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"STUDY ON KINETICS AND MECHANISM OF OXIDATIVE DE-CARBOXYLATION LACTIC ACID BY SELENIUM DIOXIDE IN WATER ACETIC ACID MEDIUM"

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Abstract

The kinetics of oxidative de-carboxylation of lactic acid by seleninium dioxide (SeO_2) has been investigated in water - HOAc medium. The reaction is of pseudo first-order in [SeO_2], first order in [LA] and first order in [H^+] ion. The velocity of the reaction increases with increase the Di electric constant of medium and solvent polarity. Effect of temperature has been studied and thermodynamic parameters are calculated and a suitable mechanism has been suggested.

Key words: Lactic acid; seleninium dioxide (SeO_2); pseudo first order; oxidative de-carboxylation; thermodynamic parameters

INTRODUCTION

Kinetics aims fundamentally at the details of the process in which a system converts from one state to another and the time required for the transformation. Hence, chemical kinetics provides information about the rate of reaction on possible pathways, by which the reactants are transformed into products. Thus, the fundamental of objective of the study of the kinetics of chemical The kinetics of oxidation reactions and the investigation of the reaction mechanisms from the kinetic data have been always the most interesting subjects in chemistry. In any kinetic investigation, one may be interested to arrive at (i) the relationship between the rate and the various factors like concentrations of the reactants, temperature, reaction medium etc., and, (ii) interpretation of the empirical rate laws in the light of the mechanism proposed [1].

In present paper we have explored the oxidative de-carboxylation of lactic acid by selenium dioxide. The potential of selenium dioxide as an oxidizing agent for organic compounds was first realized in the early 1930's by Riley [2]. Since this initial discovery, selenium dioxide has found wide application as a selective reagent in organic synthesis [3]. Literature survey revealed that selenium dioxide has been used as oxidant to oxidized ketones[4-14], alcohols[15-25], aldehyde[26], paraffin's[27-28], desoxybenzoin**[29-30]**, Esters[31-32], substituted mandelic acids[33-34], olefins**[35-41]**, amines[42-48] etc. The recent literature surveys also revealed that lactic acid have been oxidized by various oxidants viz. Pyridinium chlorochromate**[49]** (PCC), tripropylammonium fluorochromate (TriPAFC)**[50]** Vanadium (V)**[51]** and Ce (IV)**[52]** etc. However, no work seen on above topic/entitle, all these facts are inspired to me to explore mechanistic path of this problem first time.

EXPERIMENTAL

Materials

Selenium dioxide (Loba) solution was prepared by dissolving a weighed quantity of pure selenium dioxide in distilled water. Solution was standardized iodometrically. The iodine liberated was titrated against standard sodium thiosulphate solution using starch as an indicator. The stock solution of lactic acid (sigma 98%) was used to solution, prepared by dissolving a calculated quantity of the lactic acid in glacial acetic acid. Other Reagent was used analytical grade and doubly distilled water was used throughout the experiments.

Kinetic measurements

The reactions were carried out under pseudo first-order condition by taking a known excess of [Lactic acid] over [SeO_2] at 313 K. The glass stopper reaction flask made of Pyrex glass containing lactic acid, acetic acid and in other flask; solution of selenium dioxide with other reagents was kept together in a thermostat maintained at a desired temperature with an accuracy ±0.1. When the two flasks attained the temperature of thermostat, a required volume of selenium dioxide was pipette and transferred to reaction flask. At the instant half of selenium dioxide solution was added to the reaction flask, zero time was noted. Immediately 2 ml. aliquot was withdrawn into a flask containing 10ml. ice cold water and 10 ml. of 0.01 sodium thiosulphate solution along with 5ml. of 4N H_2SO_4. About 2ml of starch solution was added to it and then un-reacted sodium thiosulphate left was titrated against standard 0.01N iodine solution till a light blue color is developed. Aliquots were withdrawn at known intervals of time and concentration of selenium dioxide left un-reacted was estimated iodometrically.

