Insertion of Hydrogen Isocyanide in Acid-catalysed Reactions of Organopentacyanocobaltate(III) Ions

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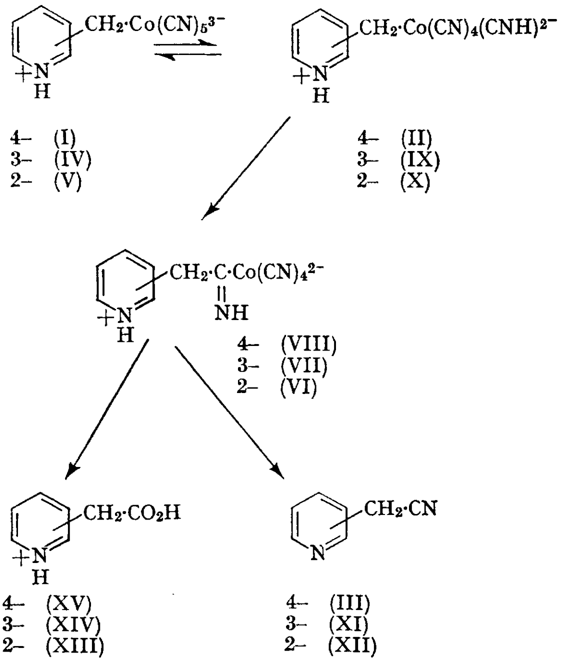
WE have recently shown[1] that the acid-catalysed decomposition of the 4-pyridiomethylpentacyanocobaltate(III) ion (I) involves the decomposition of the protonated species (II), which contains the HNC ligand. The only product that could be isolated from this reaction was the nitrile (III), and an insertion mechanism was suggested.

We now report that comparative kinetic and n.m.r. studies on the acid-catalysed decomposition of the 2-, 3-, and 4-pyridiomethylpentacyanocobaltate(III) ions (V, IV, and I, respectively) show that the primary product, in each case, is that (VI, VII, or VIII) formed by insertion of the hydrogen isocyanide ligand in the corresponding conjugate acid (X, IX, or II, respectively), between the organic group and the metal atom. Addition of base to the solution of the insertion product gave the nitrile (XII, XI, III, respectively) in 66, 26, and 20% yield respectively, but prolonged heating of the insertion product solution in 25% H_2SO_4 at 60° yields two main products; namely the ammonium ion and the corresponding pyridioacetic acid (XIII, XIV, or XV).



Thus, for example, the ^1H n.m.r. spectrum of the yellow solution of the 3-pyridiomethylpentacyanocobaltate(III) ion in 25% H_2SO_4 shows the methylene singlet at τ 6·90 which changes quite rapidly at 33° to the broad methylene singlet (τ 5·1) of the green insertion product and then, much more slowly, even at 60°, to the methylene singlet (τ 5·75) of the pyridioacetic acid and the triplet (τ 1·98, 3·04, and 3·80) of the ammonium ion. The first change exactly parallels the rate of loss of the charge transfer band (λ_{max} 320 mμ) of the 3-pyridiomethylpentacyanocobaltate(III) ion. Similar results were obtained with the 2- and 4-ions. In none of the three cases could the pyridioacetic acid have been formed by hydrolysis of the pyridioacetonitrile, because the latter is much more stable than any of the observed intermediates. The 2- insertion product is much less stable than the 3- and 4-insertion products, probably because of hydrogen bonding between the inserted and the heteroaromatic nitrogen atoms in the former, which facilitates nucleophilic attack at the iminyl carbon.

The relative rates of the insertion reactions are 3 > 4 > 2, and oxygen does not affect the products or the rate of the reactions. This appears to rule out any carbanion or radical intermediates or any carbanionoid character in the transition state,[2,3] and suggests that the insertion process is concerted.

(*Received, February 7th*, 1967; *Com.* 117.)

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[1] M. D. Johnson, M. L. Tobe, and Lai-Yoong Wong, *J. Chem. Soc.* (*A*), in the press.

[2] M. D. Johnson and J. R. Coad, *J. Chem. Soc.* (*B*), in the press.

[3] R. G. Coombes and M. D. Johnson, *J. Chem. Soc.* (*A*), 1966, 177.