Role of Potassium Cyanide.—The role of potassium cyanide in the reactions described above is a matter of considerable interest. The reduction of $K_3[Mn(CN)_6]$ and of $K_4[Mo(CN)_8]$, with attendant evolution of cyanogen, may be represented by the following equations (making a slight modification in the empirical formula of the manganese product).

$$4K_3[Mn(CN)_6] = 4K_{1.50}Mn(CN)_{3.75} + 1.5(CN)_2 + 6KCN$$
$$K_4[Mo(CN)_8] = K_2Mo(CN)_5 + 0.5(CN)_2 + 2KCN$$

Obviously, the stoichiometry of these reactions does not require potassium cyanide as a reactant, but as a product, instead. Cyanogen, too, is indicated to be a direct product of the reduction decomposition of the original cyano compound.

In an attempt to gain some insight into the mechanism of the reductions, runs were conducted in which C^{14}-labeled potassium cyanide was used. Examination of the products showed the C^{14} activity to be about uniformly distributed among the three products in each case. Therefore, whether the cyanogen originates, in part at least, from the potassium cyanide in the course of reduction of the metal compound, or from decomposition of the cyano complex subsequent to exchange of C^{14}-labeled cyanide between potassium cyanide and the complex, cannot be determined from this evidence. A sample of unlabeled $K_{1.52}Mn(CN)_{3.72}$ was found to exchange readily at the experimental temperature; presumably, $K_3[Mn(CN)_6]$ would behave similarly.

Since potassium cyanide appears as a product in the above equations, it seemed worthwhile to see whether or not these starting compounds would behave in the same manner as before if they were heated under the same conditions but in the absence of added potassium cyanide. When $K_3[Mn(CN)_6]$ was heated without potassium cyanide in this way, extensive carbonization occurred, and none of the green compound denoted by $K_{1.52}Mn(CN)_{3.72}$ could be isolated. Similar treatment of $K_4[Mo(CN)_8]$ also resulted in much decomposition, with formation of carbon and a metallic mirror. When the heating period was limited to 10 min., a small amount of $K_2Mo(CN)_5$ could be isolated; after 1 hr., none could be obtained. If $K_2[Pd(CN)_4]$ reacts to give condensed products containing cyano bridge groups, as postulated, potassium cyanide should be a product of this reaction, also. When $K_2[Pd(CN)_4]$ was heated without potassium cyanide, however, extensive decomposition occurred here, too, and the 2180 $cm.^{-1}$ band could not be detected in the infrared spectrum of the products.

It is clear that potassium cyanide plays a most important role in stabilizing the various cyano complex products described here and, therefore, in determining the course of reaction when cyanometallate compounds or their precursors are subjected to elevated temperatures.

Acknowledgment.—The authors gratefully acknowledge their indebtedness to the Atomic Energy Commission for financial support of this work and to the Stauffer Chemical Company for a fellowship held by W. L. M. during part of the time.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ARIZONA, TUCSON, ARIZONA

The Influence of Metal Chelation on the Structure of Certain Hydroxyquinaldinic Acids

BY SASWATI P. BAG, QUINTUS FERNANDO, AND HENRY FREISER

Received May 25, 1963

The acid dissociation constants and stepwise metal chelate formation constants of 4-hydroxyquinaldinic acid and 4,8-dihydroxyquinaldinic acid have been determined in 50% v./v. aqueous dioxane at 25°. Metal chelation was found to have an acid-strengthening effect on the 4-hydroxy group far in excess of that which could be attributed to a shift in the keto–enol equilibrium involving this group. Factors that contribute to this effect include the nature of the chelate ring, its position relative to the dissociating group, and the nature of the metal ion.