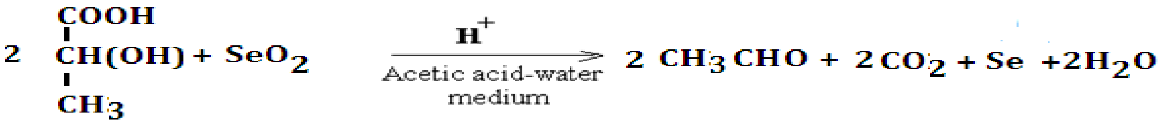
These readings are the values of (a-x) at time "t". The experimental data were fed into the integrated form of equation for first-order reactions. The values of pseudo first-order rate constant obtained from the rate equation -

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

The rate constant k was found fairly constant within the experimental error suggested that each reaction obeys first-order kinetics.

In order to study the effect of varying concentration of sulphuric acid on the reaction rate, kinetic runs have been carried out at varying concentration of acid, but at fixed substrate and oxidant concentration, solvent composition and temperature.

Stoichiometry and end-product analysis: stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of selenium dioxide over lactic acid and sulphuric acid, for 24 hrs. at, 313K. The un-reacted oxidant (selenium dioxide) was determined by iodometrically. The stoichiometric determinations have been suggested that **2:1 mole** ratio for lactic acid, and oxidant (SeO_2).



$$2\ \underset{CH_3}{\overset{COOH}{CH(OH)}} + SeO_2 \xrightarrow[\text{Acetic acid-water medium}]{H^+} 2\ CH_3CHO + 2\ CO_2 + Se + 2H_2O$$

Acetaldehyde was formed as the end-product of oxidation of lactic acid, which were identified by the determination of melting points of 2,4-dinitrophenylhydrazone derivatives of oxidation products and existing conventional methods.

RESULTS AND DISCUSSIONS

The kinetics data have been collected for variant in concentration of oxidant (SeO_2) at fixed concentration of other reactants and temperature. The linear plots of log (a-x) vs. Time, suggested that the first order rate dependency with respect to oxidant. The pseudo first-order rate increases with increase in the concentration of lactic acid, the plot of k_1 versus [lactic acid] are obtained linear passing through origin (Fig.1). The double reciprocal plot between $1/k_1$ and 1/ [lactic acid] is obtained linear with passing through origin (Fig. 1). On the basis of above results it is concluded that the reaction follows first-order behavior with respect to the lactic acid. The plot of k_1 versus [lactic acid] are obtained linear passing through origin this evidence ruled out the formation of a complex during the reaction.

Table: 1

Summary: Dependence of rate of oxidation reaction on the initial concentration of Oxidant (SeO_2)

[SeO_2] = $2.50X10^{-3}$ (mol.dm.$^{-3}$)
[LA] = $1.25X10^{-2}$ (mol.dm.$^{-3}$)
[H^+] = $1.25X10^{-3}$ (mol.dm.$^{-3}$)
HOAc-H_2O = 30%(v/v),
Temperature = 313 K.

[SeO_2]10^3 (mol.dm.$^{-3}$)	Lactic acid
	$10^5 k_1 (s^{-1})$
1.00	9.11
1.25	9.09
2.00	9.18
2.50	9.32
4.00	9.33
5.00	9.28

