PALLADIUM(II)-CATALYZED OXIDATION OF α-HYDROXY ACIDS WITH SODIUM *N*-CHLOROBENZENESULFONAMIDE IN PERCHLORIC ACID SOLUTION: A KINETIC AND MECHANISTIC STUDY

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Kinetics of oxidation of glycolic acid (GA), lactic acid (LA) and 2-hydroxybutanoic acid (BA) with Chloramines B (CAB) catalyzed by Pd(II) in a $HClO_4$ solution has been studied at 30 °C. The reaction rate shows first-order dependence each on [CAB], [hydroxy acid] and [Pd(II)] and a fractional-order dependence on $[H^+]$. Additions of chloride ions, perchlorate ions and the reduction product of CAB, benzenesulfonamide (BSA), have no effect on the reaction rate. Variations of ionic strength and dielectric permittivity of the medium have no effect on the rate. Activation parameters have been evaluated. A mechanism consistent with kinetic data is proposed. A Taft linear free-energy relationship is observed for the reaction with $\rho^* = -3.593$, indicating an increase in the rate with the presence of electron-donating substituents. An isokinetic relationship is observed with $\beta = 376$ K, indicating the effect of enthalpy factors on the rate.

Keywords: Chloramine B; α-Hydroxy acids; Kinetics; Oxidation; Palladium(II); Mechanism; Substituent effects.

The chemistry of sodium salt of aromatic *N*-halosulfonamides in aqueous solution has received considerable attention and the existing literature on Chloramine B (CAB) has been reviewed. Hydroxy acids are organic compounds containing both OH and COOH functional groups. Their industrial applications include use in processing textiles and leather, manufacturing adhesives, brightening copper, decontamination, cleaning, dyeing, and electroplating. They are used as solvents for water-insoluble dyes and in dilute solutions to irrigate tissues as an intestinal antiseptic.

A literature survey reveals the Os(VIII)-catalyzed oxidation of hydroxy acids with Chloramine T (CAT)[1], oxidation of α-hydroxy acids with CAT in aqueous perchloric acid solution[2], the kinetics of oxidation of hydroxy acids with CAB in acid solutions[3] and oxidation of lactic acid with CAT in

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presence of Cu(II) as catalyst[4], the kinetics of Pd(II) catalyzed oxidation of mandelic and tartaric acids with CAT in alkaline medium[5]. The kinetics of oxidation of malic, citric and tartaric acids in perchloric acid medium[6] have been reported. In the literature, reports are lacking on the oxidation and kinetics of hydroxy acids catalyzed by Pd(II) in $HClO_4$ solution, with CAB as oxidant. The present studies are undertaken to investigate the kinetic aspects of the oxidation with CAB of α-hydroxy acids, namely glycolic, lactic and 2-hydroxybutanoic acids, catalyzed by Pd(II) solution. Attempts have been made to arrive at a LFER through Taft treatment and isokinetic relationship with the computed activation parameters.

EXPERIMENTAL

Materials

Chloramine B was prepared and purified by the method described earlier[7]. An aqueous solution of the compound was standardized iodometrically and preserved in brown bottles to prevent its photochemical deterioration. Aqueous solutions of glycolic (Merck), lactic (Merck) and 2-hydroxy butanoic (Sigma) acids were prepared. A solution of $PdCl_2$ (Arora Matthey) in 0.01 M HCl was used as a catalyst. Allowances were made for the amount of HCl present in the catalyst solution while preparing the solutions for kinetic runs. All other chemicals used were of acceptable grades of purity. Ionic strength of the reaction mixture was kept constant with a concentrated solution of $NaClO_4$ (Merck). Triply distilled water was used for preparation of aqueous solutions.

Kinetic Measurement

The kinetic runs were performed under pseudo-first-order conditions, when $[\text{hydroxy acid}]_0 >> [CAB]_0$. Required amounts of solutions of the hydroxy acid, $NaClO_4$, $PdCl_2$ and $HClO_4$ were charged into a stoppered Pyrex glass tubes whose outer surfaces were black to eliminate photochemical effects. In each case, a required amount of water was added to maintain a constant total volume. The tube was thermostatted in a water bath set at a given temperature (30 ± 0.1 °C). To this solution, a measured amount of pre-equilibrated CAB solution was added to give a known concentration. The progress of the reaction was monitored iodometrically for two half-lives by withdrawing aliquots of the reaction mixture at regular time intervals. The rate constants *k* were reproducible within ±3%.

