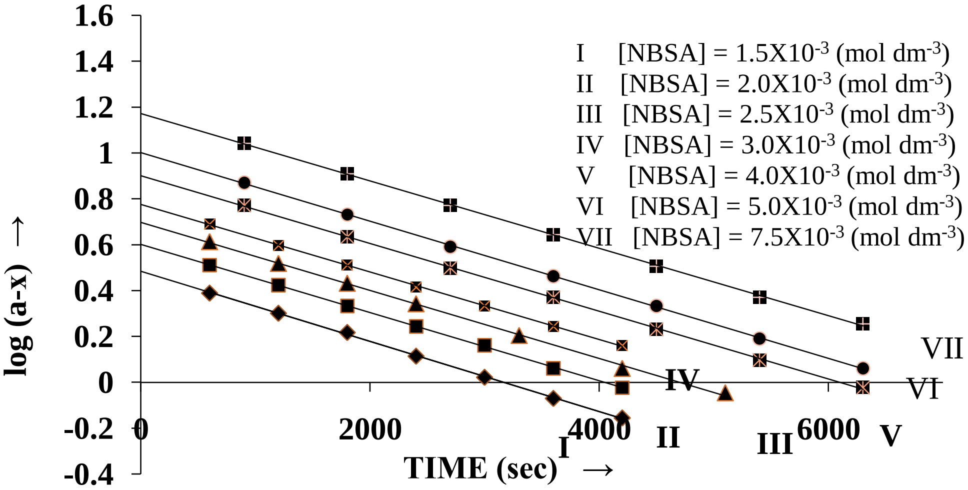


Fig. 1: The plot of log (a-x) vs time. Conditions are given in table 1.

Effect of variation of $[OsO_4]$: The concentration of **OsO_4**was varied while the concentration of *butane-2,3-diol* and, [NBSA] kept constant. Reaction is **OsO_4**catalysed with in a limit. The plot of k_1 vs. 10^2[**OsO_4**] is obtained straight line without intercept on gradual increment of concentration,and at higher concentration rate become constant, indicate complex formation (**Fig. 2 , Table 1**).

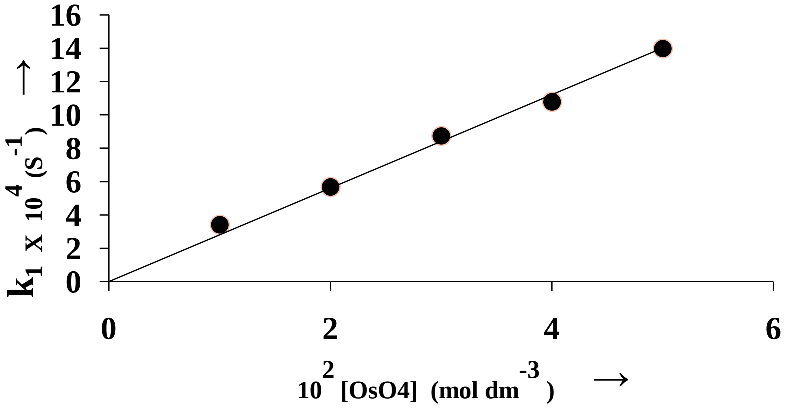


Figure 2: Dependence of the reaction rate on the concentration of OsO_4. Conditions are given in Table 1.

Table 1: Effect of variation of reactants on pseudo order rate constant k_1 at 303K

10^2[Substrate] (mol dm^{-3})	10^3[NBSA] (mol dm^{-3})	[NaOH] (mol dm^{-3})	[OsO_4] (mol dm^{-3})	[$Hg(OAc)_2$] (mol dm^{-3})	$k_1 x 10^4$ (s^{-1})
1.25	2.50	4.00	1.00	2.00	3.418
1.66	2.50	4.00	1.00	2.00	3.417
2.50	2.50	4.00	1.00	2.00	3.419
3.33	2.50	4.00	1.00	2.00	3.416
5.00	2.50	4.00	1.00	2.00	3.421
6.66	2.50	4.00	1.00	2.00	3.419
2.50	1.50	4.00	1.00	2.00	3.433
2.50	2.00	4.00	1.00	2.00	3.437
2.50	2.50	4.00	1.00	2.00	3.419
2.50	3.00	4.00	1.00	2.00	3.426
2.50	4.00	4.00	1.00	2.00	3.422
2.50	5.00	4.00	1.00	2.00	3.429
2.50	7.50	4.00	1.00	2.00	3.424
2.50	2.50	4.00	1.00	2.00	3.419
2.50	2.50	5.00	1.00	2.00	4.185
2.50	2.50	8.00	1.00	2.00	6.254
2.50	2.50	10.00	1.00	2.00	7.651
2.50	2.50	20.00	1.00	2.00	15.653
2.50	2.50	4.00	1.00	2.00	3.419
2.50	2.50	4.00	2.00	2.00	5.678
2.50	2.50	4.00	3.00	2.00	8.748
2.50	2.50	4.00	4.00	2.00	10.784
2.50	2.50	4.00	5.00	2.00	13.989
2.50	2.50	4.00	1.00	2.00	3.419
2.50	2.50	4.00	1.00	4.00	6.414
2.50	2.50	4.00	1.00	5.00	7.416
2.50	2.50	4.00	1.00	10.00	14.701