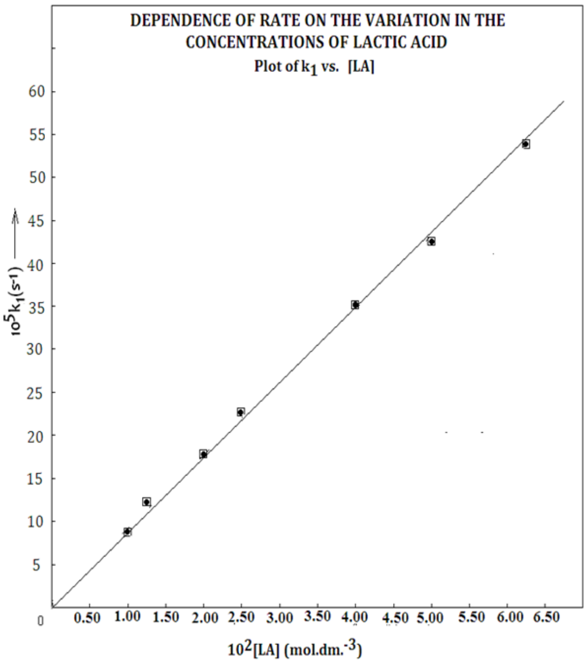


Fig.1

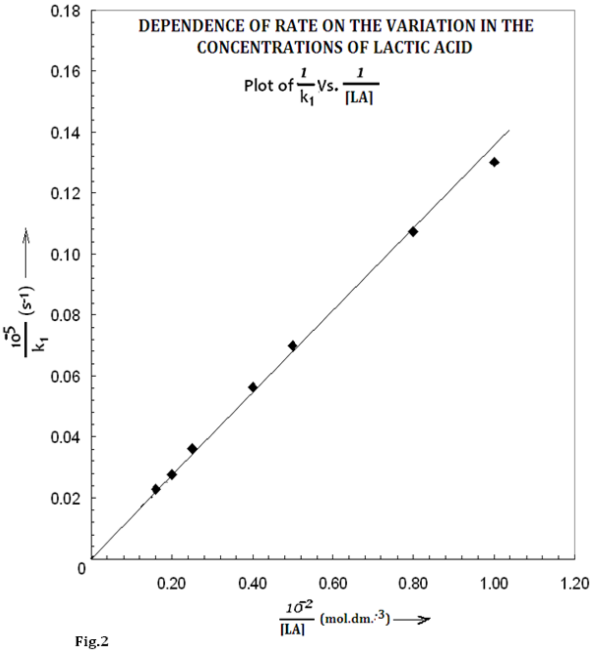


Fig.2

Reactions are fully acid catalyzed but velocity of the reaction slightly increases with increase the concentration of H_2SO_4 acid. The plot of k_1 vs. $[H_2SO_4]$ and plot of log k_1 vs. log $[H_2SO_4]$ is obtained linear with the positive unit slope, confirming that the reactions are fully acid catalyzed (Fig.3).

