

Kinetic study on acid catalysed oxidation of nitrogenous compound by selenium dioxide in aqueous acetic acid medium

Rajesh Singh^{1*}, S.S. Saket², H.P. Dwivedi³, Sharmila Singh⁴

^{1,3}S.G.S. Govt. P.G. (Auton.) College Sidhi (M.P.), India

^{2,4}Govt. Girls P.G. College Satna (M.P.) India

*Corresponding Author: Rajesh Singh

ABSTRACT

In this paper, we reported model studies on mechanistic oxidation of some nitrogenous compounds with selenium dioxide. The dependence of rate on temperature was studied at four different temperature for para propyl aniline with selenium dioxide while keeping the concentration of other reactants constant. The stoichiometry of the reaction of oxidation of para propyl aniline with SeO_2 in presence of sulphuric acid, in aqueous-acetic acid medium was determined. Various activation parameters namely temperature coefficient, energy of activation, frequency factor, free energy, enthalpy of activation and entropy of activation for each reaction are calculated.

Keywords: Nitrogenous compounds selenium dioxide aqueous-acetic acid medium, para propyl aniline, activation.

INTRODUCTION

The potential of selenium dioxide as an oxidizing agent for organic compounds was first realized in the early 1930's by Rileyⁱ. Since this initial discovery, selenium dioxide has found wide application as a selective reagent in organic synthesisⁱⁱ. Selenium dioxide most commonly oxidizes carbon-hydrogen bonds attached to various activating groups such as olefins, aldehydes, ketones, acetylenes, esters, amides, carboxylic acids, anhydrides, and aromatic nuclei. Aldehydes, ketones and olefins are oxidized in good yields under relatively mild conditions. Alcohols, amines, phenols, and mercaptans are oxidized in poor yields under vigorous conditions. Alkanes, ethers, and alkyl halides are usually not attacked by selenium dioxide, and when they are, only under severe reaction conditions. 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 SeO_2 can be purified by sublimation, SeO_2 is an acidic oxide and dissolves in water to form selenous acid, H_2SeO_3 .

In the present work, selenium dioxide has been employed as an oxidant. It has been, therefore, thought worthy to give a brief account regarding the work done with this oxidant. Rileyⁱⁱⁱ introduced selenium dioxide as an oxidant to oxidize some ketone. They obtained glyoxals as the product of the oxidation of these compounds. Mel'nikov and Rokitskaya^{iv} have studied the kinetics of oxidation of some ketones. They have observed that the oxidation by SeO_2 is a bi-molecular reaction and the rate is measured on the basis of degree of enolization of the carbonyl group of these compounds. Duke^v studied the kinetics of oxidation of acetone by selenious acid in each of the experiment, the reactants concentrations were kept such that only the concentration of selenious acid changed. While that of other reactants remained unchanged. The plots of $\log [\text{H}_2\text{SeO}_3]$ vs. Time were found to be straight lines, the slope being first order in oxidant. The selenium dioxide-catalyzed hydrogen peroxide oxidation of ketones was discovered by Payne and Smith^{vi} in 1957. The reaction involves a migration of an alkyl substituent,

EXPERIMENTAL

MATERIALS AND METHODS

In the kinetic investigation of para propyl aniline by selenium dioxide acetic acid-water medium in presence of sulphuric acid, different chemicals were used in the form of solutions. The procedure employed for the preparation of these solutions and for the kinetic study is mentioned in the following sections: —

PREPARATION OF SELENIUM DIOXIDE SOLUTION AND STANDARDIZATION –

Selenium dioxide (Loba) 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 a 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.

PREPARATION OF SUBSTRATES SOLUTION – The stock solutions of substrates were prepared by dissolving a calculated quantity of the substrate in glacial acetic acid.

IODINE SOLUTION –

3.32 gram of KI weighed and transferred to a 500 ml. volumetric flask. About 10 ml. of water was added to it. Now about 5 to 5.2 grams of iodine were weighed and transferred to the same volumetric flask. When iodine was completely dissolved, the solution was diluted with distilled water and makeup to the mark. The iodine solution thus prepared was standardized as-% ml of standard sodium thiosulphate solution was taken with graduated pipette in conical flask. To this 1 ml. of 4N HCl and about 2 ml. of 1% starch solution were added. This was titrated with iodine solution till light blue color is developed.

SOLUTION OF SULPHURIC ACID –

Stock solution of H₂SO₄ (Analar E. Merck) of desired strength was prepared by diluting the calculated volume (from specific gravity) of acid with distilled water and finally its concentration was determined by titrating it against standard NaOH solution using phenolphthalein as an indicator.

