Research Articles

"SPECTROPHOTOMETRIC STUDY OF OXIDATION OF α- HYDROXY ACIDS BY SELENIUM DIOXIDE IN AQUEOUS ACETIC ACID MEDIUM"

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ABSTRACT

The spectral kinetic investigation of oxidation of Glycolic acid and Mandelic acid by SeO_2 in aqueous acetic acid medium in presence of H_2SO_4 was followed at measurable temperature 308 K. The Lambert-Beer's law was verified and emblematic k_{obs} was determined from the slope of optical density vs. $[SeO_2]$ plots. The study reveals first-order rate with respect to oxidizing agent SeO_2, and α-hydroxy acids. The reaction rate was accelerated by addition of H^+ ion. The positive slope of Amis plot indicated that two dipoles in reactions are involved. The stoichiometric mole ratio was found 1:2. The corresponding products formaldehyde and benzaldehyde were identified by modern methods. The probable reaction mechanism was proposed and rate law was derived.

INTRODUCTION

The potentiality of selenium dioxide was realized in the history of chemistry when this oxidant was utilized in the synthesis of compounds.[1] This valuable oxidizing agent produces active species $H_3SeO^+_3$ and AcH_2SeO_3 . The recent available survey indicates that involving SeO_2, a number of organic compounds containing various functional groups viz. alcohols,[2] ketones,[3,4] aldehydes,[5] etc. have been kinetically oxidized. The kinetic studies on the oxidation of α–hydroxy acids have been documented with several oxidants such as Cr(VI),[6] NBP,[7] N-bromosuccinimide,[8] NCSA,[9] N-chlorosuccinimide,[10] and $KBrO_3$[11]. However, the spectrophotometric study of oxidation of α–hydroxy acids, glycolic acid and mandelic acid with SeO_2 in aqueous acetic acid medium in presence of H_2SO_4 have not been reported. In order to bring out the hidden potentiality of the oxidant SeO_2 and mechanism of substrates, the authors have probed the reactions spectrophotometrically.

EXPERIMENTAL

All the solvents and reagents employed in the spectrophotometric study were of analytical grade, used without further decontamination. SeO_2 (Loba), glycolic acid (AR), mandelic acid (Fluka) were used. The required, standard solutions of reagents were prepared of definite concentrations in doubled distilled water.

KINETIC STUDY

The experiments were performed in a thermostat, in which the solutions of oxidant, α–hydroxy acids and other reagents kept in a pyrex reaction vessel equilibrated at 308 in a thermoregulated thermostat. The accuracy of temperature was maintained within $\pm 0.1^0C$.

The reaction was initiated by mixing definite volume of SeO_2 with α–hydroxy acid. The entire reaction was monitored spectrophotometrically at required wave lengths (λ_{max} 242,and 309 nm) by recording decreasing absorbance of reactions with time respectively. The observed rate constant was determined from the plots of optical density against [SeO_2], which are expected to be linear for more than 75% completion of the reactions. The pseudo first-order rate constant was calculated by

$$k = \frac{1}{t} \ln \frac{(D_o - D_e)}{(D_t - D_e)}$$

RESULTS AND DISCUSSION

(a)   The spectral kinetic studies were initiated for the reactions under the conditions $[\alpha\text{-HA}] \gg [SeO_2]$ at measurable temperature. The rate of reaction was studied at their maximum wave lengths (λ_{max}) of absorption 242nm and 309nm respectively. The Lambert-Beer's law was verified to λ_{max}. The rate constant was determined from the slope of optical density vs. time plots from the spectral kinetic data recorded in Tables: 1 and 2, (Figs. 1 and 2). The stoichiometrically of the reactions indicate that for 1 mole of oxidant, 2 moles of α–hydroxy acid are consumed. The corresponding end-products of oxidation of glycolic and mandelic acids were identified by modern techniques as formaldehyde and benzaldehyde respectively.

