

Nobel studies on some nitrogenous organic molecules by potential applications of selenium dioxide as an oxidizing agent

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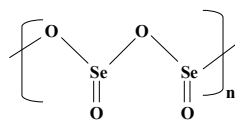
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Abstract: Selenium dioxide is a colorless solid. It exists as one dimensional polymeric chain with alternating selenium and oxygen atoms. In this paper, we reported model studies on mechanistic oxidation of some nitrogenous compounds with selenium dioxide. The dependence of rate on temperature was studied at four different temperature for secondary benzyl alcohols with selenium dioxide while keeping the concentration of other reactants constant. The stoichiometry of the reaction of oxidation of some secondary benzyl alcohols 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.)

Introduction

Selenium dioxide is a colorless solid. It exists as one dimensional polymeric chain with alternating selenium and oxygen atoms (Scheme 1). 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 .



Scheme 1.

The potential of selenium dioxide as an oxidizing agent for organic compounds was first realized in the early 1930's by Riley¹. Since this initial

discovery, selenium dioxide has found wide application as a selective reagent in organic synthesis². 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. Riley³ introduced selenium dioxide as an oxidant to oxidize some ketone. They obtained glyoxals as the product of the oxidation of these compounds. They pointed out that the active species of oxidant was selenious acid not the selenium dioxide. They observed that when a mixture of acetone with a little water was added to selenium dioxide in cold, the reddish color due to liberation of Se developed more rapidly than the case when dry acetone was used. Mel'nikov and Rokitskaya⁴ 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. Duke⁵ 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 $\log [H_2SeO_3]$ vs. Time were found to be straight lines, the slope being first order in oxidant.

2. Experimental

2.1 Materials and methods : In the kinetic investigation of some secondary benzyl alcohols 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: -

2.2 Preparation of Solutions and Their Standardization :

2.2.1 Preparation of selenium dioxide solution and its 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 H_2SO_4 and one gram of solid KI were added. The iodine liberated was titrated against standard sodium thiosulphate solution using starch as an indicator.

2.2.3 Preparation of Substrates solution : The stock solutions of substrates were prepared by dissolving a calculated quantity of the substrate in glacial acetic acid.

2.2.4 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 a graduated pipette in a conical flask. To this 1 ml. of 4 N HCl and about 2 ml. of

1% starch solution were added. This was titrated with iodine solution till light blue color is developed.

2.2.5 Solution of Sulphuric Acid : Stock solution of H_2SO_4 (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.

2.2.6 Sodium thiosulphate solution : Sodium thiosulphate solution was prepared and standardized by the method prescribed in the literature.

2.2.7 Starch solution : 1% starch solution was prepared as per procedure given in the literature; this starch solution was used as an indicator.

2.2.8 Salts Solutions : The salts solutions of desired concentration were prepared by dissolving required quantities of salts in distilled water in a volumetric flask and made up to the mark.

2.2.9 Kinetic Measurements : Kinetics of oxidation of some secondary alcohols 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

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

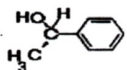
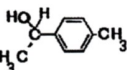
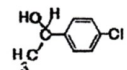
Where found fairly constant within the experimental error suggested that each reaction obeys first-order kinetics. In order to study the effect of varying concentration of sulphuric acid on the reaction rate, kinetic runs have been carried out at varying concentration of acid, at fixed substrate and oxidant concentration, solvent composition and temperature.

2. Results and Discussion

3.1 Isolation: The stoichiometry of the reaction of oxidation of some secondary benzyl alcohols

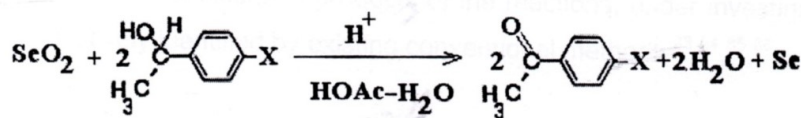
with SeO_2 in presence of sulphuric acid, in aqueous-acetic acid medium was determined in duplicate at their experimental temperature by following procedure⁷. In stoichiometric determination, the experiments were planned and designed in which the oxidant concentration was in excess (H^+ 10 times) over the concentration of substrate. The binary composition of H_2O and CH_3COOH 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 SeO_2 concentration. The SeO_2 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 SeO_2 used up to oxidize a definite quantity of each substrate under study completely is calculated. The results are recorded in Table 1.