KINETIC MEASUREMENTS –

Kinetics of oxidation of para propyl aniline under study by selenium dioxide in aqueous acetic acid as solvent has been followed iodometrically as follows –

The glass stoppered reaction flask made of Pyrex glass containing substrate, acetic acid and other reagents if any, was kept together with a stock solution of selenium dioxide 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 containing 10 ml. ice cold water and 1 ml. of 0.01 sodium thiosulphate solution along with 5 ml. of 4N HCl, About 2 ml. of starch solution was added to it and then un-reacted sodium thiosulphate left was titrated against standard 0.01 N 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 –

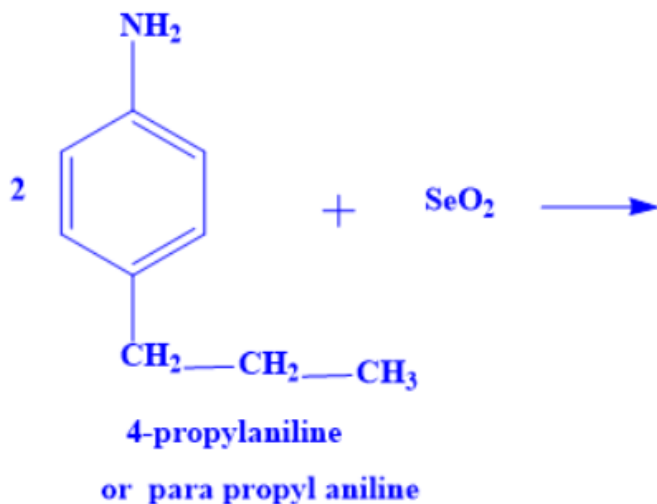
$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

Where 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, at fixed substrate and oxidant concentration, solvent composition and temperature.

RESULTS AND DISCUSSION

ISOLATION

The stoichiometry of the reaction of oxidation of para propyl aniline with SeO₂ in presence of sulphuric acid, in aqueous-acetic acid medium was determined in duplicate at their experimental temperature by following procedure⁷. In stoichiometric determination, the experiments were planned and designed in which the oxidant concentration was in excess (≈10 times) over the concentration of substrate. The binary composition of H₂O and CH₃COOH were taken similar to their respective runs. The calculation volume of the reactants were mixed and maintained in a thermostat at the experimental condition of temperature, for sufficient time that is until there is no change in SeO₂ concentration. The SeO₂ un-reacted in each reaction mixture is, then estimated separately, periodically by titrating a definite volume of the reaction mixture iodometrically¹. Thus, the quantity of SeO₂ used up to oxidize a definite quantity of each substrate under study completely is calculated.

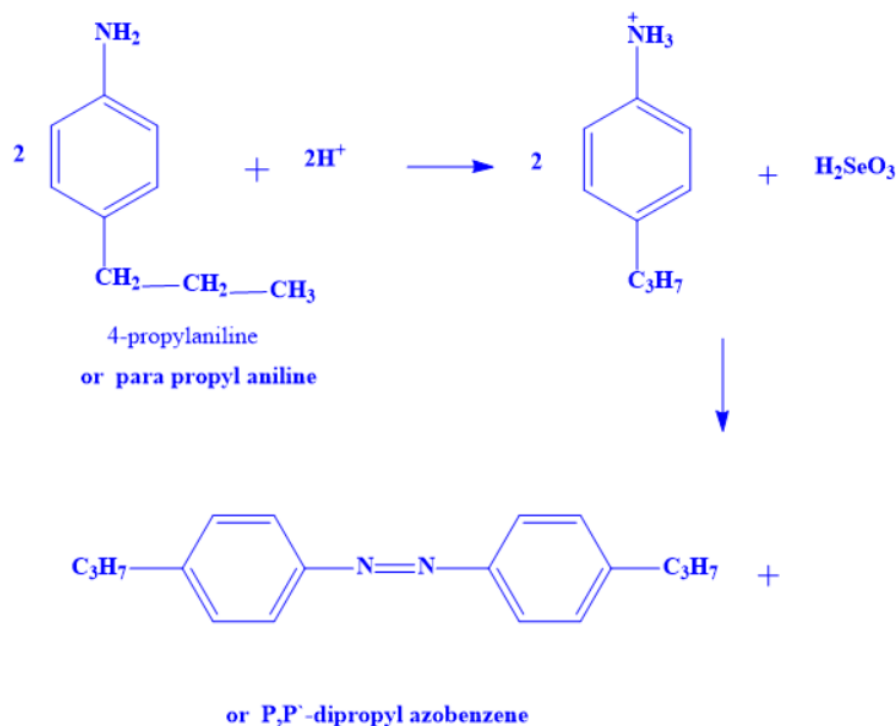
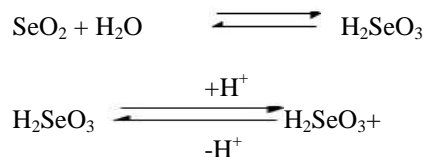