Table 1 : Variation of concentration of SeO₂ on rate of reaction

[Glycolic acid] $= 5.0 \times 10^{-2}$ (mol dm^{-3}) ; $[H^+] = 1.0 \times 10^{-3}$ (mol dm^{-3}) ;

CH$_3$COOH-H$_2$O $= 20\,\%$ (v/v) ;   Temp. $= 308$ K ;

$\lambda_{max} = 242$ nm

S. No.	Time (Min.)	Optical density	$[SeO_2] \times 10^{-3}$ (mol dm^{-3})
1.	0.00	0.779	7.00
2.	0.50	0.711	6.00
3.	1.50	0.552	5.00
4.	2.00	0.461	4.00
5.	3.00	0.383	3.30
6.	4.00	0.350	3.00
7.	5.00	0.302	2.50
8.	6.00	0.235	2.00
9.	7.00	0.176	1.50
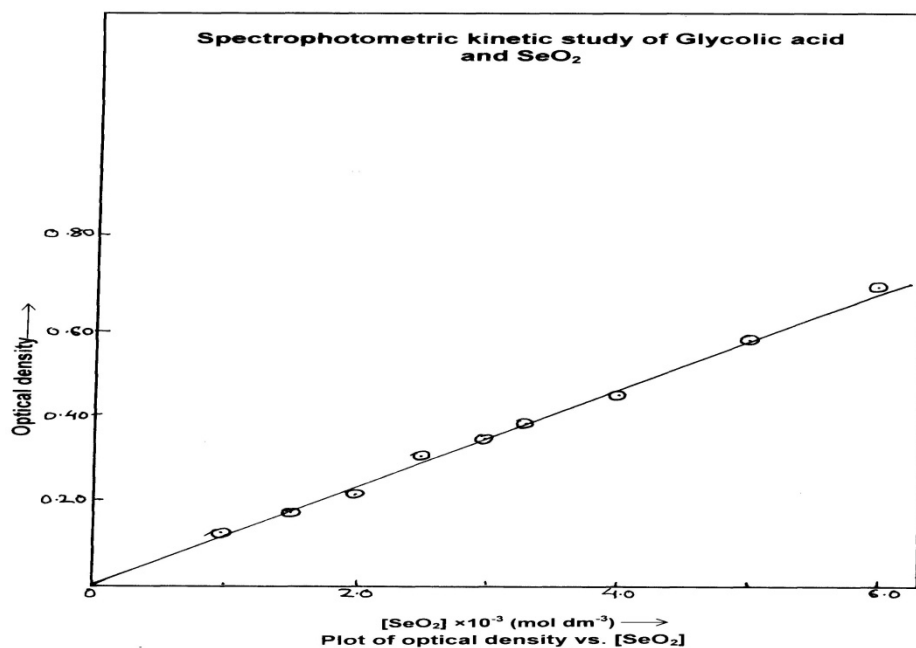
Fig. 1 [Glycolic acid] = 5.0×10^{-2} (mol dm^{-3}) ; [H$^+$] = 1.0×10^{-3} (mol dm^{-3})
CH$_3$COOH-H$_2$O = 20 % (v/v) ;   Temperature = 308 K
λ$_{max}$ = 242 nm

Table 2 : Variation of concentration of SeO$_2$ on rate of reaction

[Mandelic acid] = 2.50×10^{-2} (mol dm^{-3}) ; [H$^+$] = 1.0×10^{-3} (mol dm^{-3}) ;

HOAc-H$_2$O = 30 % (v/v) ;   Temp. = 308 K ;

λ$_{max}$ = 309 nm

S. No.	Time (Min.)	Optical density	[SeO$_2$] ×10^{-3} (mol dm^{-3})
1.	0.00	0.736	6.00
2.	0.50	0.630	5.00
3.	1.50	0.531	4.00
4.	2.00	0.374	3.00
5.	3.00	0.318	2.50
6.	4.00	0.250	2.00
7.	5.00	0.172	1.50
8.	6.00	0.179	1.25
9.	7.00	0.121	1.00