Table 1. Summary: Stoichiometry of the oxidation of sec. Benzyl alcohol- SeO_2 system.

$[\text{H}^+] 10^3 (\text{mol dm}^{-3})$		: 1.25 (1 – 3);			
$\text{HOAc-H}_2\text{O} \% (\text{v/v})$		: 30 (1 – 3);			
Temperature, K		: 313 (1 – 3)			
Sr. No.	[substrate] 10^3 (mol.dm. ⁻³)	Initial [SeO_2] 10^2 (mol.dm. ⁻³)	Final [SeO_2] 10^3 (mol.dm. ⁻³)	Consumer [SeO_2] 10^2 (mol.dm. ⁻³)	Mole ratio [SeO_2] [substrate]
(1) 1-phenylethanol					
					
1.	2.50	2.50	19.80	2.46	2.08
2.	2.25	2.25	16.01	2.32	1.99
(2) 1-(4-methylphenyl)ethanol					
					
1.	4.00	4.00	31.89	8.11	2.02
2.	5.00	5.00	39.99	10.01	2.00
(3) 1-(4-chlorophenyl)ethanol					
					
1.	3.00	3.00	24.03	5.97	1.99
2.	3.00	3.00	23.93	6.07	2.02

From these stoichiometric data, it is found that for complete oxidation of one mole of each *sec.* benzyl alcohols, one mole of SeO_2 is required. The

stoichiometric equations empirically can therefore, be represented as:

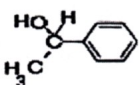
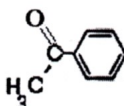
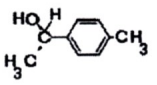
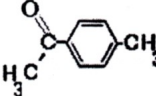
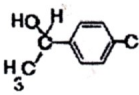
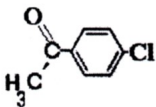


X = -H- CH_3 and -Cl are stand for 1-phenylethanol, 1-(4-methylphenyl) ethanol and 1-(4-Chlorophenyl) ethanol respectively. The oxidation

products of various *sec.* benzyl alcohols are presented in Table-2.

Table-2.

Oxidation products of *sec.* benzyl alcohols – SeO_2 system

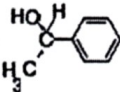
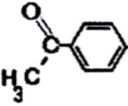
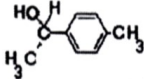
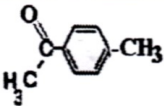
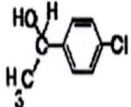
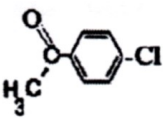
Substrate	Mole ration substrate SeO_2	Products
(1) 1-phenylethanol 	2:1	 + H_2O + Se
(2) 1-(4-methylphenyl)ethanol 	2:1	 + H_2O + Se
(3) 1-(4-chlorophenyl)ethanol 	2:1	 + H_2O + Se

3.2. Identification of oxidation main end-products –

A 0.25 M solution of 2, 4-dinitrophenylhydrazine, may be used for the preparation of derivatives of keto compounds. Dissolve 25 g of 2, 4-dinitrophenylthdrazine in 300 ml. of 85% perchloric acid in a 600 ml. beaker on a stream bath, dilute the solution with 200 ml. 95% ethanol, allow to stand and filter through a sintered glass funnel. It must be emphasized that this reagent is not suitable for the routine detection of carbonyl compounds since it also gives a

precipitate in cold with certain amine, esters, and other compounds; if, however, a dilute solution of the keto compound in ethyl alcohol is treated with a few drops of the reagent and mixture diluted with water and heated, the precipitate produced with keto compounds generally not dissolves. Collect the crystals of 2, 4-dinitrophenyl hydrazone of keto and re-crystallized again wash, dried it, then determine the melting points to compare with reported melting points as following Table-3.

Table-3.