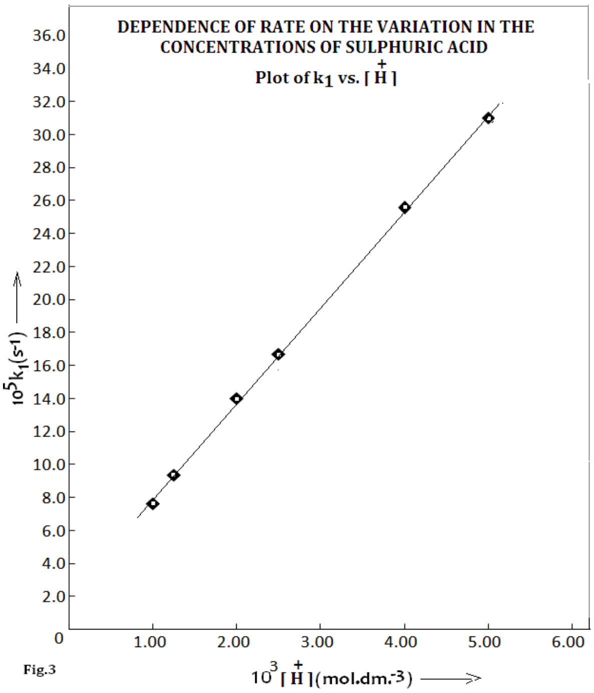


Fig.3

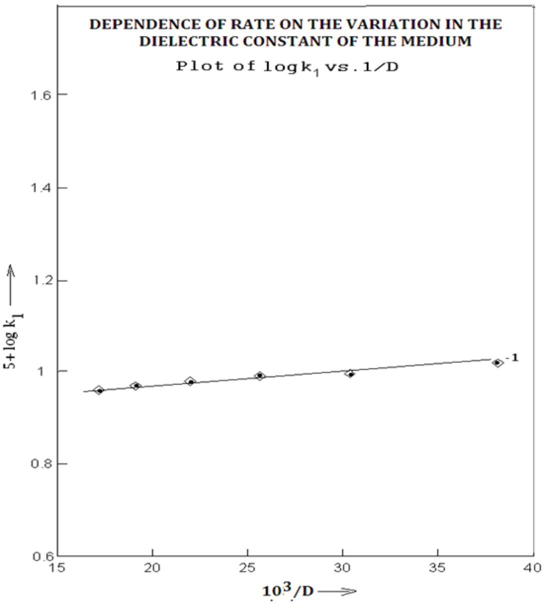


Fig. 4

Table: 2

THERMODYNAMIC PARAMETERS

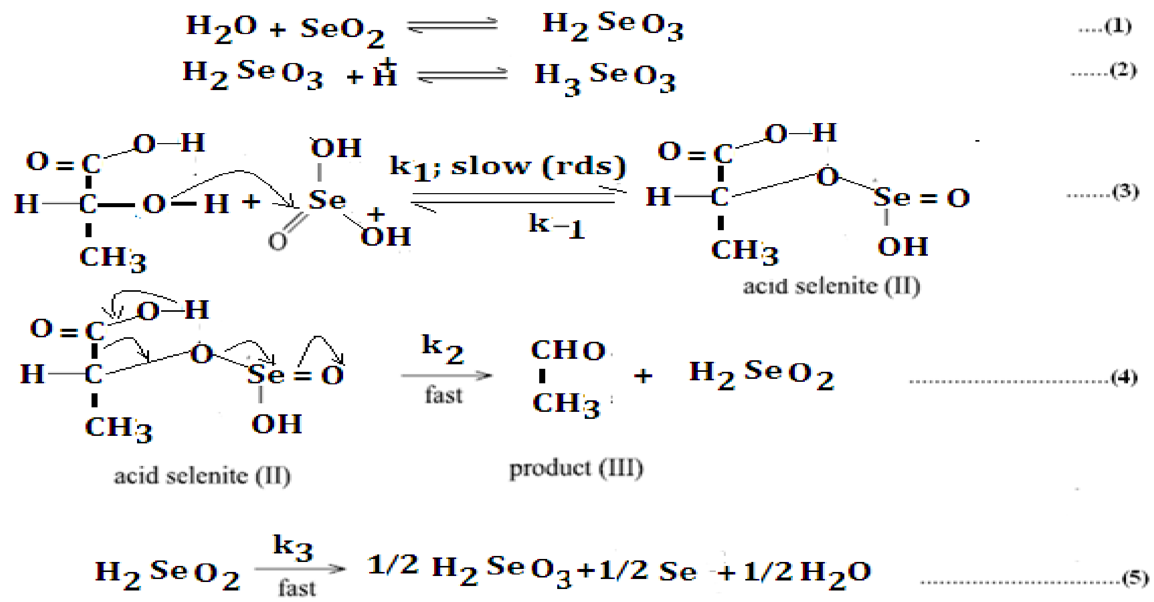
$[SeO_2]$ = 2.50×10^{-3} (mol.dm^{-3})
$[H^+]$ = 1.25×10^{-3} (mol.dm^{-3})
HOAc-H_2O = 30% (v/v)
Temperature = 313 K.