Effect of variation of [solvent]: The catalyzed kinetics was observed by the addition of sodium hydroxide. On varying sodium hydroxide concentration there is an increase in reaction rate (**Table 1**). rate of oxidation of diols under probe retard with increase the water content of the medium. The plot of log k_1 vs. [OH^-] was obtained linear.

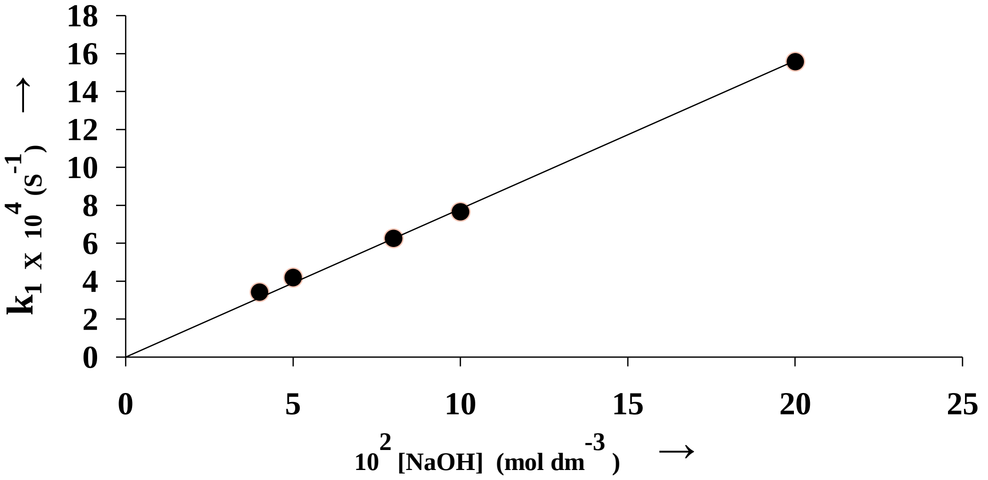


Figure 3: Dependence of k_1 on [OH^-]. Conditions are given in Table 1.

Effect ofionic strength and saccharin: The reaction rate was not influenced by the addition of chemically neutral salt. Hence the ionic behaviour of slow step in the reaction mechanism is ruled out. Saccharin was identified as the reduction product of the oxidant. Hence the effect of addition of saccharin to the reaction mixture plays a vital role to deciding reaction mechanism. That was studied at different concentrations of saccharin. It was found that rate of oxidation is unaffected with increase in the concentration of saccharin for diol-NBSA system in presence of Os(VIII).

Effect ofionic strength and Mercuric Acetate: Mercuric acetate has been utilised as a Br^- ions scavenger in the current study. The oxidation of the vicinal diols by NBSA produces bromide ions that combine with hypobrominus ions to produce bromine, setting off a parallel oxidation reaction. As a result, $[Hg\,Br_4]^{2-}$ complex, which is formed by mercuric acetate, has been employed to trap Br^- ions.

Effect of Product and Free Radical Inhibitor: Variation of saccharin, one of the products of oxidation, had negligible effect on the rate of reaction. The oxidation reactions of butane-2,3-diol with NBSAcatalyzed by OsO_4 at different initial concentrations of acrylonitrile have been investigated. The reaction neither induces polymerization nor retards the reaction rate which may be attributed to the inertness shown by free radicals.

Effect of temperature: The effect of temperature on the reaction of butane-2,3-diol with NBSA in presence of OsO_4 was also studied. The value of energy of activation,ΔS& ΔG were computed. These values are summarized in **Table 2** along with the other parameters.