Identification of oxidation products by the compared observed melting points and reported melting points			
Substrate	Main oxidation product	Melting points of 2, 4-dinitrophenylhydrazone derivatives of oxidation products	
		Observed melting point ($^{\circ}\text{C}$)	reported melting point ($^{\circ}\text{C}$)
(1) 1-phenylethanol 		146 (lit.)	146.2
(2) 1-(4-methylphenyl)ethanol 		260 (lit.)	259.9
(3) 1-(4-chlorophenyl)ethanol 		231 (lit.)	231.1

3.3 Test for selenium, reduction product of SeO_2

Free selenium – The red precipitated selenium formed by the reduction of selenium dioxide in each reaction was tested as a small quantity of red precipitated se was dissolved in the CS_2 . The surface of a piece of silver foil was roughened with fine emery paper. The metal foil was thoroughly cleaned. A drop of test solution was placed the foil and solvent (CS_2) was allowed to evaporate. A gray fleck (of silver selenide) appeared, indicating that the red precipitate obtained was of free selenium.

3.4 Interpretation of Results

The problem entitled “Kinetic study on reactions of some secondary benzyl alcohols with selenium dioxide in water acetic acid medium” deals with the mechanism of oxidation of some secondary benzyl alcohols suggested that these reactions occur at measurable rate within a range of temperature ($35^{\circ} - 50^{\circ}\text{C}$). The detailed study of

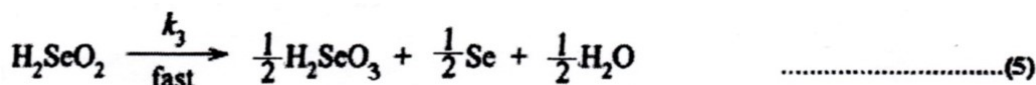
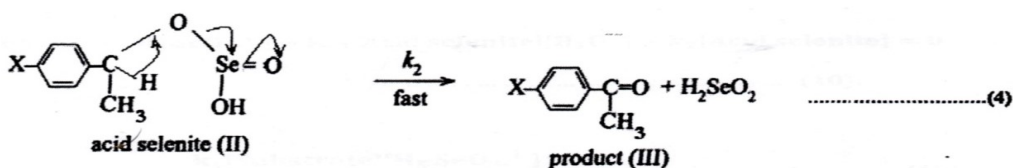
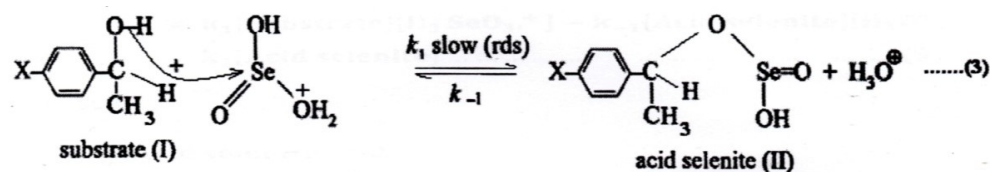
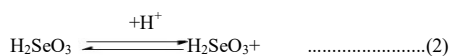
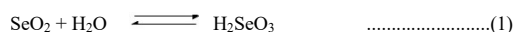
rate was switched on at measurable temperature i.e. 40°C for respectively. Since there is a little difference between the activity of these compounds and therefore this point will be discussed in subsequent pages. It is found that under the condition $[\text{SeO}_2] \ll [\text{substrate}]$, is reaction 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.

3.4 Mechanism of the Oxidation

The kinetic data reveal that the reaction velocity follows first-order kinetics⁸. In the oxidation of sec. benzyl alcohols with SeO_2 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 SeO_2 the mechanism could be proposed as per following scheme:



3.4.1 Rate Expression

Taking into the consideration of various steps involved in the proposed mechanism, the rate equation could be derived as follows :

$$-\frac{dc}{dt} = [\text{H}_3\text{SeO}_3^+] = k_1 [\text{Substrate}] [\text{H}_3\text{SeO}_3^+] - k_{-1} [\text{Acid selenite}] [\text{H}_3\text{O}^+] \quad \text{.....(6)}$$

The rate of formation of the main product cited by

$$-\frac{dc}{dt} = [\text{Product}] = k_2 [\text{Acid selenite}] \quad \text{.....(7)}$$

One the execution of steady – state approximation

$$-\frac{dc}{dt} = [\text{H}_3\text{SeO}_3^+] = +\frac{dc}{dt} = [\text{Product}] \quad \text{..... (8)}$$

