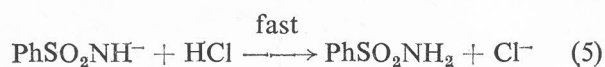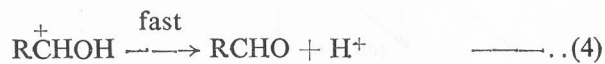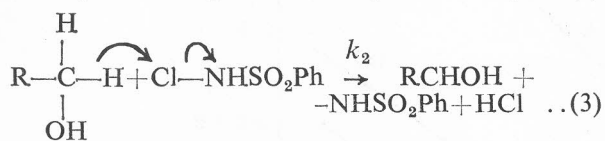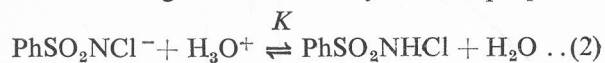constants at 298K and 313K are —2.20 ($r = 0.9993$) and —1.80 ($r=0.9999$) respectively. The large negative reaction constant and substantial kinetic isotope effect indicate a considerable carbonium ion character in the transition state. The above results point to a hydride ion transfer in the rate-determining step.

The following mechanism may then be proposed.

$$PhSO_2NCl^- + H_3O^+ \overset{K}{\rightleftharpoons} PhSO_2NHCl + H_2O \quad ..(2)$$

$$R\!-\!\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}\!-\!H + Cl\!-\!NHSO_2Ph \xrightarrow{k_2} \overset{+}{R}CHOH + \\ -NHSO_2Ph + HCl \quad ..(3)$$

$$\overset{+}{R}CHOH \xrightarrow{fast} RCHO + H^+ \quad \text{———} ..(4)$$

$$PhSO_2NH^- + HCl \xrightarrow{fast} PhSO_2NH_2 + Cl^- \quad (5)$$

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Kinetics of Oxidative Deamination & Decarboxylation of Some Amino Acids by Diperiodatocuprate(III) in Alkaline Medium

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The kinetics of oxidation of glycine, alanine, phenylalanine, valine, leucine and serine by diperiodatocuprate(III) in alkaline medium has been studied. The order in [amino acid] and [Cu(III)] is one each. The rate decreases with increase in [OH⁻] and [periodate]. The products of oxidation are CO_2, NH_3 and the corresponding aldehydes. A probable mechanism consistent with the observed results is discussed.

DIPERIODATOCUPRATE(III) (DPC) has been used in the estimation of amino acids[1]. Cu(III) is also shown to be an intermediate in the Cu(II)-catalysed oxidation of amino acids by peroxodisulphate[2]. Therefore it was worthwhile to study the kinetics of oxidation of amino acids by diperiodatocuprate(III) in alkaline medium.

All the chemicals used were of AR(BDH) grade. Amino acids were either Fluka or BDH products. DPC was prepared by a method given earlier[3]. The course of the reaction was followed by measuring the absorbance of unreacted DPC at 413 nm at regular time intervals, using Carl Zeiss spectrophotometer. The reactions were usually followed upto 50 to 60% completion. The molar absorption coefficient of Cu(III) under our experimental conditions was 1.0×10^4 litre mol^{-1} cm^{-1}. Blank reactions were carried out and necessary corrections made for any self-decomposition of DPC during the reaction.

Under the conditions employed the products of the reaction were identified[4] as ammonia, carbon dioxide and the corresponding aldehydes. Stoichiometric studies, carried out by adding dropwise DPC of known concentration to 0.1 M glycine until no further decolourisation occurred, revealed that one mol of amino acid required 2 mol of DPC.

Under the conditions [AA] ≫ [DPC] the plot of log [absorbance] versus time was linear showing that the reaction is first order in [DPC] (Fig. 1A). This was also confirmed by varying [DPC], which did not show any change in pseudo-first order rate constants (k'). The reactions also exhibited a first order dependence in [AA] (Fig. 1B). At constant [DPC], [AA] and temperature the rate decreased with increasing [OH⁻] and also [periodate] (Table 1).

The diperiodatocuprate(III), $[Cu(IO_6)_2]^{7-}$ has been demonstrated to exist as an aquo or hydroxyhydroperiodatocuprate(III)[5] which we prefer to express as $Cu(HL)_2$ in our discussion. The effect of periodate on the rate of oxidation is similar to that observed in our earlier work[3] suggesting monoperiodatocuprate(III) to be the active species of DPC in the oxidation of amino acids.

