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9893076404

J. Chemtracks 21(1&2) 103-106, 2019

Abstracted / Indexed in
CAS
A division of the American Chemical Society
Chemical Abstract U.S.A.

ISSN 0973-239X
CODEN:JCOHF7
IMPACT FACTOR : 1.930

Physical and chemical study of mechanistic oxidation of some nitrogenous compounds by selenium dioxide

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Manuscript received online 21 November 2018, accepted on 27 July 2019

Abstract: Study on mechanistic oxidation of o-c hylaniline and m-ethylaniline nitrogenous compound by selenium dioxide was carried out in aqueous acetic acid medium at 308 K. These follows pseudo first-order kinetics each in nitrogenous compound and selenium dioxide. The reaction is acid catalysed. The study completely discarded the formation of complex and rules out the involvement of free radicals in mechanism. The study reveals that the reaction velocity retarded with increases in solvent composition. Thermodynamic parameters were computed. A suitable mechanism consistent with the kinetic results have been proposed.

(Key words : Resonance involvement, consistent, composition, deterioration)

Introduction

The present proposed study envisaged with the kinetic of reactions involving the redox system¹. The selenium dioxide can be successfully exploited as an input technology and first of all employed as an oxidant for kinetic aspect for the oxidation of phenyl methyl sulphoxide. Kinetic and mechanistic of oxidation of some nitrogenous compounds with selenium dioxide has been received much attention and attracted to chemists in several laboratories kinetic of some nitrogenous compound with variety of oxidants. However there seems to be no work carried out till date with SeO₂. Selenium dioxide (SeO₂) oxidation shows that it has been used as an oxidising agent to oxidise ketones,^{2,3} aldehydes,⁴ esters,^{5,6} acids,⁷ alifines,⁸⁻¹⁰ and alcohols,^{11,12} kinetically as well as in chemical synthesis of 3α-

hydroxy-5α-cholesterol-8(14), 16-diene-15-one. The oxidative nature of aromatic hydroxy acid has also been examined by selenium dioxide.¹³

Experimental Material and Methods

Kinetic investigation of some nitrogenous compounds by Selenium dioxide acetic acid water medium in resonance of sulphuric acid, different chemicals were used in the form of solutions. Selenium dioxide solution was prepared by dissolving a weighed quantity of pure selenium dioxide in distilled water. Solution was standardized iodometrically as 2 ml. of selenium dioxide solution was taken with graduated pipette in a conical flask. 10 ml. of 2N H₂SO₄ and one gram of solid KI were added. The iodine liberated was titrated against standard sodium thiosulphate solution using starch as an indicator. Selenium dioxide was prepared in acetic acid (B.D.H.). The solution thus obtained was standardized by an iodometric method⁸. Aqueous solution of ortho-ethylaniline (A.R.B.D.H.) and meta-ethylaniline (E. Merck) in acetic acid were used. Other chemicals were either B.D.H. or Riedel grade. All the standard solutions were prepared in double distilled water. The several determinations indicated 1:1 stoichiometry.

Results and Discussion

The kinetics was studied over a wide range of concentrations. The actual nature of reaction can be shown by the plots of lg (a-x) against time, where the slope values give the


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reaction rate. The pseudo-first order reaction is quite obvious from the data in Table 1, where k_1 values remain fairly constant, confirming first order dependence in $[\text{SeO}_2]$.

Table -1
Effect of $[\text{SeO}_2]$ on the rate constant [ortho-ethylaniline] = 2.5×10^{-3} (mol dm⁻³)
[meta-ethylaniline] = 2.5×10^{-3} (mol dm⁻³); $[\text{H}^+] = 1.25 \times 10^{-3}$ (mol dm⁻³); HOAc-H₂O %, (v/v) = 30 (1, 2); Temperature K = 308 (1,2)

S.N.	$[\text{SeO}_2] \times 10^3$ mol dm ⁻³	$10^3 \times k_1$ mol dm ⁻³	
		ortho-ethylaniline	meta-ethylaniline
1	1.25	12.35	20.21
2	1.36	13.37	20.35
3	2.00	11.52	19.67
4	2.50	13.72	20.41
5	3.25	14.04	19.36

The complex feature of the reaction was obtained by the variation of [ethylaniline]. The reaction rate which followed nearly first order kinetics with respect to low [ethylaniline], tended to zero order at higher concentration (Fig. 1). Further more the double reciprocal plots of k_1 vs. [ethylaniline] are linear with positive intercept on the Y axis. Both results indicate that an intermediate complex is formed with oxidant species in a pre-equilibrium step.

The various activation parameters were computed from the rate study measurements carried out at four different temperatures (the results are given in Table 2). A plot of $\log_2 k$ vs. $1/T$ is linear showing thereby that Arrhenius equation is followed. The reaction is characterized by a low energy of activation giving a large negative value of entropy of activation.