The net rate of formation of acid selenite is given

$$\begin{aligned} \text{as } +\frac{dc}{dt} &= [\text{Acid selenite}] \\ &= k_1 [\text{substrate} [\text{H}_3\text{SeO}_3^+] - k_{-1} [\text{Acid selenite}] [\text{H}_3\text{O}^+]] \\ &\quad - k_2 [\text{Acid selenite}] \quad \text{.....(9)} \end{aligned}$$

At stationary state

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

Therefore,

$$= k_1 [\text{substrate} [\text{H}_3\text{SeO}_3^+] - k_{-1} [\text{Acid selenite}] [\text{H}_3\text{O}^+]] - k_2 [\text{Acid selenite}] = 0 \quad \text{.....(10)}$$

Since

$$[\text{Acid selenite}] = \frac{k_1 [\text{substrate}] [\text{H}_3\text{SeO}_3^+]}{\{k_{-1} [\text{H}_3\text{O}^+] + k_2\}} \quad \text{.....(11)}$$

$$\text{Since the, } [\text{H}_3\text{SeO}_3^+] \propto [\text{H}_2\text{SeO}_3] [\text{H}^+] \quad \text{.....(12)}$$

On inserting the value of acid selenite from equation (11) to (6)

The reaction rate of take the form as

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

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

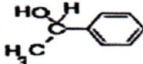
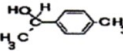
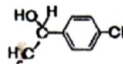
The rate of reaction becomes

$$k_{\text{abs.}} = k_1 [\text{Substrate}] [\text{H}_2\text{SeO}_3] [\text{H}^+] \quad \dots(13)$$

The derived rate equation (13) 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 and are shown in Table 4.

Table-4.

Thermodynamic Parameters.					
$[\text{SeO}_2] 10^3 (\text{mol. dm.}^{-3})$: 2.50 (1 – 3);		$[\text{H}^+] 10^3 (\text{mol. dm.}^{-3})$: 1.25 (1 – 3);		$\text{HOAc-H}_2\text{O} \% (\text{v/V})$: 30 (1 – 3);	
		Temperature K : 313 (1 – 3)			
Substrate	Ea kJ mol^{-1}	A S^{-1}	$\Delta H^\ddagger$ kJ mol^{-1}	$\Delta G^\ddagger$ kJ mol^{-1}	$\Delta S^\ddagger$ JK mol^{-1}
(1) 1-phenylethanol 	51.27 ± 0.56	4.12×10^5 ± 0.89	52.87 ± 0.92	-89.32 ± 0.27	-103.35 ± 0.48
(2) 1-(4-methylphenyl)ethanol 	48.03 ± 0.66	2.36×10^7 ± 0.89	49.83 ± 0.97	-87.68 ± 0.58	-99.45 ± 0.57
(3) 1-(4-chlorophenyl)ethanol 	53.34 ± 0.91	7.75×10^5 ± 0.59	56.03 ± 0.96	-89.73 ± 0.62	-104.85 ± 0.71

3.4.2 Isokinetic Relationship

The largest activation energy for the slowest reaction (Table-4) 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.

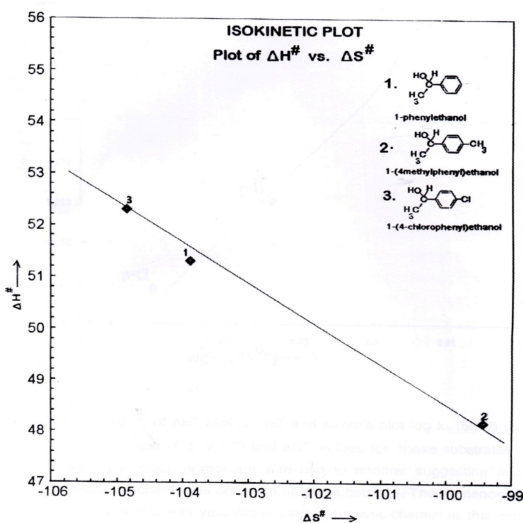


Figure-1. Benzyl alcohols oxidations are linearly related by plotting " $\Delta H^\ddagger$ vs. " $\Delta S^\ddagger$ "

