Kinetics and Mechanism of Oxidation of Neutral α-Amino Acids by Sodium N-Chloro-*p*-toluenesulfonamide in Acid Medium

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ABSTRACT: Kinetics of oxidation of α-amino acids, glycine, valine, alanine, and phenylalanine, by sodium N-chloro-*p*-toluenesulfonamide or chloramine-T (CAT) has been investigated in $HClO_4$ medium at 30°C. The rate shows first-order dependence on both CAT and amino acid concentrations and an inverse first-order on $[H^+]$. The variation of ionic strength and the addition of *p*-toluenesulfonamide and Cl^- ion had no effect on the reaction rate. Decrease of dielectric constant of the medium by increasing the MeOH content decreased the rate. Rate studies in D_2O medium showed the inverse solvent-isotope effect of $k_{D_2O}/k_{H_2O} = 0.50$. Proton-inventory studies were carried out using H_2O–D_2O mixtures. The activation parameters have been computed. The proposed mechanism and the derived rate law are consistent with the observed kinetic data. An isokinetic relationship is observed with $\beta = 323$ K, indicating enthalpy as a controlling factor. The rate of oxidation increases in the following order: Gly < Val < Phe < Ala.
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INTRODUCTION

The chemistry of sodium *N*-chloroarylsulfonamides in aqueous solutions has received considerable attention [1,2]. The prominent member of this class of compounds, namely, sodium *N*-chloro-*p*-toluenesulfonamide or chloramine-T (p-$CH_3C_6H_4SO_2NClNa{\cdot}3H_2O$ or CAT), is a by-product in the manufacture of saccharin. Generally CAT undergoes a two-electron change in its reactions resulting in the formation of the reduction products, *p*-toluenesulfonaminde or PTS (p-$CH_3C_6H_4SO_2NH_2$) and sodium chloride. The oxidation potential of the CAT–PTS couple varies with pH of the medium (1.139 V at pH 0.65, 0.778 V at pH 7.0, and 0.614 V at pH 9.7). A detailed review of the chemistry of CAT and related *N*-haloarylsulfonamides has been reported [3].

In the present paper, we report the kinetic and mechanistic study of the oxidation of four neutral α-amino acids, glycine, valine, alanine, and phenylalanine, by CAT, performed under the same experimental

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conditions including the $HClO_4$ medium and the temperature. The main objective of this investigation was twofold: (1) to ascertain whether the neutral α-amino acids follow a common mechanism of oxidation, which they do, and (2) to compare these new kinetic results with those of the earlier studies [1,2] so that the main differences could be identified. The following differences between the earlier studies and the present work are noted:

i. Unlike the present case, in the earlier studies [1,2], oxidation kinetics were performed on individual amino acids under different reaction conditions, including acid and base media, resulting in different experimental rate laws and mechanisms. For example, one of the previous studies [1] involved the oxidation of L-threonine by CAT, in HCl, $HClO_4$, and H_2SO_4 media, while the present study involves the oxidation of four neutral amino acids in $HClO_4$ medium by CAT. The threonine oxidation shows the following kinetic orders, which differ from the present data: a first-order in [CAT], a negative first-order in $[H^+]$, and a fractional-order each in [threonine] and $[Cl^-]$.
ii. Similar differences can be found between the kinetic results and mechanisms for several amino acids reported earlier [2].
iii. A part of the earlier study [2] involved the kinetics of oxidation of glycine, valine, alanine, and phenylalanine with CAT performed in HCl medium, but not in $HClO_4$ medium. Hence the two sets of kinetic data in two acid media for the same four amino acids are different.
iv. There are differences in the reaction stoichiometries and in the products formed. Under the experimental conditions used in this work, the mole-to-mole ratio of the amino acid to CAT is 1 : 1 with NH_4^+ ion, CO_2, and the corresponding aldehyde as oxidation products of the substrate. In contrast, under the experimental conditions used in the previous studies [2], the stoichiometry involved 2 mol of CAT consumed per mole of the amino acid, yielding a nitrile and CO_2 as oxidation products.
v. In the present study, a proton-inventory experiment has been performed showing the involvement of H^+ in the transition state. The earlier studies [1,2] do not report this experiment.
vi. The applicabilities of the Taft equation and single-parameter correlations have been explored to elucidate stereochemical information of the reactions in the present study. These data are lacking in the earlier investigations [1,2]. The differences described above justify the present study.

