Here a five membered cyclic intermediate is known to be involved.

Hydrolysis of the cyclic anhydride (III, R = H) can proceed by the attack of a water molecule at phosphorus or at the carbon atom of the carbonyl group. Two of our experiments indicate that the former is more likely. (i) Reversal of the hydrolytic sequence is observed when the dianion (IV, R = H) as the monocyclohexylammonium monopyridinium salt is heated to reflux in methanolic solution. After 5 hr. the starting material had disappeared and comparable amounts of inorganic phosphate and the monomethyl ester (IV, R = CH_3) could then be detected.[11] (ii) Treatment of the monocyclohexylammonium phosphoenol pyruvate with a 10% excess of dicyclohexylcarbodiimide in dry pyridine solution gave a readily hydrolyzed compound which we believe to be the cyclic anhydride (III, R = H). Removal of N,N-dicyclohexyl urea and solvent left a viscous oil having a *single* carbonyl absorption at 1785 cm.$^{-1}$ and P=O and P—O—alkyl bonds at 1290 and 1110 cm.$^{-1}$.[12] Addition of methanol to a pyridine solution of the compound prepared in this way gave immediately the monomethyl ester (IV, R = CH_3)[14] *but no carboxylic ester*.

Addition of an excess of cyclohexylamine to a pyridine solution prepared as before gave the enol phosphoramidate {(IV, $-NH\cdot C_6H_{11}$). *Anal.* Found for the barium salt: C, 29.1; H, 5.12; N, 3.58. $C_9H_{14}PO_5NBa\cdot H_2O$ requires C, 29.1; H, 4.53; N, 3.77.} *but no carboxylic amide*. Thus, the cyclic anhydride appears to be a powerful *phosphorylating* agent. This is in contrast to open-chain acyl phosphates, which are normally acylating agents.[15-17]

However, this behavior is not entirely unexpected, as four-covalent phosphorus in a five-membered ring is known to be exceptionally susceptible to nucleophilic attack.[18,19] The participation of a neighboring carboxyl group has been implicated by Chanley, *et al.*,[11,20] in the hydrolysis of salicyl phosphate near pH 5; this ester, too, is stable at pH 8.5.

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(10) The vicinal hydroxyl also catalyzes the removal of the second esterifying group in basic solution. Presumably a neutral (OH) can approach the negatively-charged phosphate residue more effectively than carboxylate anion, removal of a proton taking place after this has occurred.

(11) *Cf.* J. D. Chanley, E. M. Gindler, and H. Sobotka, *J. Am. Chem. Soc.*, **74**, 4347 (1952).

(12) Each of these three absorption bands is at a higher frequency than usual[13] as would be expected for the cyclic structure III.

(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1958, pp. 178, 311.

(14) Isolated as the barium salt in 60% yield within 10 min.

(15) F. Lipmann, and N. O. Kaplan, *Ann. Rev. Biochem.*, **18**, 267 (1949).

(16) D. E. Koshland, *J. Am. Chem. Soc.*, **73**, 4103 (1951).

(17) F. Cramer and K.-G. Gärtner, *Chem. Ber.*, **91**, 1562 (1958).

(18) J. R. Cox, R. E. Wall, and F. H. Westheimer, *Chem. Ind.* (London), 929 (1959).

(19) P. C. Haake and F. H. Westheimer, *J. Am. Chem. Soc.*, **83**, 1102 (1961).

(20) J. D. Chanley and E. M. Gindler, *ibid.*, **75**, 4035 (1933).

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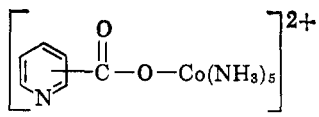
Isomeric Pyridinecarboxylates as Bridging Groups in Oxidation–Reduction Reactions. Electron Transfer through Nitrogen

Sir:

Comparison of the rates of reduction of the isomeric pyridinecarboxylatopentaamminecobalt(III) ions



(2-, 3-, 4-)

with Cr(II) indicates that electron transfer may occur through nitrogen, resulting ultimately in reduction of tripositive cobalt bound to the carboxylate group. Like other conjugation-related effects exhibited by pyridine derivatives, this path may be observed for α and γ substituents, but not for β.