In this study, enthalpy and entropy of activation are correlated by " $H^\ddagger = H_0^\ddagger + \beta$ ", " $S^\ddagger$ ", which is called the isokinetic relationship where 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 " $H^\ddagger$ vs. " $S^\ddagger$ " (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

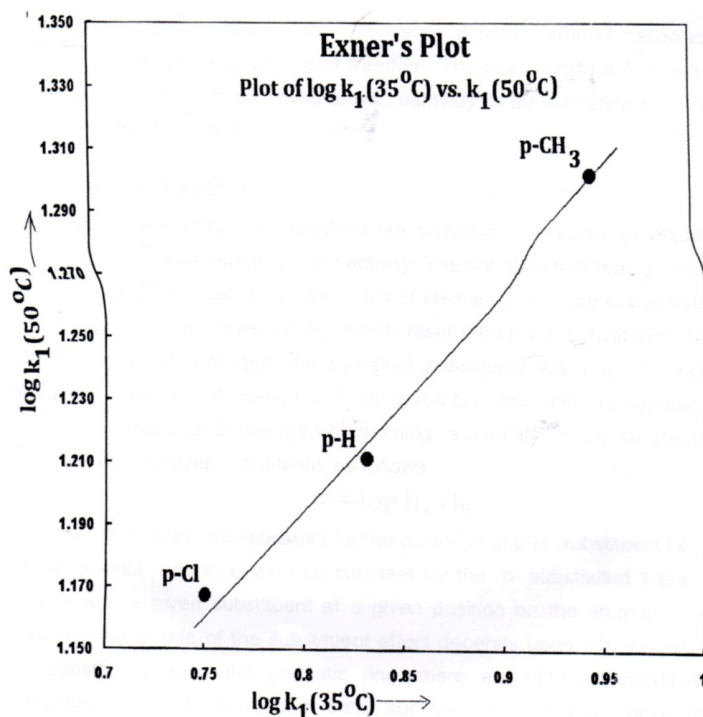


Figure 2. The iso-kinetic plot of " $H^\ddagger$ versus - " $S^\ddagger$ " and Exner's plot $\log k_1(50^\circ\text{C})$ vs. $\log k_1(35^\circ\text{C})$, are linear (Figure 2) and " $G^\ddagger$ " values for these substrates – SeO_2 system.

The iso-kinetic plot of " $H^\ddagger$ versus - " $S^\ddagger$ " and Exner's plot $\log k_1(50^\circ\text{C})$ vs. $\log k_1(35^\circ\text{C})$, are linear (Figure 2) and " $G^\ddagger$ " 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 " $S^\ddagger$ " indicates a more ordered associative transition state with less degree of freedom. The near

constant " $G^\ddagger$ " values show an identical common mechanistic pathway in the oxidation of all the substrates under studied.

3.4.3 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 i.e. 1-phenyl ethanol and k_1 is the rate constant for the p- substituted 1- phenyl

ethanol with a given substituent at a given position on the aromatic ring. Since the magnitude of the substituent effect depends upon the position of the substituent upon the aromatic ring. There are different substituent constants for *para*, *meta*, and *ortho* substituents. Typically, these are distinguished as σ_p , σ_m and σ_o . If the ratio $(k_1/k_0) > 1$, i.e., the substituent has increased the acidity of the substrates, σ is positive.

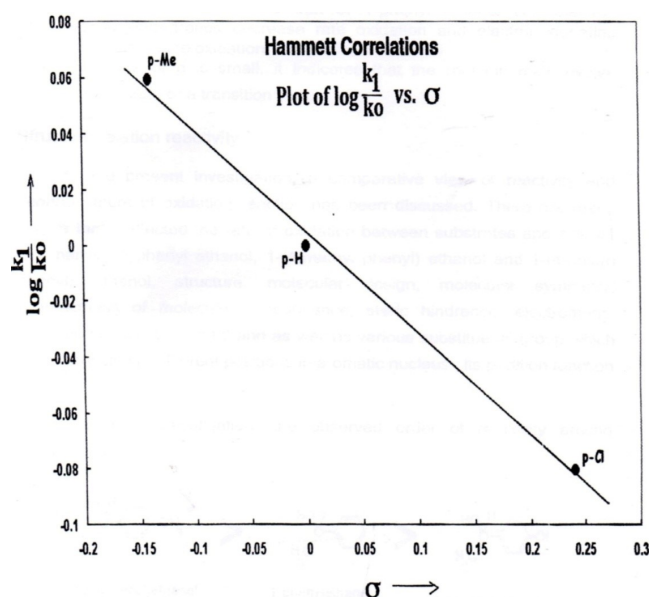


Figure 3. Hammett Correlation plot given substituent.