EXPERIMENTAL

Chloramine-T (Merck) was purified by a standard method [3] and its purity was checked by iodometry and by its ^1H and ^{13}C NMR spectra. An aqueous solution of the compound was prepared and preserved in a brown bottle to prevent its photochemical deterioration. The chromatographically pure glycine (S.D. Chem.), DL-valine, L-alanine, and L-phenylalanine (Loba Chemie) were further assayed by the acetous perchloric acid method [4]. All other chemicals used were of analytical reagent grade. Solvent-isotope studies were made with D_2O (99.4%) supplied by BARC, Trombay, Mumbai, India. Triply distilled water was used in the preparation of aqueous solutions. The dielectric constant of the medium was varied by the addition of MeOH and the values of dielectric constant for MeOH–water mixtures reported in literature [5,6] were employed.

Kinetic Procedure

The reaction was carried out in glass-stoppered Pyrex boiling tubes whose outer surface was coated black to eliminate photochemical effects. Requisite amounts of the solutions of the amino acid and perchloric acid were taken in the tube and thermostated at 30°C. A measured amount of CAT solution, also thermostated at the same temperature, was rapidly added with stirring to the mixture in the tube. The progress of the reaction was monitored by the iodometric determination of the unreacted CAT in aliquots of the reaction mixture withdrawn at different intervals of time. The course of the reaction was studied for at least two half-lives. The pseudo first-order rate constants, k_{obs}, calculated from the plots of log [CAT] vs. time were reproducible within ±3%.

Regression analysis of experimental data, to obtain regression coefficient r and the standard deviation s, was performed with an EC-72 statistical calculator.

Stoichiometry and Product Analysis

The reaction mixtures containing the amino acid and perchloric acid with excess of CAT were kept for 24 h at 30°C. Iodometric determination of the unconsumed CAT showed that 1 mol of the oxidant was consumed per mole of the amino acid forming the corresponding aldehyde. The stoichiometry of the reaction can be represented by Eq. (1).

$$R'CH(NH_2)COOH + RNCl^- + H_3O^+ \rightarrow R'CHO + NH_4^+ + CO_2 + RNH_2 + Cl^- \quad (1)$$

Here R′ = H for glycine, $(CH_3)_2CH$ for valine, CH_3 for alanine, and $C_6H_5CH_2$ for phenylalanine while R represents p-$CH_3C_6H_4SO_2$.

Ammonia and CO_2 were identified by the conventional tests. The aldehydes were characterized by preparing the DNP derivatives and by their spectral data in comparison with the authentic aldehyde samples. The reduction product of CAT, RNH_2, among the reaction products was detected by TLC using dichloromethane and petroleum ether (7:3 v/v) as the solvent system and iodine as the detecting reagent ($R_f = 0.34$).

RESULTS

Effect of Varying Reactant Concentration on the Rate

The kinetics of oxidations of neutral α-amino acids by CAT were investigated at several initial concentrations of the reactants in perchloric acid medium at 30°C. With the $[substrate]_0$ in excess and at constant $[HClO_4]$, plots of log [CAT] vs. time were linear ($r > 0.9930$, $s \leq 0.05$) for each $[CAT]_0$. The reaction showed a first-order dependence of rate on [CAT] (Table I). Values of k_{obs} increased with increase in [amino acid]. The plots of log k_{obs} vs. log $[amino\ acid]_0$ were linear ($r > 0.9990$, $s < 0.02$) with unit slopes (Table I). Also, the second-order rate constants $k_2 = k_{obs}/[S]_0$ were constant confirming the first-order dependence on [S].