One of the useful techniques of evaluating the influence of metal ion chelation on the physical and chemical properties of a ligand is the measurement of the change in pK_a of an appropriate acidic or basic substituent suitably located on the ligand.[1,2] The phenolic group, whose pK_a is significantly higher than the pH range in which most metal chelation occurs, has been shown to be of value in this type of investigation.[2,3] Of course, the phenolic group can itself in certain types of compounds influence the properties of the ligand. In compounds such as 4-hydroxypyridine, the phenolic group interacting through keto–enol tautomerism exerts a profound influence on the coordinating properties of the nitrogen atom. In the case of 2,6-dicarboxy-4-hydroxypyridine, for example, the presence of the hydroxy group results in a tautomeric change to the pyridone. Instead of being a disadvantage, however, such a tautomeric transforma-

(1) T. R. Harkins and H. Freiser, *J. Am. Chem. Soc.*, **78**, 1143 (1956).
(2) A. Corsini, Q. Fernando, and H. Freiser, *Inorg. Chem.*, **2**, 224 (1963).
(3) S. P. Bag, Q. Fernando, and H. Freiser, *ibid.*, **1**, 887 (1962).

TABLE I

ACID DISSOCIATION CONSTANTS OF QUINALDINIC ACIDS, DETERMINED POTENTIOMETRICALLY IN 50% V./V. DIOXANE–WATER AT 25 ± 0.1°

Compound	pK_1	pK_2	pK_3	pK_4
Quinaldinic acid[a]	<2	5.39	...	...
4-Hydroxyquinaldinic acid	<2	3.65 ± 0.01 ($\mu \approx 0.005$)	13.9 ± 0.2[b] ($\mu \approx 0.005$)	...
4,8-Dihydroxyquinaldinic acid	<2	3.55 ± 0.01 ($\mu \approx 0.005$)	10.05 ± 0.1 ($\mu = 0.01$)	14.5 ± 0.2[b] ($\mu \approx 0.02$)
4,8-Dihydroxyquinaldinic acid	<2[c]	3.87 ± 0.05[c] ($\mu \approx 0.005$)	7.90 ± 0.05[c] ($\mu \approx 0.01$)	10.35 ± 0.1[c] ($\mu \approx 0.01$)

[a] F. Holmes and W. R. C. Crimmin, *J. Chem. Soc.*, 3467 (1955). [b] Determined spectrophotometrically. [c] Determined in water.

tion serves to augment the change in pK_a value on metal ion chelation.[3]

In this regard then it is of interest to extend this type of investigation to ligands containing other ring systems; for example, how does the effect of metal ion chelation on the keto–enol tautomerism in a 4-hydroxyquinoline system compare with that in the 4-hydroxypyridine system? By including 4,8-dihydroxyquinaldinic acid in this study it might be possible to assess the effect of changing the nature of the chelate ring on the keto–enol tautomerism in the 4-hydroxyquinoline system.

Experimental

Materials.—4-Hydroxyquinaldinic acid and 4,8-dihydroxyquinaldinic acid were obtained from K and K Laboratories, Inc., New York, N. Y. Both compounds were purified by the following procedure: the crude acid was dissolved in the minimum quantity of dilute NaOH, the resulting solution was warmed with animal charcoal, filtered, and acidified with dilute HNO_3 to precipitate the acid. 4-Hydroxyquinaldinic acid on recrystallization from hot ethanol formed colorless needles which melted with decomposition at 274° (lit.[4] 277°). 4,8-Dihydroxyquinaldinic acid was obtained in the form of pale yellow needles after recrystallization from hot ethanol. The compound melted with decomposition at 277° (lit.[5] 284°).

Methods for the preparation and standardization of NaOH and metal perchlorate solutions as well as for the purification of dioxane have been previously described.[6]

Acid Dissociation Constants.—The acid dissociation constants of 4-hydroxyquinaldinic acid and 4,8-dihydroxyquinaldinic acid were determined potentiometrically in a 50% v./v. dioxane–water medium at 25 ± 0.1°. A detailed description of the method has been published in an earlier paper.[3] The results obtained are summarized in Table I.