Table 2: Thermodynamic parameters of Butane-2,3-diol-NBSA system

Substrate	Ea (kJ mol^{-1})	A (s^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	$-\Delta S^*$ (JK^{-1} mol^{-1})
Butane-2,3-diol	61.01	1.08 $x10^6$	58.91	83.71	89.56

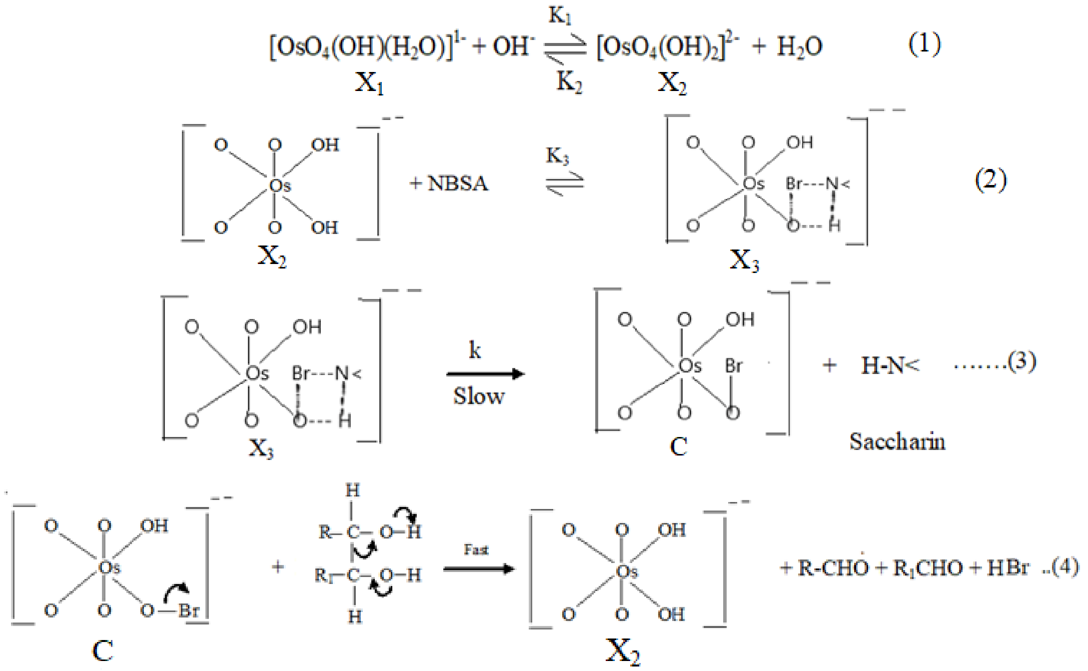
Reactive Species and Mechanism: It is already known that in alkaline medium, NBSA hydrolyses according to the following equilibria.[37]

$$\underset{(NBSA)}{>NBr} + H_2O \rightleftharpoons \underset{(NSH)}{>NH} + HOBr \;......(I)$$

$$>NH + OH \rightleftharpoons >N + H_2O \;.....(II)$$

Thus either NBSA, HOBr or $>N^-$ may be involved in the oxidation process. In view of zero effect of $[OH^-]$ on the rate, the species $>N^-$ is not likely to occur. Zero effect of saccharin on the rate also neglects the role of HOBr as oxidizing species. So we have only choice left to assume molecular NBSA is a prime oxidizing species.[38] Based on the above experimental facts, the following mechanism for the OsO_4catalyzed oxidative degradation of Butane-2,3-diol byNBSA is proposed.

Based upon the experimental observations, the most probable mechanism is as following.



Where R &R_1= CH_3

On the basis of the aforementioned steps involved in the proposed mechanism and at steady state approximation condition, the final rate law is derived as;

$$\text{Rate} = \frac{k\,k_2\,[NBSA]\,K_1\,[OH^-][OsO_4]_T}{(1 + K_1\,[OH^-] + k_2\,[NBSA]\,K_1\,[OH^-]}$$

This proposed rate law explained all experimental facts.

IV. CONCLUSION

Butane-2,3-diol is a vicinal diol. At first oxidant formed a complex with OsO_4 which is rearranged by intramolecular rearrangement and yields saccharin as by-product in a slow rate determining step. After it, rearranged complex is reacted with vicinal diol and gives acetaldehyde as product. The reaction obeys Arrhenius relation-ship. The proposed mechanism is in good accordance with experimental findings.