Fig. 2

Spectrophotometric kinetic study of Mandelic acid and SeO₂

Plot of optical density vs. [SeO₂]
Lambert-Beer's law
[Mandelic acid] = 2.50 ×10⁻² (mol dm⁻³) ; [H⁺] = 1.0 ×10⁻³ (mol dm⁻³)
CH₃COOH-H₂O = 30 % (v/v) ; Temperature = 308 K
λmax = 309 nm
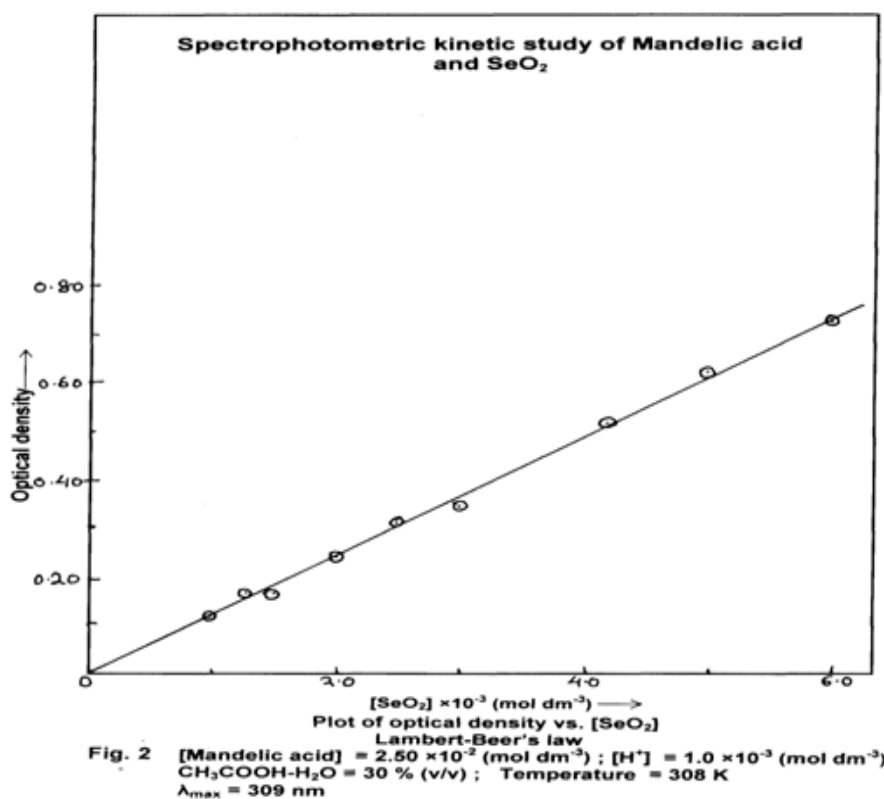
(b)   The spectral data have been collected for the effect of variation of concentration of SeO_2 ranging from 1.50 x 10^{-3} to 7.0 x 10^{-3} (mol dm^{-3}) at 308 K, keeping the other participating moiety constant. The values of rate constant obtained from the slopes of the plots log (a-x) against time clearly indicate that the order with respect to oxidant (SeO_2) is unity.

(c)   The effect of varying concentrations of glycolic acid and mandelic acid were studied by SeO_2 spectrophotometrically at previous conditions. The study rules out the formation of any complex in the reaction under investigation. The overall first-order rate was observed with respect to α–hydroxy acids.

(d)   The spectral data have been collected for the variation of concentrations of H^+ ions at fixed concentration of other participating reagents, temperature and wave lengths. The analysis indicates that the rate of oxidation of substrates proportionally accelerate with the rising concentration of acids. The study concludes that reaction is acid catalysed.

(e)   The effect of dielectric constant of the medium was examined by varying the

composition of acetic acid 10-50% (v/v) maintaining the reagent constant at fixed experimental temperature and wave lengths. The results are reflected in Table 3. The liner Amis plot (log k vs. 1/D) with positive intercept (Fig.3) indicates that rate constant increases with increase in percentage composition of acetic acid.