Such a substituent is considered to be an electron-withdrawing group (EWG), because electron density is decreased at the reaction site, and an EWG will favor this change by withdrawing electron density away from the reaction site. Group such as p-Cl, etc. which have relatively large dipole moments oriented with the positive end directed towards the reaction site are EWG's. On the other hand, electron donating groups i.e. EDG's (groups which tend to increase the electron density near the reaction site) disfavor the ionization to a negatively charged ion and have $k_1/k_0 < 1$. These groups have negative sigma values.

These include alkyl groups (at both the *meta* and *para* positions), such as *para* p-methyl groups. It should be noted that, by definition, Hammett substituent constants are relative to hydrogen as a basis of comparison. That is to say, $\sigma_H = 0.0$.

3.4.4 Inference from the Hammett Plot –

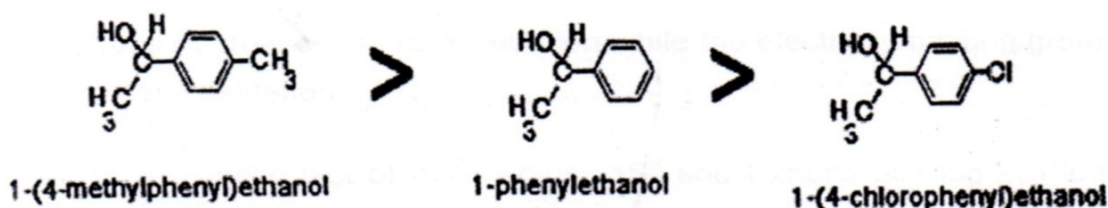
- I. A straight line plot obtained indicates that the free energy relation of the reaction is valid.
- II. The slope of the line is the ρ of the reaction.

- III. Value of ρ ($\rho = 0.72$) $\rho > 1$ indicates that the influence of the substituent is opposite to that of 1-phenyl ethanol i.e., electron withdrawing groups decrease rate oxidation and electron donating groups increase oxidation.
- IV. The value of ρ is small, it indicates that the reaction may involve intermediate or a transition state.

3.4.5 Structure Relation reactivity –

In the present investigation, a comparative view of reactivity and general nature

of oxidation reaction has been discussed. There are many factors those effected the rate of oxidation between substrates and oxidant i.e. namely 1-phenyl ethanol, 1-(4-methyl phenyl) ethanol and 1-(4-chlorophenyl) ethanol, structure, molecular design, molecular symmetry, compactness of molecules, resonance, steric hindrance, electromeric, mesomeric, inductive effect and as well as various substituent's group which are introducing at different positions in aromatic nucleus, its partition function etc. In the present investigation, the observed order of reactivity among substrates are:



The value of ρ (0.72) indicate that the influence of the substituent is opposite to that of 1-phenyl ethanol i.e., electron withdrawing groups decrease rate oxidation and electron donating groups increase oxidation. From the above observed order of reactivity, it is crystal cleared that the reactivity order is influenced through the nature of the various substituent group attached on the para position of aromatic ring. +I influenced group like $-\text{CH}_3$ at para position in aromatic ring and also attached through C_1 , both have increased electron density at secondary carbon atom, provides the high electron density site to attack protonated electrophile H_3SeO_3^+ . Due to this the oxidation process become more easily than both 1-phenyl ethanol and 1-(4-chloro phenyl) ethanol. While in case of 1-(4-chloro phenyl) ethanol, the observed reactivity is much slower than the 1-phenyl ethanol, because $-\text{I}$ influenced group (an electron withdrawing group) $-\text{Cl}$, is attached at the para position in aromatic nucleus decreased the electron density at the reaction site. Due to

this, the rate of oxidation becomes slow. Similar order of reactivity of various nucleio substituted alcohols were reported by other workers ^{7,8}.

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 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 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, 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.

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