REFERENCES

[1]. Priya V., Subalakshmi M., International Journal of Innovative Science, Engineering & Technology. 6, 12, ***2019***.
[2]. Ramasamy V.andNambi.K. AsianJ.Chem.,18(4):2605, **2006**.
[3]. Pushplatha L. International Letters of Chemistry, Physics and Astronomy 52, 111-119, **2015**.
[4]. Mathiyalagan N., Sridharan R., Vani P , J. Indian Chem. Soc 82(9), 795-798, **2005**.
[5]. Mathiyalagan N., Shenbagan K., Kavita M., Asian Journal of Chemistry 22(1), 265-270, **2010**.
[6]. D.,Mathur, , P.K ,Sharma,., K.K. Banerji, Proc. Ind. Acad. Sci., **1995**, 107 (2), 133.
[7]. G.,Goswami, , S.Kothari, , K.K. Banerji, Proc. Ind. Acad. Sci., **2001**, 113 (1), 43.
[8]. J.Gosain, ,P.K Sharma,. Proc. Ind. Acad. Sci., **2003**, 115 (2), 135.
[9]. S.Saraswat, ,V.Sharma, , K.K. Banerji, Proc. Ind. Acad. Sci., **2003**, 115 (41), 75.
[10]. M.Bhatt, ,P.K.Sharma, , K.K. Banerji, Indian J. Chem. Sec. B, **2002**, 41 (4), 826.
[11]. Singh B., Indianjournalofchemistry, 49A,756-759, **2010**.
[12]. Singh, S.K., Gupta, H.D., Baghel, S.S., Tiwari S.S., J. Chem. Bio. Phy. Sci. Sec.A, **2011**, 2, 1, 560-567.
[13]. Kaur R., Arora M., Gujral H.,Kaur G., Nayak S.N., Singh S.K., Int. J. Chem. Tech Research, **2010**, 2 (3),1480-1485.
[14]. Singh S.K., Kaur R., Arora M., Gujral H., Kaur G., Orbital Elect. J. Chem**., 2011**, 3 (2),80-88.
[15]. Mansoor S.S., Syed Shafi S., Arabian Journal of Chemistry **2016** 9, S602–S609
[16]. Dayo Felix Latona, Advanced Journal of Chemistry-Section A, **2019**, 2(3), 225-233
[17]. Pandey D., Kothari S., Indian Journal of Chemistry, **2011**, 50B, 918-925
[18]. Banerji, J., Sharma, P.K., Banerji, K.K., Indian J.Chem., **2008**, 47A, 1213
[19]. Banerji, J., Sharma, P.K., Banerji, B.K., Indian J.Chem., **2008**, 47A, 1218
[20]. Pohani, S., Pancharia, P., Purohit, P., Vyas, S., Sharma, P.K., Int. J. Chem. Sci., **2010**, 8 (3), 1365.
[21]. Sharma K R. Mehrotra N., polyhedron, 27,17,3425-3432, **2008**.
[22]. Gupta M , Srivastava A , Srivastava S, Verma A., Chem. Chem. Technol., **2019**, 13, 3, 326–333
[23]. Das A., Coord Chem., **2001**, 213, 307.
[24]. Srivastava S., Patel R., World J. Phar. Pharm. Sc., **2014**, 3, 365
[25]. Gupta M., Srivastava S., Bull. Catal. Soc. India, **2015**, 14, 1.
[26]. P. K. Sapathy, G. C. Das, P. Mohanty, *Indian J. Chem.,* **2008**, 47A**,** 1199.
[27]. D. S. Rajmane, K. V. Kapshikar, G. S. Gokavi, *Indian J. Chem.,* **2006**, 45 A**,** 1626.
[28]. P. K. SaPTAthy, G. C. Dash, S. Acharya, P. Mohanty, *J. Indian Chem. Soc*., **2006**, 83**,** 891.
[29]. K. Amani, F. Maleki, *J. Iran. Chem*. Soc., **2007**, 4**,** 238.
[30]. S. P. Maradur, G. S. Gokavi, *Bull. Catal.Soc. India.***2007**, 6**,** 42.
[31]. H. Firouzabadi, N. Iranpoor, K. Amani, *Green. Chem.*, **2001**, 3, 131.
[32]. H. Firouzabadi, N. Iranpoor, K. Amani, *Synthesis,* **2003**, 408.
[33]. J. Bharad, B. Madje, F. Chavan, M. Farooqui, M. Ubale, *Bull. Catal. Soc. India*., **2008**.7,168.
[34]. L. I. Kuznetsova, R. I. Maksimovskaya, M. A. Fedotov, *InzvestiyaAkademiiNauk SSSR*.**1985**, 3, 537.
[35]. Koteswara Rao K. V. S., Venkata Nadh R.,Rasayan J. Chem. Vol., 12, 4 ,1681 – 1687**2019**.
[36]. Devra V., Yadav M.B., Rasayan J. Chem. **2012**, Vol. 5, No.1,| 67-73.
[37]. Singh R.A., Singh K., Singh S.K., J. Chem. Pharm. Res., , 2(3):684-690**2010**
[38]. Kumar A., Ph. D. Thesis, , V.B.S. PurvanchalUniversity Jaunpur (U.P.)**2012.**