Effect of $[HClO_4]$

The rate decreased with increase in $[HClO_4]$ for each amino acid and the plot of log k_{obs} vs. log $[HClO_4]$ was linear ($r > 0.9979$, $s \leq 0.04$; Table I) with a slope of −1.

Effect of RNH_2 and Cl^- Ion

Addition of the reaction products, *p*-toluenesulfonamide and chloride ions, the latter in the form of NaCl, did not affect the rate. It may thus be inferred that the sulfonamide is not involved in a pre-equilibrium with the oxidant.

Effect of Ionic Strength

Variation of the ionic strength of the medium by adding $NaClO_4$ (0.20–1.0 mol dm^{-3}) had no effect on the reaction rate. This effect supports the involvement of at least one nonionic species in the rate-limiting step.

Effect of Varying the Solvent Composition

The solvent composition and dielectric constant (D) of the reaction medium were varied by adding MeOH (0–40% Vol%). The rate decreased with increase in the MeOH content. Plots of log k_{obs} vs. $1/D$ were linear ($r > 0.9896$, $s \leq 0.05$) with a negative slope. Control experiments performed showed that MeOH was not oxidized by CAT under the experimental conditions.

Table I Effect of Varying Reactant Concentrations on the Rate of Oxidation of Neutral α-Amino Acids at 30°C

$10^3[CAT]_0$ (mol dm^{-3})	$10^2[S]_0$ (mol dm^{-3})	$10^2[H^+]$ (mol dm^{-3})	$10^4 k_{obs}(s^{-1})$			
			Glycine	Valine	Alanine	Phenylalanine
2.00	5.00	6.00	2.06	4.72	5.28	5.38
2.50	5.00	6.00	2.25	5.05	5.75	5.45
3.00	5.00	6.00	2.40	5.45	5.92	5.63
3.50	5.00	6.00	2.44	5.60	5.96	5.68
4.00	5.00	6.00	2.53	5.68	6.03	5.73
4.50	5.00	6.00	2.67	5.88	6.20	5.93
3.00	1.00	6.00	0.64	1.50	1.52	1.28
3.00	3.0	6.00	1.75	3.98	4.03	3.55
3.00	7.00	6.00	3.83	7.89	8.46	7.98
3.00	9.00	6.00	4.80	9.80	10.6	9.74
3.00	10.0	6.00	5.92	11.52	12.8	11.0
3.00	5.00	2.00	7.98	17.50	21.5	19.6
3.00	5.00	4.00	4.29	9.11	11.0	9.13
2.0	5.00	8.00	1.75	4.20	4.50	4.15
3.0	5.00	10.0	1.20	3.07	2.92	3.20
3.00	5.00	20.0	0.63	1.66	1.60	1.50

Effect of Temperature

The reaction was studied at different temperatures (298–313 K). From the linear Arrhenius plots of log k_{obs} vs. $1/T$ ($r > 0.9998$, $s \leq 0.01$), the activation energy E_a was calculated. Values of the other activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, were computed from the E_a values (Table II).

Effect of Solvent Isotope

The reaction was studied in D_2O medium in the presence of $HClO_4$. The rate decreased with increase in D_2O content. The inverse solvent-isotope effect $k_{obs}(D_2O)/k_{obs}(H_2O)$ was found to be 0.50, showing a retardation of the reaction rate in D_2O medium. Proton-inventory studies were carried out performing the reaction in H_2O–D_2O mixtures with varying deuterium atom fractions n. The proton-inventory plots relating the rate constants k^n_{obs} with n are given in Fig. 1.

Test for Free Radicals

Addition of the reaction mixture to aqueous acrylamide solution did not initiate polymerization, showing the absence of free radical species.