RESULTS

Stoichiometry and Product Analysis

Reaction mixtures containing different amounts of the hydroxy acid and CAB were equilibrated in the presence of 1×10^{-3} M $HClO_4$ and 45×10^{-6} M palladium chloride catalyst at 25 °C for 24 h. Iodometric titration of unreacted CAB in the reaction mixture showed that 1 mol of CAB was consumed per mol of hydroxy acid according to Eq. (*1*).

$$\begin{aligned} &\mathrm{R{-}CH(OH){-}COOH + PhSO_2NClNa} \rightarrow \\ &\mathrm{R{-}CO{-}COOH + PhSO_2NH_2 + Na^+ + Cl^-}, \end{aligned} \qquad (1)$$

where R = H for glycolic acid (GA), CH_3 for lactic acid (LA) and CH_3CH_2 for 2-hydroxybutanoic acid (BA).

The presence of the corresponding keto acid (aldehydo acid in the case of glycolic acid) in the reaction mixture was detected by preparing their 2,4-dinitrophenylhydrazones and by characteristic spot tests[8]. The formation of benzenesulfonamide was confirmed by TLC [6] in petroleum ether–chloroform–1-butanol (2:2:1 v/v) with iodine as the detection reagent (R_F 0.88). The presence of BSA was further confirmed by mass spectral analysis. The parent molecular ion peak at *m/z* 157 confirms the presence of benzenesulfonamide in the reaction mixtures.

Effect of Varying Reactant Concentrations

The stoichiometry of the hydroxy acid–CAB reaction was found to be of 1:1 mole ratio. The reaction was performed in the presence of palladium chloride catalyst and $HClO_4$, under pseudo-first-order conditions of $[\text{hydroxy acid}]_0 \gg [\text{CAB}]_0$. Plots of log [CAB] versus time were linear. The linearity of these plots, together with the constancy of the slope for various $[\text{CAB}]_0$, indicates a first-order dependence of the reaction rate on [CAB]. The pseudo-first-order rate constants *k* obtained at 30 °C are listed in Table I. The reaction rate increased with increase in [hydroxy acid] and the plot of log *k* versus log [hydroxy acid] was linear with a slope of unity indicating the first-order dependence on [hydroxy acid] (Table I, Fig. 1).

Effect of Catalyst

At constant $[\text{CAB}]_0$, $[\text{hydroxy acid}]_0$, $[HClO_4]$ and temperature, the rate of reaction increased with increasing [Pd(II)] (Table II). The plots of log *k* versus log [Pd(II)] (Fig. 2) were linear, with a slope equal to unity indicating a first-order dependence on [Pd(II)].

TABLE I
Effect of varying reactant concentration on the reaction rate constant: $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[Pd(II)] = 45 \times 10^{-6}$ mol dm^{-3}; $I = 0.3$ mol dm^{-3}; temperature 30 °C

$[CAB] \times 10^4$ mol dm^{-3}	[hydroxy acid] $\times 10^4$ mol dm^{-3}	$k \times 10^4$, s^{-1}		
		GA	LA	BA
2.0	10.0	0.87	2.19	6.48
5.0	10.0	0.86	2.18	6.46
7.0	10.0	0.84	2.16	6.47
10.0	10.0	0.85	2.17	6.45
15.0	10.0	0.87	2.16	6.47
20.0	10.0	0.85	2.15	6.45
5.0	2.0	0.17	0.44	1.28
5.0	5.0	0.43	1.09	3.22
5.0	10.0	0.86	2.18	6.46
5.0	12.0	1.03	2.62	7.70
5.0	15.0	1.29	3.28	9.63
5.0	18.0	1.55	3.94	11.56
5.0	20.0	1.72	4.37	12.84

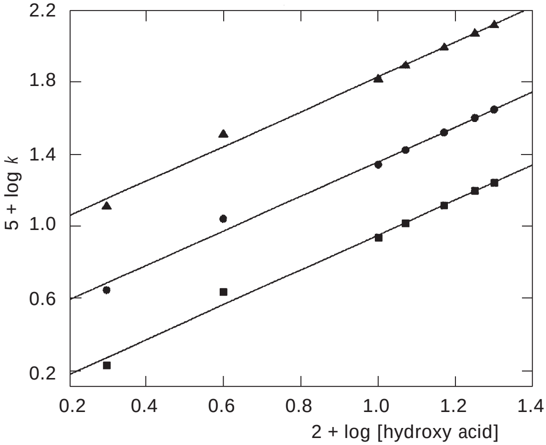

FIG. 1
Plots of log *k* vs log [hydroxy acid]. Slopes: BA 0.96219 (▲), LA 0.95985 (●), GA 0.9657 (■). $[CAB] = 5 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[Pd(II)] = 45 \times 10^{-6}$ mol dm^{-3}; $I = 0.3$ mol dm^{-3}; temperature 30 °C