Contrary to the earlier observation in the oxidation of alcohols by DPC[3] the rate decreased with the increasing [OH⁻] at constant [DPC], [AA] and [IO₄⁻]. This could be due to the existence of the equilibrium (1) in alkaline medium.

$$R\!-\!\underset{\underset{+NH_3}{|}}{CH}\!-\!COO^- + OH^- \rightleftharpoons R\!-\!\underset{\underset{NH_2}{|}}{CH}\!-\!COO^- + H_2O \quad ..(1)$$
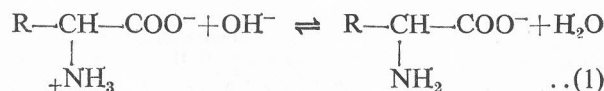
According to equilibrium (1) the rate should decrease with the increasing [OH⁻] if the dipolar form of the amino acid is the reactive species. This was found to be true, indicating that dipolar form of the amino acid is the reactive species even in alkaline medium.

TABLE 1— EFFECT OF VARYING [KOH] AND [KIO₄] ON RATE OF OXIDATION OF GLYCINE

[Cu(III)] = $5.10 \times 10^{-5}M$; [Glycine] = $2.00 \times 10^{-3}M$; temp = 300K

[KOH] $\times 10^2$ (M)	[KIO₄] $\times 10^4$ (M)	$k' \times 10^3$ (min⁻¹)	[KOH] $\times 10^2$ (M)	[KIO₄] $\times 10^4$ (M)	$k' \times 10^2$ (min⁻¹)
1.0	6.8	5.40	4.0	6.8	2.40
2.0	6.8	3.70	1.0	3.4	7.10
2.5	6.8	3.20	1.0	10.2	4.03
3.0	6.8	2.80	1.0	20.4	2.80
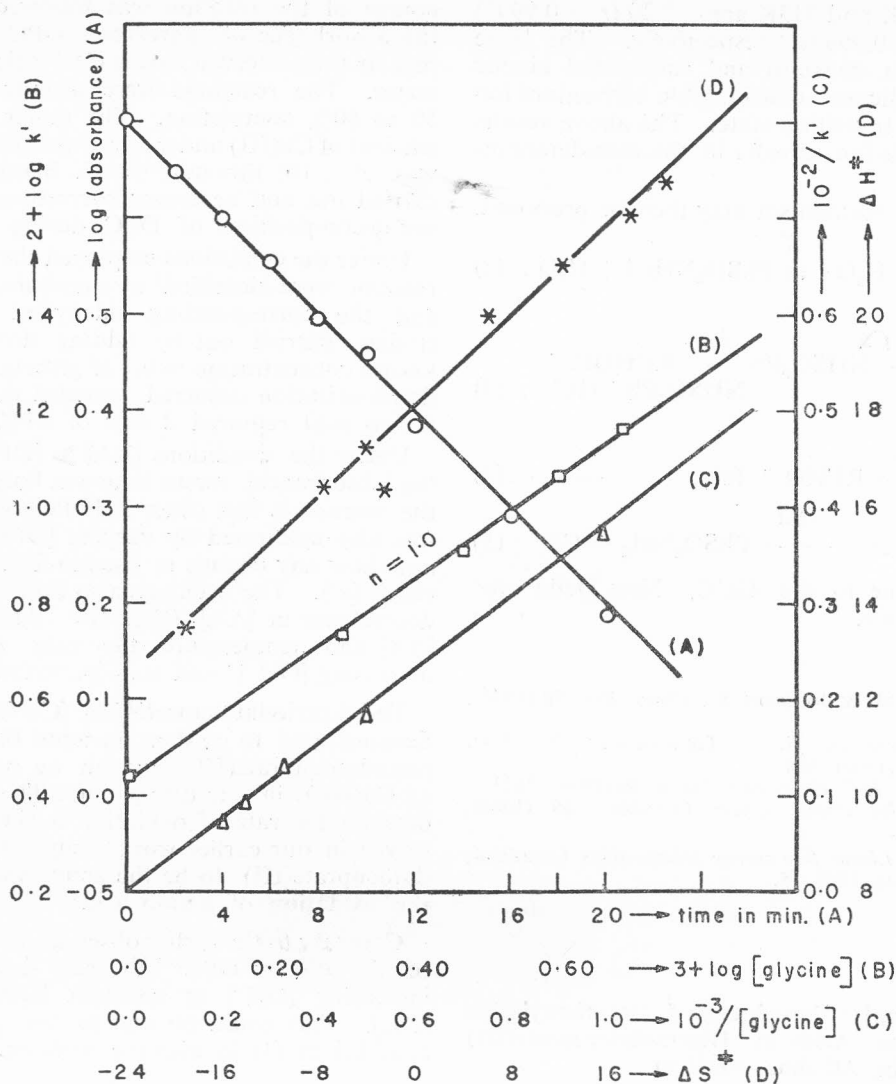
Fig. 1 — (A) Plot of 1+log (absorbance) versus time; [Cu(III)] = 5.100 × 10⁻⁵ M; [KIO₄] = 6.80 × 10⁻⁴ M [glycine] = 2.00×10⁻³M [KOH]=0.01M temp.=300 K. (B) Plot of 2 + log k′ versus 3 + log [glycine] [Conditions same as in A] (C) Plot of 10⁻²/k′ versus 10⁻³/[glycine]: [Conditions same as in A] (D) Plot of $\triangle H\ddagger$ versus $\triangle S\ddagger$