DISCUSSION

A detailed study of monochloramines shows that similar equilibria exist in aqueous solutions of these compounds. Chloramine-T ionizes in aqueous solution and the anion picks up a proton in acid medium to give the free acid [7], monochloramine-T, RNHCl:

Table II Kinetic and Activation Data for the Oxidation of Neutral α-Amino Acids by CAT in $HClO_4$ Medium

Amino Acid	Temp (K)	$10^4 k_{obs}$ (s^{-1})	E_a (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J $mol^{-1}K^{-1}$)
Glycine	298	1.38	95.8	93.3	−6.8
	303	2.40			
	308	4.25			
	313	7.68			
Valine	298	3.98	73.6	71.0	−73.3
	303	5.45			
	308	7.68			
	313	13.1			
Alanine	298	4.00	72.2	69.7	−77.0
	303	5.92			
	308	8.79			
	313	14.1			
Phenyl-alnine	298	4.20	65.7	63.2	−99.0
	303	5.63			
	308	9.47			
	313	13.8			

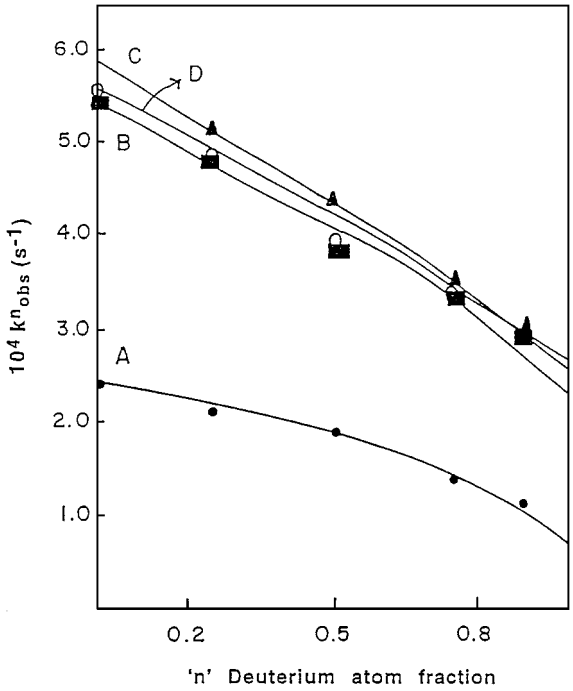


Figure 1 Proton-inventory plots for the oxidation of α-amino acids by CAT in H_2O–D_2O mixtures at 30°C: $[CAT]_0 = 3.00 \times 10^{-3}$ mol dm^{-3}; [amino acid]$_0 = 5.00 \times 10^{-2}$ mol dm^{-3}; $[HClO_4] = 6.00 \times 10^{-2}$ mol dm^{-3}; A: Gly; B: Val; C: Ala; D: Phe.

$$RNClNa \rightleftharpoons RNCl^- + Na^+ \quad (2)$$

$$RNCl^- + H^+ \overset{K_a}{\rightleftharpoons} RNHCl, \quad K_a = 2.82 \times 10^{-5} \text{mol dm}^{-3} \text{ at } 18^\circ\text{C} \quad (3)$$

Although the free acid has not been isolated, there is sufficient experimental evidence for its formation in solution [8]. It can further undergo disproportionation/hydrolysis giving RNH_2, dichloramine-T ($RNCl_2$), and HOCl:

$$2RNHCl \overset{K_d}{\rightleftharpoons} RNH_2 + RNCl_2, \quad K_d = 6.1 \times 10^{-2} \text{at } 25^\circ\text{C} \quad (4)$$

$$RNHCl + H_2O \overset{K_h}{\rightleftharpoons} RNH_2 + HOCl, \quad K_h = 4.88 \times 10^{-8} \text{at } 25^\circ\text{C} \quad (5)$$