Substrate	**Ea** KJ mol^{-1}	**A** s^{-1}	**$\Delta H^{\#}$** KJ mol^{-1}	**$\Delta G^{\#}$** KJ mol^{-1}	**$\Delta S^{\#}$** JK mol^{-1}
LACTIC ACID	51.20 ±0. 56	4.14×10^5 ±0.89	52. 78 ±0.92	-89.39 ±0.27	-108.39 ±0.71

The first-order rate constant increases with increase composition of acetic acid i.e. rate accelerated with increase in dielectric constant of the medium. The plot of log k_1 versus $10^3/D$ were obtained linear with positive slope (Fig.4). The presence of free radicals in the system understudy was tested qualitatively by addition of 1-2 ml of acrylonitrile (monomer) in about 5-6 ml of the reaction mixture employing trapping method. The non-occurrence of turbidity and white precipitate clearly indicates the absence of free radicals in the system. Various activation parameters namely temperature coefficient, energy of activation (Ea), frequency factor (A), enthalpy of activation ($\Delta H^{\#}$), free energy of activation ($\Delta G^{\#}$), and entropy of activation ($\Delta S^{\#}$) for each reaction are calculated for lactic acid–SeO_2 system and according to the reaction mechanism, rate equation and order of reaction have been discussed. The iso-kinetic and Exner's have been explained.

MECHANISM

In view of the above experimental kinetic data, facts and finding, a suitable mechanism has been proposed for the oxidation of lactic acid – SeO_2 system as:



The finally derived rate of reaction is

$$k_{obs} = k_1 [LA][H_2SeO_3][\overset{+}{H}] \quad \text{.....................} (6)$$

The derived rate equation (5) explains all the experimental facts, which are in good agreement with our experimental kinetic data i.e. the observed first order kinetic in [lactic acid], [oxidant] and [H^+] ion etc.

REFERENCES

1. K.J. Laidler, Chemical Kinetics, McGraw-Hill, Mumbai, 1965.
2. H. L. Riley and N. A. Friend, *J. Chem. Soc., 2342 (1932).*
3. N.N. Mel'nikov and M.S. Rokitskaya, *Chem. Abs. ,33,3194(1939)*
4. F.R. Duke, *J.Amer.Chem.,Soc.,70,410(1948)*
5. G. B. Payne and C. W. Smith, *J. Org. Chem., 2_2, 1680 (1957).*
6. J.P. Schefer, *J.Amer.Chem. Soc., 84, 713,(1962).*
7. B. Sharpless and Gorden, *J.Amer.Chem.,Soc.,98,300,(1976)*
8. E.J. Corey and J.P. Schefer , *J.Amer.Chem.,Soc.,82,918,(1960)*
9. K.J. Singh and S.N. Anand, *J. Indian Chem., Soc.,56,363(1979)*
10. N.D.Valechha, A. Pradhan, *J. Indian Chem.,Soc.,61, 495(1984)*
11. Sanjay Tiwari, M.U.Khan, N.D. Valechha; *Oxid. Commn. 22, No. 3, 424-431(1999).*
12. J.P. Sewanee; *Ph.D. Thesis(1986), central library, A.P.S. University Rewa (M.P.), India*
13. N. Sonoda and S. Tsutsumi, *Bull, Chem. Soc. Japan, 32, 505(1959).*
14. N. Sonoda, T. Yamaguchi, and S. Tsutsumi*, J. Chem. Soc. Japan, Ind.Chem. Soc., 63, 737 (1960).*