Such presumptions are not uncommon in literature; e.g. Bell and Ramsden[6] postulated free amine as the reactive species in the bromination of alkylamines even at as high a concentration of H_2SO_4 as 8M. Recently Rao et al.[7] also reported free amine as the reactive form instead of RNH^+ in the oxidation of aliphatic amines by Ce(IV) in HNO_3 medium.
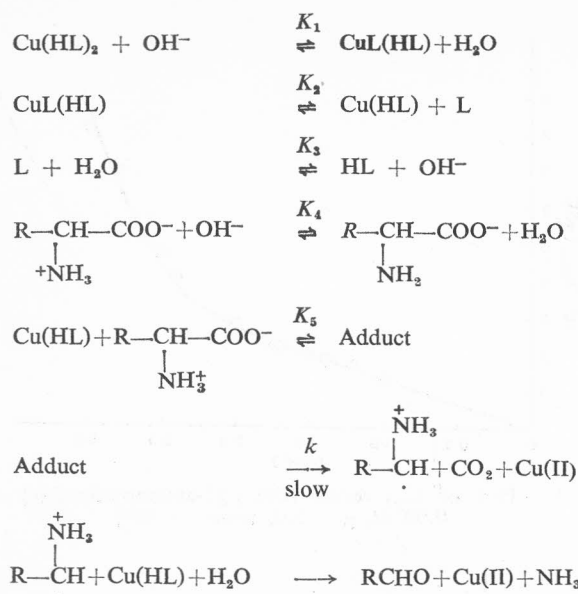
The plot of 1/k′ versus 1/[AA] was linear (Fig. 1C) passing through the origin indicating absence of any complex formation between the substrate and the oxidant. The observed negative salt effect suggests that the reaction is of the ion-dipole type. The mechanism consistent with the observed results is shown in Scheme 1.

The product analysis, observed stoichiometry and induced polymerisation of acrylamide supports the proposed mechanism. The rate law comes out to be

$$-\frac{d[DPC]}{dt} = \frac{k\,K_1\,K_2\,K_5\,[Cu(HL)_2]\,[R—CH—COO^-]\{1+K_3([HL]+[OH^-])\}}{K_3K_4[OH^-][HL]\{1+K_1[OH^-]\}}$$

with the NH_2 group indicated on the $R—CH—COO^-$.

which substantiates the rate data obtained.

The presence of electron withdrawing groups at α-carbon such as —CH_2Ph, —CH_2OH etc. increased the rate, whereas electron releasing groups such as —CH_3 decreased the rate (see Table 2). The decrease in the rate of oxidation with increasing chain length (Table 2) among the amino acids can be ascribed to the difficulty in the formation of the adduct due to the decrease of positive charge on the N atom caused by +I effect of alkyl groups and also steric effect. But the same analogy cannot be extended to the greater oxidation rate of serine as compared to alanine in which —I effect of OH group induces a more posi-

$$Cu(HL)_2 + OH^- \underset{}{\overset{K_1}{\rightleftharpoons}} CuL(HL) + H_2O$$