The acid dissociation constants of the 4-hydroxy groups in a series of transition metal chelates of 4-hydroxyquinaldinic acid and 4,8-dihydroxyquinaldinic acid were determined potentiometrically at 25 ± 0.1° in a 50% v./v. dioxane–water medium by titrating solutions containing a 1:2 metal ion:ligand ratio.[3] These titrations, when repeated with solutions containing a 1:2 ratio of metal ion:quinaldinic acid, did not show a second buffer region. It could therefore be concluded that the second buffer regions in the titration curves of the 4-hydroxy and 4,8-dihydroxy compounds are caused by proton release from the 4-hydroxy groups and not from metal ion hydrolysis. The pK and pK' values, calculated from the second buffer region of each of these titration curves, are given in Table II.

Formation Constants of Metal Chelates.—The chelate formation constants of 4-hydroxyquinaldinic acid with several transition metal ions were determined potentiometrically at 25 ± 0.1° in a 50% v./v. dioxane–water medium. Formation constants for the copper(II) chelates could not be obtained since precipitation occurred at low pH values. The calculation of chelate formation constants from potentiometric data has been described previously.[6]

The chelate formation constants of 4,8-dihydroxyquinaldinic acid with a number of transition metal ions were determined potentiometrically at 25 ± 0.1° in a 50% v./v. dioxane–water medium. In this case it was assumed that chelation involved only the nitrogen atom and the 8-hydroxy group (see Discussion). The chelate formation constant data are collected in Table III.

TABLE II

ACID DISSOCIATION CONSTANTS OF THE 4-HYDROXY GROUPS IN METAL CHELATES OF 4-HYDROXY-AND 4,8-DIHYDROXYQUINALDINIC ACIDS, AT 25 ± 0.1° IN 50% V./V. DIOXANE–WATER ($\lambda \approx 0.01$)

Metal ion	4-Hydroxyquinaldinic acid[c]		4,8-Dihydroxyquinaldinic acid	
	pK[b]	pK'[b]	pK[b]	pK'[b]
Mn(II)	...[a]	...[a]	10.7	...[a]
Co(II)	7.3	9.0	9.9	11.7
Ni(II)	7.2	9.5	10.0	11.8
Cu(II)	6.2	7.3	9.5	11.0
Zn(II)	7.0	8.1	9.7	11.3

[a] These values were not obtained since hydrolysis products precipitated. [b] pK refers to the dissociation of the proton from one of the coordinated ligands and pK' refers to that from the other. [c] NOTE ADDED IN PROOF.—These values are maximum values that approximate the true values since ligand:metal ratios greater than 2:1 are required to ensure complete formation of the 2:1 chelate [G. Anderegg, *Helv. Chim. Acta*, **46**, 1011 (1963)].

TABLE III

FORMATION CONSTANTS OF CERTAIN TRANSITION METAL CHELATES OF QUINALDINIC ACIDS AT 25 ± 0.1° IN 50% V./V. DIOXANE–WATER ($\lambda \approx 0.01$)

Metal ion	Quinaldinic acid[a]		4-Hydroxyquinaldinic acid		4,8-Dihydroxyquinaldinic acid	
	log k_1	log k_2	log k_1	log k_2	log k_1	log k_2
Mn(II)	...	...	...	...	5.5	5.0
Co(II)	5.3	4.9	3.3	2.9	6.7	5.6
Ni(II)	5.3	5.1	3.5	2.7	7.1	5.5
Cu(II)	...	...	...	...	9.4	7.2
Zn(II)	5.1	4.6	3.4	3.1	7.7	6.0

[a] F. Holmes and W. R. C. Crimmin, *J. Chem. Soc.*, 3467 (1955).

Spectra.—A Beckman Model DB recording spectrophotometer and stoppered 1-cm. quartz cells were used for all spectrophotometric measurements.