INTERPRETATION OF RESULTS

The problem entitled "Kinetic study on reactions of para propyl aniline with selenium dioxide in water acetic acid medium" deals with the mechanism of oxidation of para propyl aniline suggested that these reactions occur at measurable rate within a range of temperature ($35^{\circ} - 50^{\circ}\text{C}$). The detailed study of rate was switched on at measurable temperature i.e. 40°C for respectively. Since there is a little difference between the activity of these compounds and therefore this point will be discussed in subsequent pages. It is found that under the condition $[\text{SeO}_2] \ll [\text{substrate}]$, its reaction follows first order kinetics in $[\text{SeO}_2]$, all these reactions are homogeneous and characterized by induction period. The induction period can be accounted in terms of slow approach of steady-state. In these subsequent pages we will give a comparative account of all the reaction studied. Chemical kinetics play very important role and adds valuable and precious wealth of information's towards its literature as is obvious. The study of mechanism of organic compounds is a subject of major importance to all chemists for not only does it require consideration of the properties and reaction of both organic and inorganic compounds, but above all, it has vast implications in connective with the understanding of the nature of life.

MECHANISM OF THE OXIDATION

The kinetic data reveal that the reaction velocity follows first-order kinetics⁸. In the oxidation of sec. benzyl alcohols with SeO₂ it was found that the respective kinetic findings in their finality are similar for substrate. It can, therefore, be concluded that for the oxidation of sec. benzyl alcohols with SeO₂ the mechanism could be proposed as per following scheme:



RATE EXPRESSION

Taking into the consideration of various steps involved in the proposed mechanism, the rate equation could be derived as follows $-\frac{dc}{dt} = [\text{H}_3\text{SeO}_3^+] =$

$$k_1 [\text{Substrate}] [\text{H}_3\text{SeO}_3^+] - k_{-1} [\text{Acid selenite}] [\text{H}_3\text{O}^+]$$

The rate of formation of the main product cited by

$$-\frac{dc}{dt} = [\text{Product}] = k_2 [\text{Acid selenite}]$$

One the execution of steady – state approximation

$$-\frac{dc}{dt} = [\text{H}_3\text{SeO}_3^+] = + \frac{dc}{dt} = [\text{Product}]$$

The net rate of formation of acid selenite is given as

$$\begin{aligned}
 + \frac{dc}{dt} &= [\text{Acid selenite}] \\
 &= k_1 [\text{substrate } [\text{H}_3 \text{SeO}_3 \cdot ^+]] - k_{-1} [\text{Acid selenite}] [\text{H}_3\text{O}^+] \\
 &\quad - k_2 [\text{Acid selenite}]
 \end{aligned}$$

At stationary state

$$+ \frac{dc}{dt} = [\text{Acid selenite}] = 0$$

Therefore,

$$\begin{aligned}
 &= k_1 [\text{substrate } [\text{H}_3 \text{SeO}_3 \cdot ^+]] - k_{-1} [\text{Acid selenite}] [\text{H}_3\text{O}^+] \\
 &\quad - k_2 [\text{Acid selenite}] = 0
 \end{aligned}$$

Since

$$[\text{Acid selenite}] = \frac{k_1 [\text{substrate}] [\text{H}_3 \text{SeO}_3 \cdot ^+]}{\{k_{-1} [\text{H}_3\text{O}^+] + k_2\}}$$

Since the, $[\text{H}_3 \text{SeO}_3 \cdot ^+] \propto [\text{H}_2 \text{SeO}_3] [\text{H}^+]$

On inserting the value of acid selenite from equation

The reaction rate of take the form as

$$\begin{aligned}
 \frac{dc}{dt} \quad [\text{Product}] &= \frac{k_2 k_1 [\text{substrate}] [\text{H}_2 \text{SeO}_3] [\text{H}^+]}{\{k_{-1} [\text{H}_3\text{O}^+] + k_2\}}
 \end{aligned}$$

When, $k_2 \gg k_{-1}$

The rate of reaction becomes $k_{\text{abs.}} = k_1 [\text{Substrate}] [\text{H}_2\text{SeO}_3] [\text{H}^+]$

The derived rate equation explains all the experimental facts which are in good agreement with our experimental kinetic data i.e. the observed first order kinetic in [substrate], and $[\text{H}^+]$ ion etc

ISOKINETIC RELATIONSHIP

The largest activation energy for the slowest reaction indicates that the reaction is enthalpy controlled, within the reaction series. The variation in the rate may be caused by changes in either the enthalpy or entropy of activation or both.