The rates of reduction of these carboxylato complexes and of two pyridinedicarboxylato complexes are compared with rates for the corresponding N-methyl derivatives[1] in Table I. For the nonmethylated complexes,

TABLE I

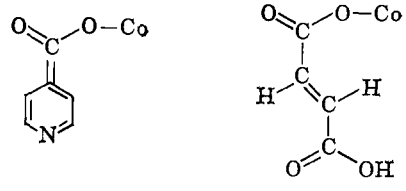
SPECIFIC RATES FOR REDUCTION OF PYRIDINECARBOXYLATOPENTAAMMINECOBALT(III) IONS WITH Cr^{2+}

Ligand	pK_{BH^+}	k_{BH^+} (acid path)	k_B (basic path)	k_{Me} (N-methyl deriv.)
	(l. mole^{-1} sec.$^{-1}$, 25°, μ = 3.0)			
Pyridine-2-carboxylato	4.49	...	2×10^5	0.087
Pyridine-3-carboxylato	4.73	0.11	...	0.13
Pyridine-4-carboxylato	4.79	1.3	1.5×10^3	1.4
Pyridine-2,5-dicarboxylato	<0	...	>200	8
Pyridine-2,6-dicarboxylato	<0	...	>150	...

rates may be expressed as the sum of two terms, pertaining, respectively, to the protonated form of the complex ($HPyCOORo^+$) and to the nonprotonated form (PyCOORo)

$$-[d(Co(III))/dt] = k_{BH^+}(Cr^{2+})(HPyCOORo^+) + k_B(Cr^{2+})(PyCOORo)$$

where k_{BH^+} and k_B, the specific rates for the acidic and basic forms, are evaluated from the dependence of rate on acidity and from K_{BH^+}, the acidity constants of $HPyCOORo^+$. As indicated in Table I, only the basic path was detected for the 2-isomer, even in 3 M $HClO_4$. Both paths are observed with the 4-isomer, whereas only the acidic path appears with the 3-isomer, which reacts at a rate comparable to the N-methylated complexes. The marked similarity between the 4-carboxylato complex and the fumarato complex



which is known to undergo reduction by attack on the noncoordinated carboxyl group,[2] strongly suggests that the basic path for reduction of the 4-carboxylato complex is associated also with remote attack by Cr(II), in this case on the nitrogen atom. However, the spectrum of the product (ϵ_{max} 23.6 (410 mμ), 19.5 (579 mμ)), is very similar to that obtained from reduction of the isomeric 3-carboxylato complex (ϵ_{max} 22.6

(1) Cobalt analyses for complexes described (prepared as the perchlorates) were in agreement with indicated formulas. Preparations, as well as analyses, will be described subsequently in a more detailed report.

(2) D. K. Sebera and H. Taube, *J. Am. Chem. Soc.*, **83**, 1785 (1961); R. T. M. Fraser and H. Taube, *ibid.*, **83**, 2239 (1961).

(410 mμ), 21.2 (577 mμ)), and to that of the acetato complex, $(H_2O)_5CrOAc^{2+}$ (ϵ_{max} 20.7 (406 mμ), 21.6 (568 mμ)).[3] Apparently, then, the N–Cr bond does not survive, but the N-coordinated Cr(III) complex is rapidly re-equilibrated, possibly by Cr(II) catalysis, to the more stable carboxylato-coordinated complex.

The much higher absorbance of the product derived from reduction of the 2-carboxylato complex (ϵ_{max} 50.8 (406 mμ), 32.8 (553 mμ)) indicates that here the product is chelated and thus features a Cr(III)–N bond. Because Cr is bound both to oxygen and nitrogen, the identity of the product does not identify the atom through which electron transfer has occurred. The very high rate of reduction, *i.e.*, about one million times that associated with the pentaamminemalonato complex (which also forms a chelated product) indicates transfer through nitrogen.

Reductions of the complexes of pyridine-2,5-dicarboxylic and 2,6-dicarboxylic acids, even in 3 *M* $HClO_4$, are immeasurably fast under our conditions. Almost certainly, these proceed predominantly by the basic path. Our lower limits for the rate constants fall so much below the values for the 2- and 4-monocarboxylato complexes because the dicarboxylato complexes are much the weaker bases. Both complexes appear to yield chelated chromium products (ϵ_{max} for the 2,5-derivative: 40.9 (403 mμ), 29.2 (562 mμ); ϵ_{max} for the 2,6-derivative: 44 (428 mμ), 102 (557 mμ)). It is likely that the 2,6-derivative is reduced in the same manner as the 2-carboxylate complex, but another route must be considered for the 2,5-complex. The nonprotonated form of the 2,5-complex is twice as strongly basic as the corresponding form of the 2,6-complex (pK_A values of 3.80 and 3.45, respectively), suggesting that the acid-strengthening Co^{3+} ion is coordinated to the 5-, rather than the 2-, carboxyl group. Since the coordinated and noncoordinated carboxy groups lie *para* to each other, remote attack, as has been demonstrated for reduction of the terephthalato complex in this series,[1] may occur, but in this case it is facilitated by chelation to nitrogen.

