



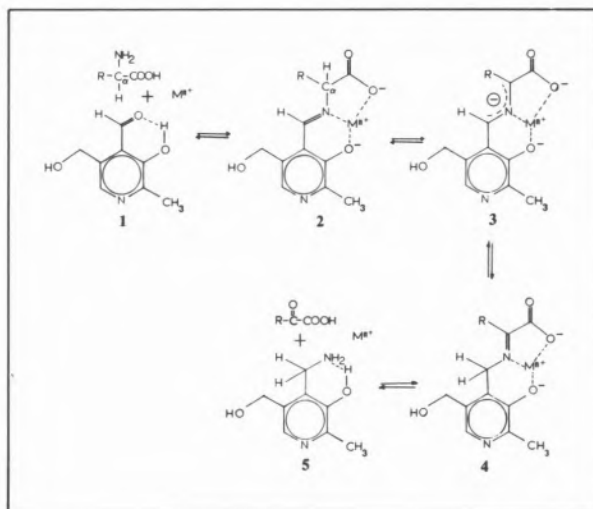
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A PROTON-NMR STUDY OF THE KINETICS OF FORMATION OF THE GENERAL INTERMEDIATE IN VITAMIN B-6-CATALYZED TRANSAMINATION

The rates of the transamination reactions of α -amino acids and α -keto acids have been determined by measurement of the 200 MHz proton NMR spectra of the functional groups of the Al(III) complexes of the Schiff bases **2**, **4** formed with pyridoxal **1** and pyridoxamine **5** respectively. Reaction systems measured in D₂O at 10°C consisted of 1:1:1 molar ratios of pyridoxal: α -amino acid:Al(III) or pyridoxamine: α -keto acid:Al(III). Amino and keto acids employed are alanine, α -aminoisobutyric acid, valine, phenylglycine, pyruvic acid, and α -ketobutyric acid. A negative deprotonated intermediate **3** was detected in all systems that undergo transamination (*i.e.*, except α -aminoisobutyric acid). The intermediate resembles the aldimine with NMR resonances shifted upfield in accordance with its greater negative charge. With Al(III) and pyridoxal as catalysts the equilibrium concentrations of the intermediate formed from α -amino acids are reached in the time required to reach transamination equilibrium and is maintained in solution at a fraction (± 10 -20%) of the aldimine Schiff base concentration. In the reverse reaction with Al(III) and pyridoxamine as catalysts, α -keto acids produce the intermediate initially at higher concentrations than those of the aldimine reaction product. The ratios of these species change as equilibrium is reached, to give the same fraction of Al(III)-stabi-

lized intermediate as that obtained in the forward reaction. The relative changes in concentration of the α -deprotonated carbanion **3** and reaction products (the Schiff base chelates **2** and **4**) with time clearly demonstrate it to be the common mandatory intermediate in both the forward and reverse metal ion-catalyzed transamination reactions.



For the metal-free enzyme systems it is suggested that the active intermediate is an analogous deprotonated intermediate with a proton coordinated to the azomethine nitrogen in place of the metal ion in **3**. This type of intermediate, first suggested by ABBOTT and MARTELL [1], is suggested as the transamination intermediate in place of the quinonoid-type Schiff base tautomer previously suggested [2,3].

REFERENCES

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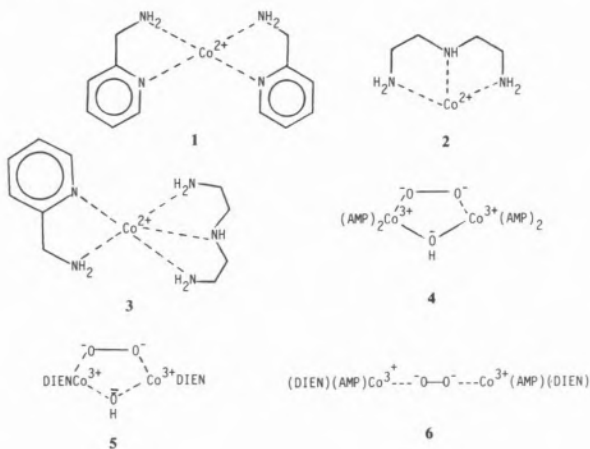


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REACTIONS OF DIOXYGEN COMPLEXES. AUTOXIDATION OF 2-AMINOMETHYL- PYRIDINE THROUGH COBALT DIOXYGEN COMPLEX FORMATION

The metal complex formation constants and the oxygenation constants of the cobalt(II) complexes of diethylenetriamine (DIEN) and 2-aminomethylpyridine (AMP) have been determined by potentiometric measurements under N_2 and O_2 . In the mixed ligand system three cobalt complexes are formed which are capable of combining with dioxygen: the 2:1 AMP complex, **1**, the 1:1 DIEN complex, **2** and the 1:1:1 mixed ligand DIEN, AMP complex, **3**. The corresponding dioxygen complexes are indicated by formulas **4**, **5**, and **6**. The equilibrium constants for the mixed ligand system have been employed to determine the conditions under which the concentration of **3** has its maximum value, and the conditions that favor the formation of the mixed ligand dioxygen complex **6**.



The kinetics of oxidative dehydrogenation of **3** through the formation and degradation of **6** have been measured spectrophotometrically and rate constants are reported. The reaction has been found to be second order, first order in the concentration of the dioxygen complex and first order in the concentration of hydroxide ion. The reaction product in the two-electron oxidation of AMP is the corresponding imine, which under the reaction conditions employed is converted to pyridine-2-carboxaldehyde, determined quantitatively as the 2,4-dinitrophenylhydrazone. The proposed reaction mechanism involves deprotonation of the amino group, through the influence of the Co^{3+} center, as a pre-equilibrium step. This is followed by a concerted process involving homolytic fission of dioxygen, shift of an electron through the metal ion to the coordinated oxygen, and transfer of the α -proton to the oxygen atom. The two-electron oxidation of each AMP ligand is thus balanced by conversion of half of the dioxygen to water, with regeneration of cobalt(II). The proximity of the dioxygen to the α - CH_2 of the ligand is considered an important requirement for this concerted mechanism.



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COORDINATION ABILITIES OF SUBSTITUTED PHENOLATES — A SPECTROPHOTOMETRIC AND CONDUCTOMETRIC STUDY

The copper(II) — phenolate oxygen interaction in several mixed-ligand complexes of copper(II) containing a heterocyclic amine and a phenol has been studied by electronic spectral,