Table - 2

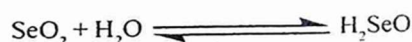
Activation parameters

Nitrogenous compounds	E_a kJ mol ⁻¹	A s ⁻¹	ΔS^\ddagger JK ⁻¹ mol ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔG^\ddagger kJ ⁻¹ mol ⁻¹
ortho-ethylaniline	52.31	4.13×10^5	-87.31	49.87	-102.34
meta-ethylaniline	48.06	3.36×10^5	-85.43	48.72	-104.84

Mechanism

Before attempting to propose the oxidation mechanism of these ortho-ethylaniline and meta-ethylaniline it is noteworthy at this stage to discuss the species of SeO_2 in acidic medium. A close examination of SeO_2 oxidation of nitrogenous compounds in aqueous acetic acid medium leads us to decide the reactive species of SeO in solution.

SeO_2 like other oxidants may exist in the presence of H^+ as free oxidant. The protonated species are HOAc or H_2O .



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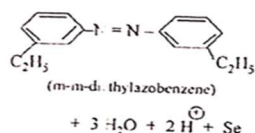
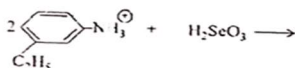
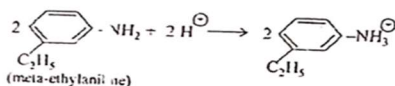
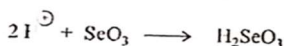
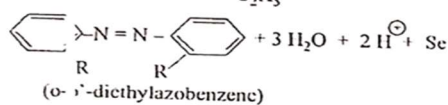
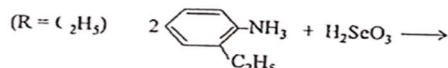
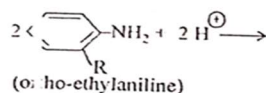
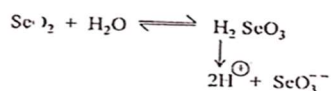
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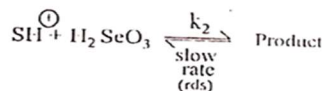
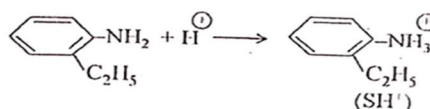
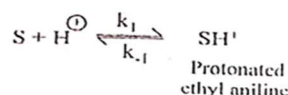
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The careful perusal of the effect of perchloric acid which causes retardation of oxidation rate and the first order inhibition of azobenzene on rate indicate that azobenzene is produced in pre-equilibrium step; both of these facts rule out the possibility of involvement of protonated species and SeO_2 as oxidant. The plot of $1/k_1$ vs. [azobenzene] for all ethylaniline is linear. Based on above experimental facts the following overall mechanism can be proposed.



S = Substrate (o,m,ethyl aniline)



$$\frac{dx}{dt} = \text{Rate of reaction} =$$

$$k_2 [SH^+] [H_2SeO_3]$$

(Protonated ethyl aniline)

$$\frac{-dx}{dt} = \frac{-d}{dt} [SH^+] = \text{zero}$$

$$= k_1 [S] [H^+] - k_{-1} [SH^+]$$

$$= k_1 [S] [H^+] - k_{-1} [SH^+]$$

which is confirmed by the validity of rate law by writing it as,

$$k = - \frac{d}{dt} [SeO_2]$$

The rate of oxidation of the SeO_2 was found to follow the order of reactivity ortho-ethyl-aniline and meta-ethyl-aniline.

Stoichiometric study and product analysis

Stoichiometric: Investigations revealed that one mol of SeO_2 was required to completely oxidise one mol of ethylaniline.

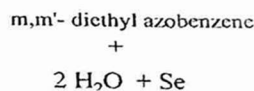
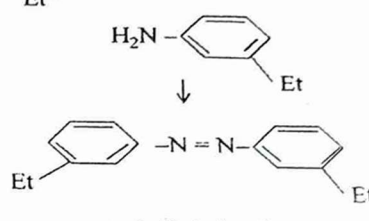
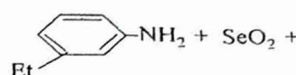
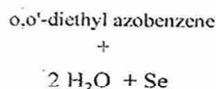
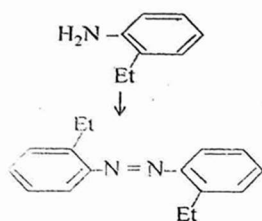
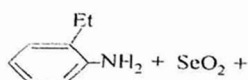
In the light of the above observations the following probable oxidation mechanism is proposed.


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Acknowledgements : We thanks to Head, Department of Chemistry, Govt. S.G.S. P.G. College Sidhi-486775 (Madhya Pradesh); Govt. Girls P.G. College, Rewa-486003(Madhya Pradesh) and Govt. Model Science College Rewa-486003 (Madhya Pradesh) for making available analysis for this manuscript.

Conclusion : Selenium dioxide is a colorless solid. It exists as one dimensional polymeric chain with

alternating selenium and oxygen atoms. It sublimes readily and hence the commercial samples of SeO₂ can be purified by sublimation, SeO₂ is an acidic oxide and dissolves in water to form selenous acid, H₂SeO₃. In conclusion, the potential of selenium dioxide as an oxidizing agent for organic compounds was studied. Since this initial discovery, selenium dioxide has found wide application as a selective reagent in organic synthesis.

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Abstracted / Indexed in : Chemical Abstract U.S.A.

ISSN - 1315/2K19 (ISSN:0973-239X), INDIA

Journal Chemtracks Vol. 21 (1&2), 103-106, January to December 2019


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