Effect of $HClO_4$

At constant $[CAB]_0$, [hydroxy acid]$_0$, [Pd(II)] and temperature, the reaction rate increased with increasing $[HClO_4]_0$ (Table III). The plots of log *k* versus log $[HClO_4]$ (Fig. 3) were linear with a slope smaller than unity (≈0.5) indicating a fractional-order dependence on $[HClO_4]$.

TABLE II

Effect of varying [Pd(II)] on the reaction rate constant: [CAB] = 5×10^{-4} mol dm^{-3}, [hydroxy acid] = 10×10^{-2} mol dm^{-3}, [H$^+$] = 1.0×10^{-3} mol dm^{-3}; I = 0.3 mol dm^{-3}; temperature 30 °C

[Pd(II)] × 10^6 mol dm^{-3}	$k \times 10^4$, s^{-1}		
	GA	LA	BA
11.25	0.21	0.55	1.61
22.50	0.43	1.09	3.21
45.0	0.86	2.18	6.46
67.5	1.29	3.28	9.63
90.0	1.72	4.37	12.80

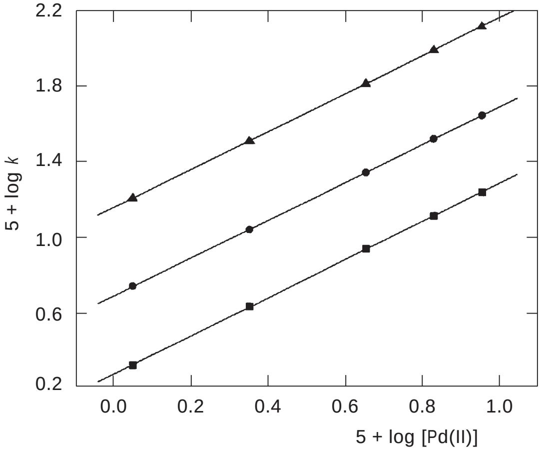

FIG. 2

Plots of log *k* vs log [Pd(II)]. Slopes: BA 0.99811 (▲), LA 0.99747 (●), GA 1.00937 (■). [CAB] = 5×10^{-4} mol dm^{-3}, [H$^+$] = 1.0×10^{-3} mol dm^{-3}, [hydroxy acid] = 10×10^{-2} mol dm^{-3}; I = 0.3 mol dm^{-3}; temperature 30 °C

Effect of ClO_4^-, Cl^- and Benzenesulfonamide

The addition of ClO_4^- in the form of $NaClO_4$ (1×10^{-2}–15×10^{-2} mol dm^{-3}) and addition of Cl^- (0.4×10^{-3}–8×10^{-3} mol dm^{-3}) at constant [H^+] did not affect the rate. Hence, the dependence of the rate on [$HClO_4$] reflects the effect of [H^+] only on the reaction rate. The addition of benzenesulfonamide

TABLE III

Effect of varying [$HClO_4$] on the reaction rate constant: [CAB] = 5×10^{-4} mol dm^{-3}, [hydroxy acid] = 10×10^{-2} mol dm^{-3}, [Pd(II)] = 45×10^{-6} mol dm^{-3}; I = 0.3 mol dm^{-3}; temperature 30 °C

[$HClO_4$] × 10^3 mol dm^{-3}	$k \times 10^4$, s^{-1}		
	GA	LA	BA
0.5	0.61	1.55	4.54
0.8	0.77	1.96	5.74
1.0	0.86	2.18	6.46
1.5	1.05	2.68	7.86
2.0	1.22	3.09	9.08
5.0	1.92	4.89	14.37
8.0	2.42	6.19	18.18