$$CuL(HL) \underset{}{\overset{K_2}{\rightleftharpoons}} Cu(HL) + L$$

$$L + H_2O \underset{}{\overset{K_3}{\rightleftharpoons}} HL + OH^-$$

$$\underset{\underset{+NH_3}{|}}{R-CH-COO^-} + OH^- \underset{}{\overset{K_4}{\rightleftharpoons}} \underset{\underset{NH_2}{|}}{R-CH-COO^-} + H_2O$$

$$Cu(HL) + \underset{\underset{NH_3^+}{|}}{R-CH-COO^-} \overset{K_5}{\rightleftharpoons} Adduct$$

$$Adduct \underset{slow}{\overset{k}{\longrightarrow}} \underset{\underset{\cdot}{|}}{R-CH} + CO_2 + Cu(II) \quad (\overset{+}{N}H_3)$$

$$\underset{\underset{\cdot}{|}}{\overset{+}{N}H_2} R-CH + Cu(HL) + H_2O \longrightarrow RCHO + Cu(II) + NH_3$$

Scheme 1

tive charge on the N-atom thus facilitating adduct formation.

The rate of oxidation increased with decrease in pK_b values of amino acids. This further supported the dipolar form of the amino acid to be the active form in the present work.

Activation parameters for all the substrates have been evaluated and are listed in Table 2. The differences in the $\triangle S\ddagger$ values were found to be higher than the corresponding changes in E_{exp} values and hence the reactions may be considered as entropy controlled. This is evident from the E_{exp}^a value which is high for the fastest reaction and vice versa. This contention receives further support from the isokinetic temperature (β) value (225 K) (obtained from the plot of $\triangle H\ddagger$ versus $\triangle S\ddagger$; Fig. 1D) which is lower than the experimental temperature range (287-307 K) used.

TABLE 2 — SECOND ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS

[Cu(III)] = $5.10 \times 10^{-5}M$; [KOH] = $0.10M$; temp. = 300 K; [KIO$_4$] = $6.80 \times 10^{-4}M$

Amino acid	pK_b	$k'' \times 10^2$ (litre mol^{-1} (sec^{-1})	E_{exp}	$\triangle G\ddagger$	$\triangle H\ddagger$	$\triangle S\ddagger$ cal deg^{-1} mol^{-1}
Glycine	9.60	45.6	25.0	18.0	21.8	12.6
β-Alanine	10.1	6.00	14.7	19.2	13.5	—19.0
α-Alanine	9.75	21.5	18.4	18.4	17.2	—4.10
Phenylalanine	8.95	921	23.9	16.3	22.7	21.0
Leucine	9.60	40.0	21.1	18.0	19.9	6.30
Valine	—	16.8	17.5	18.6	16.3	—7.70
Serine	9.15	230	23.4	16.9	22.2	18.1

Values of E_{exp} $\triangle G\ddagger$ and $\triangle H\ddagger$ in kcal mol^{-1}

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Kinetics & Mechanism of Reaction between 2-Amino-pyrimidine & Sodium Hydroxide

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The title reaction has been investigated in strong alkaline medium (1.0 to 3.0 M NaOH solution) at 95°. The reaction is psuedo-first order and the rate constants increase with increasing [alkali]. The dependence of rate on [alkali] is linear at [OH$^-$] = 1.0 to 2.0 M, thereafter a sharp increase in the reaction rate is observed. A suitable mechanism involving monoanionic and dianionic tetrahedral intermediates is suggested and the following rate equation has been derived.

$$k_{obs} = \frac{k_1 [OH^-]}{k_{-1} + k_2 + k_3 [OH^-]} (k_2 + k_3 [OH^-])$$

BROWN[1] has reported the conversion of 2-aminopyrimidine into 2-hydroxypyrimidine by heating with 10 N NaOH under reflux for 12 hr at 120°. The kinetics of this reaction has not been reported so far and the work described in the present note is an attempt in this direction.

2-Aminopyrimidine (Fluka) was used as such. The stock solution of carbonate-free sodium hydroxide was prepared and diluted to the required concentration using doubly distilled water. Other chemicals used were of reagent grade. Sodium nitrate was used for adjusting ionic strength.

Kinetic measurements — A mixture of sodium hydroxide and sodium nitrate was equilibrated at the desired temperature maintained within ± 0.1°. The reaction vessel was fitted with double walled condenser to check evaporation. 2-Aminopyrimidine solution was added and a slow stream of ammonia free nitrogen gas was bubbled through the reaction mixture.

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