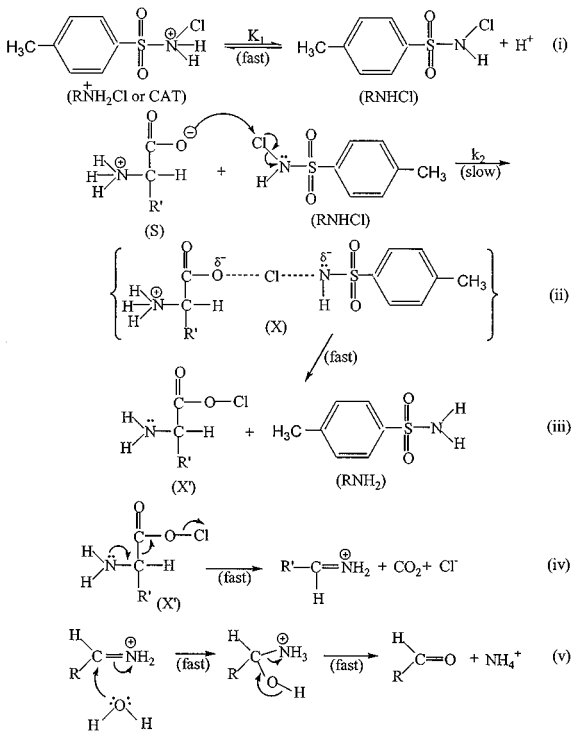
$$RNHCl + H^+ \rightleftharpoons RNH_2Cl^+ \quad (6)$$

The further protonation of RNHCl to RNH_2Cl^+ in a strong acid, $HClO_4$, is to be expected. The inverse first-order dependence of the rate on $[H^+]$ supports the involvement of RNHCl as the reactive species, as the equilibrium [Eq. (6)] predicts a retardation of

the rate with an increase in $[H^+]$. If $RNCl_2$ were to be the reactive species in the present investigations, then the rate law would predict a second-order dependence of the rate on [CAT], which is contrary to the experimental observations. If HOCl were primarily involved, a first-order retardation of the rate by the added *p*-toluenesulfonamide (RNH_2) would be expected. Since no such effect was noticed, HOCl can be ruled out as the oxidizing species. Hence, RNHCl is the reactive species of CAT responsible for the oxidation of amino acids. Furthermore, the variation of ionic strength of the medium and the addition of RNH_2 to the reaction mixture have no effect on the rate while the decrease in dielectric constant of the medium retards the rate. Bearing these facts in mind, a general scheme involving a direct interaction of the amino acid (S) with RNHCl in the rate-determining step is proposed in Scheme 1.

Amino acids are known to exist in different equilibria depending on the pH of the medium. In alkaline, neutral, and acidic media, amino acids exist as anions. ($R'CH(NH_2)COO^-$ or S^-), zwitterions ($R'CH(NH_3^+)COO^-$ or S), and cations ($R'CH(NH_3^+)COOH$ or SH^+), respectively.

In Scheme 1, the fast pre-equilibrium step (i) involving deprotonation of RNH_2Cl^+ forms the reactive oxidant species, RNHCl. In the slow step, an electrophilic attack by Cl^+ of RNHCl on the carboxylate anion of the substrate, resulting in the formation of an *N*-chloro-O bridged transition state, X, is envisaged. After the



SCHEME 1

transient state X is formed, the chlorine atom probably undergoes a Walden-type of inversion as the carboxylate anion attacks and kicks out the sulfonamide anion species, which is resonance stabilized and which later abstracts the acidic proton off the amino acid nitrogen and forms the sulfonamide product as in fast step (iii). In the subsequent fast steps (iv) and (v), the complex X′ undergoes intramolecular rearrangements and a nucleophilic attack by water to form end products including the aldehyde.

Application of the steady-state concept to the intermediate, RNHCl, in Scheme I leads to the rate law [Eq. (7)], which is in agreement with the kinetic data.

$$\text{rate} = \frac{-\mathrm{d}[\text{CAT}]}{\mathrm{d}t} = \frac{K_1 k_2 [\text{S}][\text{CAT}]}{[\text{H}^+]} \qquad (7)$$

The general mechanisms, reported by earlier workers [2], for the oxidation of several amino acids by CAT in different acid media differ from the above general Scheme I proposed for the oxidation of four amino acids in $HClO_4$ medium. They have proposed two general, mechanistic pathways leading to products involving the interaction of the substrate with different reactive species of CAT in the rate-determining step [2]. The first pathway involves RNHCl while the second one involves Cl_2 or H_2OCl^+ as reactive species. The mechanistic differences can be attributed to the following: As CAT in aqueous solutions can furnish such reactive species as $RNCl^-$, RNHCl, RNH_2Cl^+, H_2OCl^+, Cl_2, and $RNCl_2$, varying reaction conditions like acid medium and nature of the amino acid can initiate an interaction of the substrate with a known reactive species of CAT, especially in the slow step.