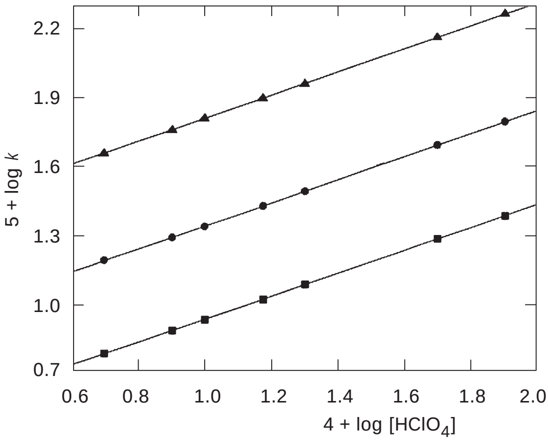

FIG. 3

Plots of log k vs log [$HClO_4$]. Slopes: BA 0.4991 (▲), LA 0.49968 (●), GA 0.49783 (■). [CAB] = 5×10^{-4} mol dm^{-3}, [hydroxy acid] = 10×10^{-2} mol dm^{-3}, [Pd(II)] = 45×10^{-6} mol dm^{-3}; I = 0.3 mol dm^{-3}; temperature 30 °C

(1×10^{-4}–8×10^{-4} mol dm^{-3}) had no effect on the rate, indicating that it is not involved in pre-equilibrium step before the rate-determining step.

Effect of Variation of Ionic Strength and Dielectric Permittivity of the Medium

The reaction rate remained unaffected by varying ionic strength of the medium through addition of sodium perchlorate (0.05–0.20 mol dm^{-3}). The solvent composition was varied by adding methanol (0 to 15%) but no significant change in the rate was observed when increasing the methanol content in the reaction medium.

Effect of Temperature

The reaction was studied at different temperatures (25–45 °C). The activation parameters namely, energy of activation (E_a), enthalpy of activation ($\Delta H^{\neq}$), entropy of activation ($\Delta S^{\neq}$) and Gibbs energy of activation ($\Delta G^{\neq}$) were obtained from the Arrhenius plot of log k versus $1/T$. The activation parameters obtained are presented in Table IV. The rate constants were also evaluated for the oxidation of α-hydroxy acid with CAB in the absence of Pd(II) at 30 °C, they are 0.43×10^{-5}, 1.21×10^{-5} and 4.40×10^{-5} for GA, LA and BA, respectively.

Test for Free Radicals

The addition of the reaction mixtures to aqueous acrylamide monomer solutions did not initiate polymerization indicating the absence of in situ formation of free radical species in the reaction sequence.

TABLE IV
Temperature dependence and activation parameters

Hydroxy acid	$k \times 10^4$, s^{-1}					E_a kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ kJ mol^{-1}
	298 K	303 K	308 K	313 K	318 K				
GA	0.50	0.86	1.51	2.51	3.80	80.84	78.27	98.14	–64.64
LA	1.44	2.18	3.39	4.90	7.24	63.60	61.03	96.08	–113.8
BA	4.47	6.46	9.35	13.09	18.07	55.18	52.2	93.44	–132.7

DISCUSSION AND MECHANISM

Pryde and Soper[9], Morris et al.[10] and Bishop and Jennings[11] have shown the existence of similar equilibria in acid and alkaline solutions of metal salts of *N*-haloarenesulfonamides. Chloramine B, an analogue to Chloramine T, behaves as a strong electrolyte in aqueous solutions forming different species as shown in Eqs (*2*)–(*6*).

$$PhSO_2NClNa \rightleftharpoons PhSO_2NCl^- + Na^+ \qquad (2)$$

$$PhSO_2NCl^- + H^+ \rightleftharpoons PhSO_2NHCl \qquad (3)$$

$$PhSO_2NHCl + H_2O \rightleftharpoons PhSO_2NH_2 + HOCl \qquad (4)$$

$$2\ PhSO_2NHCl \rightleftharpoons PhSO_2NH_2 + PhSO_2NCl_2 \qquad (5)$$

$$HOCl + H^+ \rightleftharpoons H_2O^+Cl \qquad (6)$$

In acid medium, probable oxidizing species are the free acid ($PhSO_2NHCl$), dichloroamine B ($PhSO_2NCl_2$), HOCl and H_2O^+Cl. The involvement of $PhSO_2NCl_2$ in the mechanism leads to a second-order rate law according to Eq. (*5*), which is in contrast to experimental results. As Eq. (*4*) indicates a slow hydrolysis, if HOCl were the primary oxidizing species, a first-order retardation of the rate by the added $PhSO_2NH_2$ would be expected, which is in constract to the observed results. Hardy and Johnston[12], who studied the pH-dependent relative concentrations of the species present in acidified Chloramine T solutions of comparable molar concentrations have shown that $CH_3C_6H_4SO_2NHCl$ is the probable oxidizing species in acid medium. Narayanan and Rao[13] and Subhashini et al.[14] have reported that monochloramines can be further protonated at pH < 2, as shown in the following Eqs (*7*) and (*8*) for Chloramine B and Chloramine T, respectively.