15. N. N. Mel'nikov and M. S. Rokitskaya, *J. Gen. Chem., U. S. S. R., 7, 1532 (1937).*
16. S. Astin, L. de V. Moulds, and H. L. Riley, *J. Chem. Soc., 904(1935).*
17. A. Simon and R. Paetzold, Zeitschrift Fur Anorg. and Allgeimeine; *Chemie, 303,53 (1960).*
18. B. G. Gasanov, M. A. Salinov, and Z, D. Melikova, Azerb. Khitn. *Zh.,2, 31 (1963).*
19. S. Astin, A. C. Newman and H. L. Riley, *J. Chem. Soc., 391 (1933).*
20. Rohm and Haas, *German Pat. 634,501; C. A., 31, 420 (1937).*
21. Kaulter, *U. S. Pat. 2,171,727; C. A., 34, 115 (1940).*
22. S. Austin, A.C. Newman, H.L.Riley; *J. Chemical. soc. 391,(1933)*
23. N. N. Mel'nikov and M. S. Rokitskaya,*Chem. Abs. 30,5180 (1936)*
24. A. Pandey; *Ph.D thesis, pp 93, central library A.P.S. University Rewa M.P. (India),1985* .
25. N. Rabjhon; *"Organic reactions' vol.5th, wiley newYork, Chapt. 8 (1959)*
26. M.U. Khan, N.D. Valechha, J.K. Verma, V.R. Singh; *Oxid. Commn.22, No.3, 424- 431(1999).*
27. J.P .Schaefer and Horvath, *Tetrahydron letters, 30, 2023(1964).*
28. N.D Valechha, A.Pradhan; *J. Indian chem. soc.Vol. LXI, oct. 1986.*
29. E.J Corey and J.P. Schaefer; *J. Amer. Chem. Soc. 82,918(1960)*
30. J.P. Schaefer; *J. Amer. Chem. Soc., 84,717(1962).*
31. K.K. Benerji, Borton and Cookson ; *Indian J. Chem.1980; 662, 01.*
32. N.D. Valechha; *Indian chem. soc. Vol.24A,773 (1985)*
33. Kr. Singh, O. P. Gupta. M. U. Khan, H. D. Gupta, S. K. Singh; *Oxidation Communications 33, No4, 891–897* (*2010*) .
34. S. Kr. Singh, O. P. Gupta. M. U. Khan, H. D. Gupta, S. K. Singh; *Oxidation Communications 34, No 1, 58–64 (2011).*
35. A. Guillemonat, *Ann., JA, 143 (1939).*
36. E. N. Trachtenberg, *"Selenium Dioxide Oxidations," unpublished (1967).*
37. M. Mousseron and R. Jacquier, *Bull. soc. chim. France, 467 (1952).* K. B. Wiberg and S. D. Nielsen, *J. Org. Chem., 29, 3353 (1964*).
38. E. Borgwardt and E. Schwenk, *J. Am. Chem. Soc., 56, 1185 (1934).*
39. G. Dupont, W. Zacharewicz, and R. Dulon, *Comp. Rend., 198, 1699(1934).* A. Guillemonat, *Comp. rend. 206, 1126 (1938).*
40. F. W. Bergstrom, *Chem. Revs., 35, 120, 186 (1944).*
41. D. Jerchel and J. Heider, *Ann., 613, 153 (1958).*
42. D. H. Olson, *Tetrahedron Letters, 19, 2053 (1966).*
43. Hinsberg, *Chem. Ber., 2_2, 862 (1889).*
44. Hinsberg, *Chem. Ber., 2_2, 862 (1889).*
45. Hinsberg, *Chem, Ber.,* ***23,****1393 (1890),*
46. Hinsberg, Chem. Ber., ***52,*** 21 (1919).

47. Sridhar Poloju, Kishore Cholkar, Gilles K. Kouassi, J. David Van Horn, K.S. Rangappa, Netkal M. Made Gowda ; Amer. J. Org. Chem. 2(3): 58-62(2012).
48. M. M. Girgiss . A. EL-SHATOURYAN, D Z. H. KHALILC. *Anl. J. Chem.* ***63,*** *3317 (1985).*
49. R. M. Clementin, and K. Takashima, *Quimica Nova 16(6)(1993)* .
50. Sapana Jain, B. L. Hiran and C.V.Bhatt. E-J. Chem., 6(1), 273-280(2009).
51. V. I. E. Bruyere, L. A. G. Rodenas, , P. I. Morando & M. A. Blesa; *J. Chem. Soc. Dalton Trans., (2001) 3593.*
52. R. M. Clementin, and K. Takashima; *Quimica Nova., 16 ,529(1993)*
53. R. N. Mrhrotra, *J. Chem. Soc. (B), 1563(1968).*

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