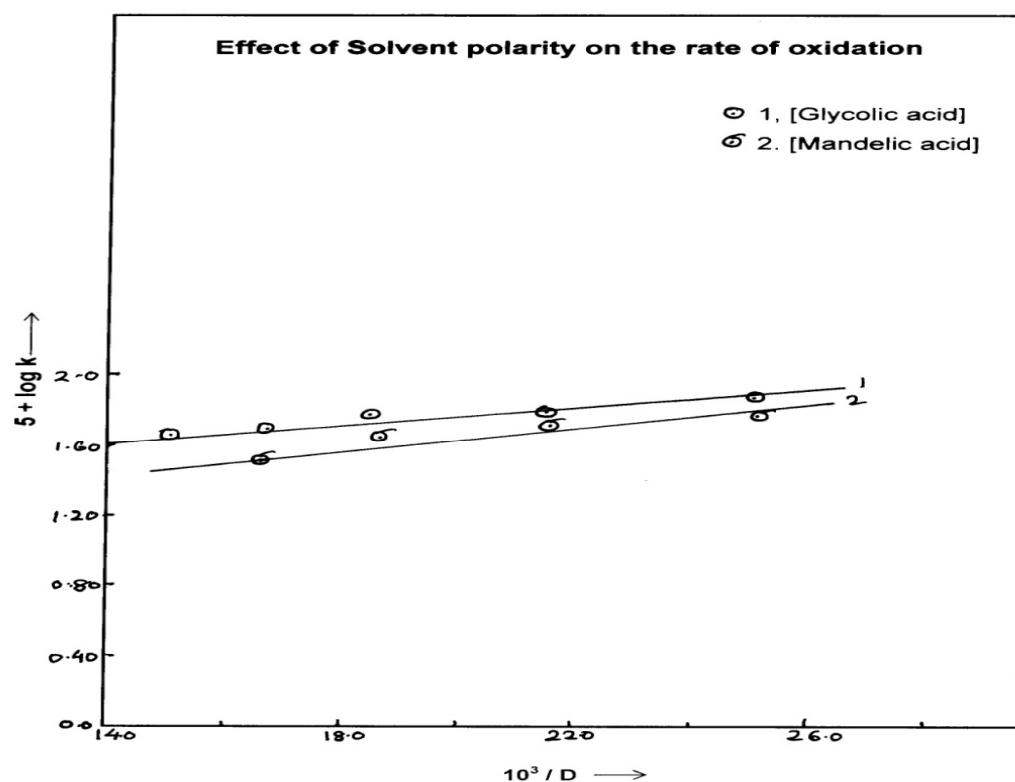**Table 3 : Effect of solvent composition on the rate of oxidation**

$10^2 \times$ [α-HA] (mol dm^{-3}) = 5.0 (1), 2.50 (2); $10^3 \times$ [SeO$_2$] (mol dm^{-3}) = 5.0 (1, 2) ;

$10^3 \times$ [H$^+$] (mol dm^{-3}) = 1.0 (1, 2) ; Temp. K = 308 (1, 2);

λ_{max} (nm) = 242 (1), 309 (2).

S. No.	HOAc-H$_2$O, % (v/v)	10^3/D*	10^5 k (s^{-1})	
			Glycolic acid (1)	Mandelic acid (2)
1.	10	15.50	44.89	-
2.	20	17.17	47.63	31.62
3.	30	19.15	52.48	44.70
4.	40	21.98	61.65	48.23
5.	50	25.64	67.51	57.50

1. Glycolic acid; 2. Mandelic acid

Fig. 3 $10^2 \times$[α-HA] (mol dm^{-3})= 5.0 (1),2.50 (2); $10^3 \times$ [SeO$_2$] (mol dm^{-3}) = 5.0 (1, 2); $10^3 \times$ [H$^+$](mol dm^{-3}) = 1.0 (1, 2); Temperature K = 308(1, 2) ; λ_{max} (nm) = 242(1), 309 (2)

(f) The neutral salt show inert effect on rate of oxidation and addition of acrylonitrile discarded the presence of the free radical in the reaction.