Results and Discussion

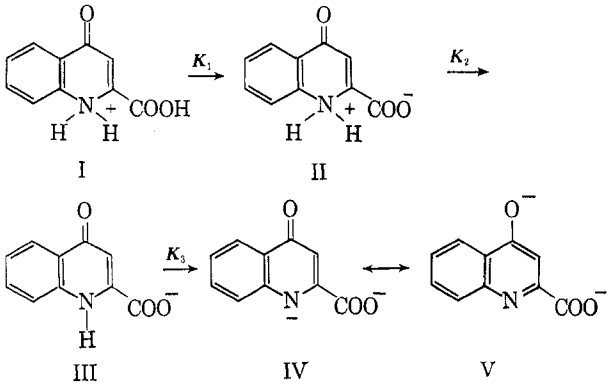
The dissociation scheme for 4-hydroxyquinaldinic acid is shown below. Since it is postulated that the enol forms are present in very small concentration

(4) B. Riegel, C. J. Albisetti, G. R. Bappin, and R. H. Baker, *J. Am. Chem. Soc.*, **68**, 2685 (1946).

(5) A. Furst and C. J. Olsen, *J. Org. Chem.*, **16**, 412 (1951).

(6) H. Freiser, R. G. Charles, and W. D. Johnston, *J. Am. Chem. Soc.*, **74**, 1383 (1952).

their structures are not shown. Likewise only the zwitterion form II is shown, since it is the predominant



I II III IV V

form of II in solution.

The acidity of the carboxylic acid group (pK_1) in the quinaldinic acids is as high as expected with heterocyclic nitrogen carboxylic acids that are capable of forming zwitterions. The drop in pK_2 of 1.74 units from the corresponding pK value of quinaldinic acid is expected from the strong electron-withdrawing effect of the >C=O group in the keto tautomer. This basicity decrease closely parallels that observed between 2,6-dicarboxy-4-hydroxypyridine and pyridine 2,6-dicarboxylic acid[3] (drop in pK_2 of 1.30).

The pK_3 value in the 4-hydroxyquinaldinic acid corresponds to the dissociation of compound III. If the expected difference between pK values measured in 50% v./v. dioxane–water and water is taken into account, this value is very similar to the corresponding value (pK_3 = 11.4) for 2,6-dicarboxy-4-hydroxypyridine.[3] In the 4,8-dihydroxy compound, pK_3 must be assigned to the dissociation of the 8-hydroxy group. This value is lower than that obtained in 8-hydroxyquinoline (pK 11.5) as a result of the influence of the predominant keto form. In the keto form the 8-hydroxy group will be involved to a lesser extent in hydrogen bonding with the nitrogen atom than in 8-hydroxyquinoline. The enhanced acidity of the 8-hydroxy group could also result from the inductive effect of the keto group. In the 4,8-dihydroxy compound, pK_4 represents the dissociation process, analogous to that of compound III. Its value is higher than pK_3 in the 4-hydroxyquinaldinic acid by virtue of the presence of an additional negative charge.

The stepwise formation constants of the 4-hydroxyquinaldinic acid chelates are each approximately 2 log units lower than those of the corresponding quinaldinic acid chelates. At first sight this difference would seem to be almost entirely accounted for by the decrease in the basicity of the 4-hydroxyquinaldinic acid. Since the metal chelate undoubtedly involves the enol form in contrast to the predominance of the keto form in the free ligand (structure III), however, a direct relation between ligand basicity and chelate stability is not meaningful. It is more likely that the stepwise formation constants of the chelates of the enol form of the 4-hydroxyquinaldinic acid should be about the same as those for quinaldinic acid, since the hydroxy group would be expected to have a relatively minor influence on the chelate formation constants. The drop in the chelate formation constants is due to the low concentration of the enol tautomer of the ligand and, in reality, measures the keto–enol tautomerism constant, K_T; *i.e.*, $k_i/k_i' = K_T$ where k_i is k_1 or k_2 observed for a 4-hydroxyquinaldinic acid chelate and k_i', that value of k_i calculated on the basis of the chelation of the enol form (assumed to be equal to the corresponding value found for quinaldinic acid). Thus, the value of K_T is seen to be of the order of 10^{-2}.