Remote attack, but not chelation, is possible also in reduction of the N-methylated 2,5-dicarboxylato derivative, and the specific rate for this complex is significantly greater than for reductions of the other N-methylated complexes. It is, however, only about one tenth as rapid as reduction of the terephthalato complex, probably because the α-carboxyl is pushed out of the plane of the ring by interference with the N-methyl group, thus diminishing conjugative effects between the two carboxyls.

The specific rates for reduction of the N-methylated and the protonated 4-carboxylato derivative[4] lie well above those for the corresponding 2- and 3-carboxylato species, and also above those for the large majority of ring-substituted pentaamminebenzoato complexes which undergo reduction by adjacent attack at specific rates clustering between 0.09 and 0.25 l. mole^{-1} sec.$^{-1}$. It is possible that this effect is associated with transitory reduction of the pyridine ring, forming a radical-like intermediate.[5] In our experience, the ring in the pyridine-4-carboxylato system is more easily reduced than in the 2- or 3-carboxylato systems.

(3) R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, *J. Am. Chem. Soc.*, **80**, 4469 (1958).

(4) Dr. R. T. M. Fraser (private communication) reports specific rates for these reductions (0.2 *M* $HClO_4$, μ = 1) as 1.2 (methylated) and 0.95 (nonmethylated). Since, in our experience, raising μ from 1.0 to 3.0 accelerates reactions of this sort by about 15%, his values are in reasonable agreement with ours.

(5) N-Ethyl-4-carbethoxypyridinyl, a stable free radical related to our N-substituted-4-carboxypyridine complexes, has been isolated: E. M. Kosower and E. J. Poziomek, *J. Am. Chem. Soc.*, **85**, 2035 (1963).

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(6) National Science Foundation Senior Postdoctoral Fellow, 1962–1963.

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RECEIVED AUGUST 22, 1963

Radical Anions of Adamantane and Hexamethylenetetramine[1]

Sir:

The prediction and observation of the radical anion of the highly strained hydrocarbon, cyclopropane, has recently been reported.[2] We now wish to report the observation of the radical anions of two bicyclic, strain-free systems, adamantane and hexamethylenetetramine. Adamantane in tetrahydrofuran–dimethoxyethane (2:1) containing sodium–potassium alloy[2,3] at −150° affords an electron paramagnetic resonance spectrum[4] consisting of five broad lines of approximately binomial intensity with a line separation a_H = 3.9 oersteds and a *g* value of 2.0029. The five-line spectrum is ascribed to principal interaction of the electron with the four equivalent bridgehead protons. This pattern seems reasonable if one assumes that the odd electron is "located" inside the molecular cavity of adamantane. The methine carbon–hydrogen bonds are oriented normal to the molecular sphere and are in best position for exchange interactions involving the back side of the sp^3 hybrid orbitals. The methylene carbon–hydrogen bonds, on the other hand, are oriented nearly tangential to the molecular sphere and might be expected to be in a less favorable position for exchange interactions. Support for this interpretation is found in the e.p.r. spectrum of the radical anion of hexamethylenetetramine (1,3,5,7-tetraazaadamantane), nine broadened lines (a_N = 4.2 oersteds, *g* value of 2.003) that approximately fit the intensity ratio of 1:4:10:16:19:16:10:4:1, expected for interaction of the electron with four equivalent nitrogen nuclei.

The significance of these results to questions of bonding and transmission of electrical effects[5] in these and related systems are under investigation.

Acknowledgment.—We are indebted to Mr. A. A. Lamola for a sample of adamantane and wish to mention his own consideration, independent of ours, of the possibility of formation of a radical anion of adamantane.

(1) This work was supported under contract No. AT(30-1)-905 with the Atomic Energy Commission. Reproduction is permitted for any purpose of the United States Government.

(2) K. W. Bowers and F. D. Greene, *J. Am. Chem. Soc.*, **85**, 2331 (1963).

(3) J. R. Bolton, *Mol. Phys.*, **6**, 219 (1963).

(4) A Varian Associates V-4500 spectrometer with 100-kc. modulation was used for this work.

(5) *E.g.*, see J. D. Roberts and W. T. Moreland, Jr., *J. Am. Chem. Soc.*, **75**, 2167 (1953).

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