$$PhSO_2NHCl + H^+ \rightleftharpoons PhSO_2N^+H_2Cl \qquad (7)$$

$$CH_3C_6H_4SO_2NHCl + H^+ \rightleftharpoons CH_3C_6H_4SO_2N^+H_2Cl \qquad (8)$$

The second protonation constant for CAB and CAT are 61 ± 5 mol^{-1} and 102 mol^{-1}, respectively, at 25 °C.

Palladium(II) chloride is soluble in hydrochloric acid, where exists[15] as $[PdCl_4]^{2-}$. Furthermore, ultraviolet spectral measurements showed that a sharp absorption band exists at 205 nm for a hydroxy acid solution, 223 nm for CAB solution and a broad band around 208 nm for Pd(II) in the presence of 1×10^{-3} M $HClO_4$. A mixture of CAB and Pd(II) in 1×10^{-3} M $HClO_4$ showed an absorption band at 223 nm, while for a mixture of hydroxy acid and Pd(II) in 1×10^{-3} M $HClO_4$ solution a sharp absorption band was observed at 220 nm, indicating that complex formation takes place only between Pd(II) and hydroxy acid. In the present case, the fractional-order in $[H^+]$ suggests that the protonation of $PhSO_2NHCl$ results in the generation of $PhSO_2N^+H_2Cl$, which is likely to be the active oxidizing species involved in the mechanism of the oxidation of α-hydroxy acids. Based on the preceding discussion, a mechanism (Scheme 1) is proposed for the reaction.

$$PhSO_2NHCl + H^+ \underset{\text{fast}}{\overset{K_1}{\rightleftharpoons}} PhSO_2N^+H_2Cl \tag{i}$$

$$\text{Sub} + \text{Pd(II)} \underset{\text{fast}}{\overset{K_2}{\rightleftharpoons}} X \tag{ii}$$

$$X + PhSO_2N^+H_2Cl \xrightarrow[\text{slow}]{k_3} X^1 \tag{iii}$$

$$X^1 \xrightarrow[\text{fast}]{k_4} \text{products} \tag{iv}$$

SCHEME 1

In Scheme 1, Sub represents the substrate, α-hydroxy acid, GA, LA or BA, and X and X^1 represent the complex intermediates.

From Scheme 1

$$\text{rate} = k_3[PhSO_2N^+H_2Cl]\,[X]. \tag{9}$$

The total effective concentration of CAB is

$$[\mathrm{CAB}]_t = [\mathrm{PhSO_2NHCl}] + [\mathrm{PhSO_2N^+H_2Cl}]. \qquad (10)$$

From step (i)

$$[\mathrm{PhSO_2NHCl}] = \frac{[\mathrm{PhSO_2\,N^+H_2\,Cl}]}{K_1[\mathrm{H^+}]}\,. \qquad (11)$$

Substituting Eq. (*11*) to Eq. (*10*) and solving for $[\mathrm{PhSO_2N^+H_2Cl}]$ gives

$$[\mathrm{CAB}]_t = \frac{[\mathrm{PhSO_2\,N^+H_2\,Cl}]}{K_1[\mathrm{H^+}]} + [\mathrm{PhSO_2N^+H_2Cl}] \qquad (12)$$

$$[\mathrm{PhSO_2N^+H_2Cl}] = \frac{K_1[\mathrm{CAB}]_t[\mathrm{H^+}]}{1 + K_1[\mathrm{H^+}]}\,. \qquad (13)$$

From step (ii)

$$[\mathrm{X}] = K_2[\mathrm{Sub}]\,[\mathrm{Pd(II)}]. \qquad (14)$$

Substituting Eqs (*13*) and (*14*) into Eq. (*9*)

$$\mathrm{rate} = \frac{K_1 K_2\, k_3[\mathrm{Sub}][\mathrm{CAB}]_t[\mathrm{Pd(II)}][\mathrm{H^+}]}{1 + K_1[\mathrm{H^+}]}\,. \qquad (15)$$

The rate law is consistent with the experimental data, including a first-order dependence of the rate each on [CAB], [Sub] and [Pd(II)] and a fractional-order dependence on $[\mathrm{H^+}]$.