(i) In the present study, tests [9] for the applicability of the Taft equation as well as single-parameter correlations for the amino acids were made. A linear regression of results yielded the following equations:

$$\log k_2 = -0.274\sigma^* - 2.003; \quad r = 0.8369 \qquad (8)$$

$$\log k_2 = -0.252E_s - 2.004; \quad r = 0.8705 \qquad (9)$$

$$\log(k_2 - E_s) = -0.393\sigma^* - 2.003; \quad r = 0.4593 \qquad (10)$$

The reasonable correlations between log k_2 and σ^* [Eq. (8)] and log k_2 and E_s [Eq. (9)] indicate that the steric effects are more important than electronic factors. However, an examination of Eq. (10) shows a poor correlation for the combined effect of polar and steric factors. A negative

value of reaction constant ($\rho^* = -0.274$ or -0.393) indicates that the presence of electron-donating groups increase the rate of reaction. It is seen from Table I that the rate of oxidation of amino acids increases in the following order: Gly < Val < Phe < Ala.

(ii) The rate of reaction decreases in D_2O medium and the values of the ratio $k_{obs}(D_2O)/k_{obs}$ (H_2O) are 0.49, 0.52, 0.49, and 0.50 for glycine, valine, alanine, and phenylalanine, respectively. The deuterated species RNClD, DOC1, and DO^- are expected to be present in heavy water under these conditions. The inverse solvent-isotope effect can be correlated with the greater acidity of D_3O^+ ions compared to H_3O^+ ions (by a factor of 2–3), resulting in a greater retardation of the rate in D_2O medium [10,11]. Proton inventory studies could throw some light on the nature of the transition state. The dependence of rate constants k^n_{obs} on n, the atom fraction of deuterium, in solvent mixtures containing H_2O and D_2O is given [12,13] by the Grass–Butler relationship [Eq. 11]

$$k^0_{obs}/k^n_{obs} = \frac{\Pi^{TS}(1 - n + n\Phi_i)}{\Pi^{RS}(1 - n + n\Phi_j)} \qquad (11)$$

where Φ_i and Φ_j are the isotopic fractionation factors (equilibrium constants for the H–D exchange) for isotopically exchangeable hydrogen sites in the transition state (TS) and the reactant state (RS), respectively. A knowledge of isotopic fractionation factors of reactants (Φ_j) would enable us to calculate the fractionation factors of the transition state (Φ_i). However, from a qualitative point of view, curvatures of the proton-inventory plots in Fig. 1 were compared with those of the standard curves in the literature [14] and it was concluded that a H^+ ion is involved in the transition state formation.

(iii) The rate decreased with decrease in dielectric constant (D) of the medium. A plot of log k_{obs} vs. $1/D$ was linear with a negative slope. The effect of D on the rate for a reaction involving two ions is given [15] by the standard relationship, Eq. (12)

$$\log k = \log k_0 - Z_A Z_B e^2/DkTd_{AB} \qquad (12)$$

where k_0 is the rate constant in a medium of infinite dielectric constant, $Z_A e$ and $Z_B e$ are the charges, d_{AB} is the activated complex size, k is the Boltzmann constant, and T is the absolute temperature. From the slope $= -Z_A Z_B\ e^2/kT\ d_{AB}$, the values of d_{AB} were computed as 2.0, 1.67, 1.51, and 1.67 Å for glycine, valine, alanine, and phenylalanine, respectively. The values are found to be reasonable in comparison with those of other reactions of similar nature [16].