Mechanism

Based on observed kinetic results, the probable mechanism of the reactions may be proposed.

$$SeO_2 + H_2O \rightleftharpoons H_2SeO_3 \qquad \text{....... (1)}$$

$$H_2SeO_3 \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} H_3SeO_3^+ \qquad \text{....... (2)}$$

.... (3)
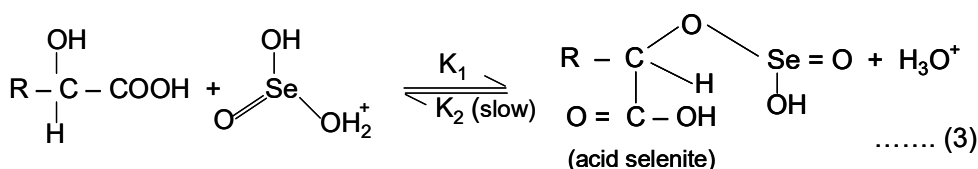
where, R= -H, and $-H_5C_6$ for glycolic acid and mandelic acid respectively.

.... (4)

$$H_2SeO_2 \xrightarrow{k_4} \tfrac{1}{2}H_2SeO_3 + \tfrac{1}{2}Se + \tfrac{1}{2}H_2O \qquad \text{....... (5)}$$
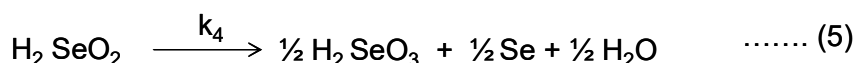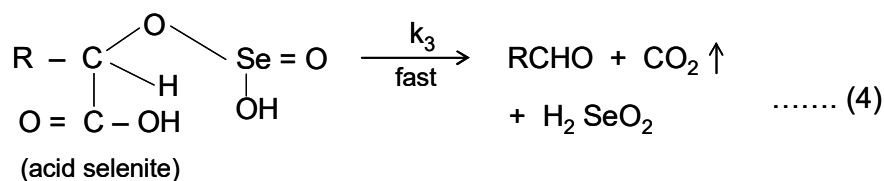
The final expression rate was obtained as :

$$\text{Rate} = \frac{k_1\, k_3\, [HA]\, [H_2SeO_3]\, [H^+]}{\{\, k_2\, [H_3O^+] + k_3 \,\}} \qquad \text{........ (6)}$$

Finally the rate under different condition, becomes

$$k_3 \gg k_2 \qquad \text{........ (7)}$$

$$k_{obs} = k_1\, [HA]\, [H_2SeO_3]\, [H^+] \qquad \text{........ (8)}$$

This mechanism is almost in close conformity with the observed facts.

REACTIVITY AND STRUCTURES

Based on observed kinetics, and thermodynamic parameters, the sequence of order of reactivity was found as:

Glycolic acid > Mandelic acid
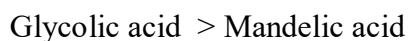
The slower rate of mandelic acid is due to the bulky design of molecular compactness and steric hindrance. The proposed mechanism and reactivity is supported by the Arrhenius parameters (Table; 4).

Table 4 : Thermodynamic parameters for α-hydroxy acid- SeO$_2$ system

S. No.	Substrate	Ea kJ (mol^{-1})	A (s^{-1})	ΔH$^{\#}$ kJ (mol^{-1})	ΔG$^{\#}$ kJ (mol^{-1})	−ΔS$^{\#}$ JK^{-1} (mol^{-1})
1.	Glycolic acid	61.68	4.16×10^3	60.85	86.87	87.90
2.	Mandelic acid	61.91	4.83×10^6	59.87	88.24	91.37

The approximate value of free energy (ΔG$^{\#}$) lying between 86.87 and 88.24 KJ (mole^{-1}) clearly shows that same type of mechanism prevailing in α–hydroxy acids. The reactivity trend and values of thermodynamic parameters also supported the C-C bond cleavage in the reactions. The mandelic acid with bulky group has ground state energy and the observed decrease in enthalpy of activation energy. A similar type of pattern in reactivity was also reported by few eminent workers.[12,13] spectrophotometrically in the oxidative studies.

CONCLUSION

The study reveals the slower rate of mandelic acid which is due to presence of bulky group (C$_6$H$_5$) of molecular compactness and steric hindrance. Rate determining oxidative de-carboxylation involves heterolytic fission of C-C bond. The H$_3$SeO$_3$$^+$ reacting species of oxidant (SeO$_2$) has been ascertained. Corresponding oxidation products, formaldehyde and benzaldehyde were identified by modern methods.

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