Variation of the dielectric permittivity (D) of the medium does not affect the rate. An explanation can be offered in terms of the Born treatment applied by Laidler[16] for dipole–dipole reactions.

Linear Free Energy Relationship

In this study, the existence of a linear free energy relationship for the oxidation of α-hydroxy acids with CAB catalyzed by Pd(II) has been evaluated[17]. Tests of the complete Taft equation as well as single-parameter correlations with polar substituent constant σ* and steric substituent constant E_s were made by plotting (log $k - E_s$) versus σ*, log k versus σ*, log k versus E_s. The following regression equations were found.

$$\log k = -0.516E_s - 1.562 \qquad (r = 0.8675) \qquad (16)$$

$$\log k = -1.274\sigma^* - 1.527 \qquad (r = 0.9175) \qquad (17)$$

$$(\log k - E_s) = -3.593\sigma^* - 1.438 \qquad (r = 0.9967) \qquad (18)$$

The implication of the steric effects on the rate is not clear from Eq. (*16*). A reasonable correlation in Eq. (*17*) shows that electronic effect has a synergistic effect in determining the rate. However, a good correlation of (log $k - E_s$) with σ* for α-hydroxy acids in Eq. (*18*) implies that both steric and electronic factors play a dominant role in determining the reaction rate. The negative values of the reaction constant ρ* (–0.516 and –3.593) suggest that electron-donating groups in the hydroxy acid substrate increases the reaction rate.

The relative magnitudes of activation energies for the oxidation of α-hydroxy acids in Table IV support the preceding trend, indicating that the reactions are enthalpy-controlled. This is verified by calculating the isokinetic temperature (β) from the slope of a linear plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ (Fig. 4; r = 0.9980). The β value of 376 K, which is higher than the experimental range used in the present study, implies that the substrate oxidation is enthalpy-controlled. A further confirmation of the existence of the isokinetic relationship was inferred from the Exner criterion[18] by plotting log k (318 K) versus log k (298 K), which yields a linear plot (Fig. 5; r = 0.9972). The Exner slope gave a β of 379 K. The fairly negative values of $\Delta S^{\neq}$ indicate the formation of a rigid associative transition state in each case.

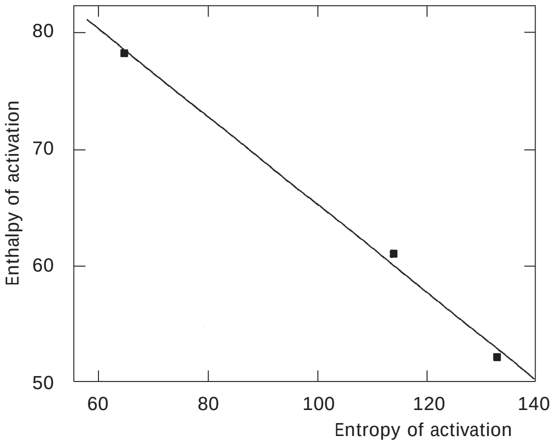

FIG. 4
Plot of $\Delta H^{\neq}$ vs $\Delta S^{\neq}$

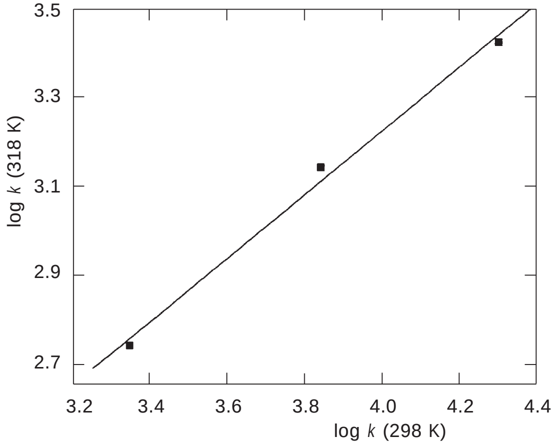

FIG. 5
Exner plot of log *k* (318 K) vs log *k* (298 K)

CONCLUSION

The rate of oxidation of α-hydroxy acids with CAB in the presence of Pd(II) catalyst increases in the order GA < LA < BA, indicating a combined effect of electronic and steric factors of alkyl groups. The reaction rate for Pd(II)-catalyzed reaction was higher than that of uncatalyzed reaction.

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