In this study, enthalpy and entropy of active tion are correlated by $\Delta H^\ddagger = \Delta H^\ddagger_0 + \beta, \Delta S^\ddagger$, which is called the isokinetic relationship were β is the isokinetic temperature. When the experimental temperature $T < \beta$, the reaction rate is controlled mainly by the enthalpy change. In the present case, sec. benzyl alcohols oxidations are linearly related by plotting ΔH^\ddagger vs. ΔS^\ddagger (Figure -1, $r = 0.9995$). From the slope, the value of isokinetic temperature (β) is computed to be 386 K. The determined β value of 386 K being higher than the experimental temperature of 308 K, suggests that the reaction is enthalpy controlled.

The iso-kinetic plot of ΔH^\ddagger versus $-\Delta S^\ddagger$ and Exner's plot $\log k_1 (50^\circ\text{C})$ vs. $\log k_1 (35^\circ\text{C})$, are linear and ΔG^\ddagger values for these substrates – SeO_2 system.

The iso-kinetic plot of ΔH^\ddagger versus $-\Delta S^\ddagger$ and Exner's plot $\log k_1 (50^\circ\text{C})$ vs. $\log k_1 (35^\circ\text{C})$, are linear (Figure 2) and ΔG^\ddagger values for these substrates – SeO_2 system is in close agreement with one to another suggesting that similar operative mechanism is prevail in all the substrates. The existence of isokinetic relationship is very valuable to the mechanistic chemist as this can be used as a supportive evidence for the mechanism along with other data. The large negative value of ΔS^\ddagger indicates a more ordered associative transition state with less degree of freedom. The near constant ΔG^\ddagger values show an identical common mechanistic pathway in the oxidation of all the substrates under studied.

HAMMETT CORRELATION

Linear free energy relationships are attempts to develop quantitative relationships between structure and activity. The correlation of reaction rates with changes in structure is a major goal of chemistry. In organic chemistry, the change in a rate constant, k_1 which results from the substitution of a specific group for hydrogen, the so-called substituent effect, is of

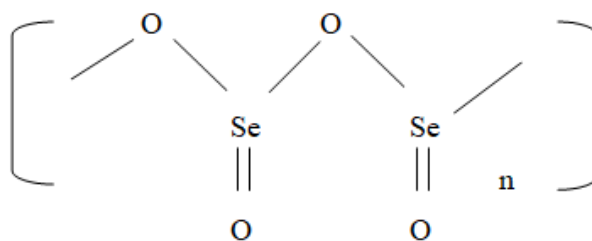
special interest. Professor L.P. Hammett, of Columbia University, systematized much of the research in this area by defining a quantity σ (the substituent constant) for any given substituent, as follows:

$$\sigma = \log k_1/k_0$$

Where K_0 is the rate constant for the oxidation of p-H substituent .

CONCLUSION

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. Selenium dioxide most commonly oxidizes carbon-hydrogen bonds attached to various activating groups such as olefins,



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.

REFERENCES

- [1]. H.L. Riley and N.A. Friend, J. Chem. Soc., 2342 (1932).
- [2]. N. Rabjohn, "Organic Reaction". Vol. V. John Wiley and Sons, Inc. New York, 1959, Chapter-8.
- [3]. 1 N. Rabjohn, "Organic Reactions". Vol. V. John Wiley and Sons, Inc. New York, 1959 Chapter-8
- [4]. N.N. Mel'nikov and M.S. Rokitskaya, Chem. Abs., 33,3194 (1939)
- [5]. R.R. Duke, J., Amer. Chem., Soc., 70,410 (1948).
- [6]. G.B. Payne and C.W. Smith, J. Org. Chem., 22, 1680 (1957).
- [7]. Santosh Kumar Singh, M.U. Khan, H.P. Dwivedi, D.B.S. Chauhan, H.D. Gupta: IJGHC; March 2013 – May 2013 Vol. 2, 189-295.
- [8]. H.D. Gupta, S.K. Singh, Manoj Kumar Solanki, O.P. Gupta and Santosh Kumar Singh: IJGHC; 2013, Vol. 2, No. 1 91-99.