(iv) The data in Table II show that the energy of activation is the highest for the slowest reaction, indicating that the reaction is enthalpy controlled. Furthermore, values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ can be correlated linearly ($r = 0.9990$, $s = 0.02$) resulting in an isokinetic relation (Fig. 2), indicating

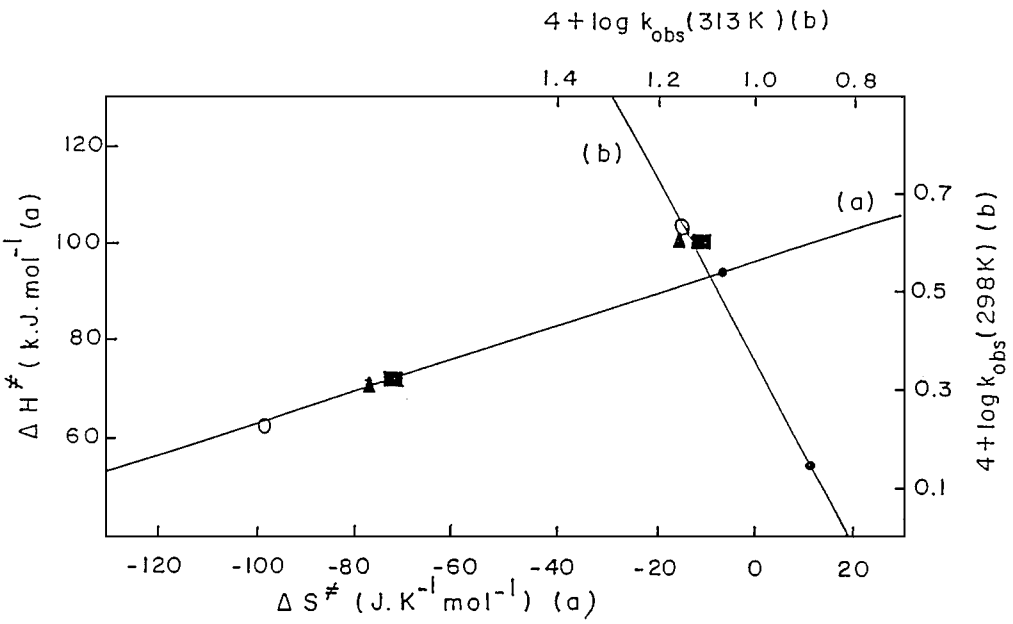


FIGURE 2 Isokinetic plots of (a) $\Delta H^{\neq}$ vs. $\Delta S^{\neq}$ and (b) log k_{obs}(313 K) vs. log k_{obs}(298 K): $[CAT]_0 = 3.00 \times 10^{-3}$ mol dm^{-3}; $[\text{amino acid}]_0 = 5.00 \times 10^{-2}$ mol dm^{-3}; $[HClO_4] = 6.00 \times 10^{-2}$ mol dm^{-3}.

that a common mechanism operates in the oxidation of the selected amino acids by CAT. The slope gives the value of the isokinetic temperature β as 323 K, which is much higher than the experimental temperature. The relationship was proved to be genuine through the Exner criterion [17] by plotting log k_{obs}(313 K) vs. log k_{obs}(298 K) ($r = 0.9955$, $s = 0.04$, Fig. 2). The value of β calculated from the relationship,

$$\beta = T_1(1 - q)/(T_1T_2) - q$$

where q is the slope of the Exner plot, was found to be 333 K, which is close to the isokinetic point (323 K) calculated from the enthalpy–entropy relationship. It is seen that the value of β is higher than the experimental temperature (303 K) indicating the reactions seem to be controlled by enthalpy.

CONCLUSION

In the present kinetic study of the oxidation of neutral α-amino acids, Gly, Val, Ala, and Phe, by CAT in $HClO_4$ medium, a general mechanism involving the interaction of the substrate (S) with the reactive species of CAT (RNHCl) in the slow step, which is different from the ones previously reported [1,2] for several amino acid substrates, has been proposed. This mechanism is supported by the experimental data such as the reaction stoichiometry, the oxidation products, the rate law, the proton-inventory plots, the activation parameters, and the Taft relationship.

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