Chelate formation in all of the quinaldinic acids occurs after the loss of the carboxylic acid proton (pH > pK_1). Consequently, chelation in the 4-hydroxy acid is accompanied by the loss of two protons (one from each of the protonated nitrogen atoms) per metal ion. Since in the chelation of the 4,8-dihydroxy acid the loss of four protons per metal ion is observed, it can be concluded that the 8-hydroxy group is involved in the metal chelate formation. Therefore the calculations of the formation constants of these chelates were based on the assumption that the ligand is the doubly charged anion. From the results shown in Table III it may be concluded that the reagent is bidentate rather than tridentate, since if the latter were true significantly higher formation constant values would be observed. Furthermore, from spatial considerations based on molecular models a tridentate chelate is highly unlikely. These chelates would therefore resemble those of other 2-substituted 8-hydroxyquinolines in that the 2-substituent exerts steric hindrance to chelate formation.[7] All of these chelates are less stable than the corresponding 8-hydroxyquinoline chelates. A significant part of this difference can be attributed to the lower basicity (particularly of the 8-hydroxy group) of the 4,8-dihydroxy compound and the involvement of the keto–enol tautomerism. The remainder of the difference, which increases in the order Mn ≈ Zn, Co, Ni ≈ Cu, reflects the adverse steric influence of the carboxylate group. Comparison of the formation constants of these chelates with those of 2-methyl-8-hydroxyquinoline, however, gives a nearly constant difference (2.8 ± 0.4 in log K_{av}). This would seem to indicate that the steric influence of the carboxylate is similar to that of the methyl group in the 2-position.

As with 2,6-dicarboxy-4-hydroxypyridine chelates, sizable enhancement of the acidity of the 4-hydroxy group is observed in the chelates of both 4-hydroxy and 4,8-dihydroxyquinaldinic acids. The changes in pK values of the 4-hydroxy groups, however, are much larger than can be attributed to a shift in the keto–enol tautomeric equilibrium alone. The major portion of the effect must be attributed to the electron-withdrawing properties of the metal ion. A close comparison of the changes in pK values of the 4-hydroxy groups must take into account the difference in the charge type of the 4-hydroxyquinaldinic acid. In both 2,6-dicarboxy-4-hydroxypyridine and 4,8-dihydroxyquin-

(7) W. D. Johnston and H. Freiser, *Anal. Chim. Acta*, **11**, 201 (1954).

aldinic acids the change in pK is the difference between two pK values involving the dissociation of doubly charged anions. Hence the comparison is uncomplicated by charge variation. In the 4-hydroxyquinaldinic acid case, however, the pK_3 of the ligand involves the dissociation of a singly charged anion whereas that of the chelate corresponds to the dissociation of a neutral species. From a comparison of the pK values of 8-quinolinol, salicylic acid, and the corresponding sulfonates, the charge effect on the change in pK can be estimated to be about 1.0 log unit. This has been subtracted from the ΔpK for the 4-hydroxy compound and the resulting values are given in Table IV.

TABLE IV
ΔpK VALUES FOR THE 4-HYDROXY GROUPS IN THE METAL CHELATES

Metal ion	ΔpK 2,6-Dicarboxy-4-hydroxypyridine	4-Hydroxyquinaldinic acid[a]	4,8-Dihydroxyquinaldinic acid
Mn(II)	...	...	3.8
Co(II)	5.9	5.6	4.6
Ni(II)	5.7	5.7	4.5
Cu(II)	6.4	6.7	5.0
Zn(II)	5.7	5.9	4.8

[a] Corrected for the charge effect.

The ΔpK values in Table IV show that in the chelates of the three compounds considered here, Cu(II) exerts a significantly greater effect than the other metal ions, although this difference seems to be almost absent in the 4,8-dihydroxy compound. Furthermore, a comparison of the corrected ΔpK values (Table IV) reveals a great similarity in the effect of metal chelation on the pK_{OH} of 2,6-dicarboxy-4-hydroxypyridine and that of 4-hydroxyquinaldinic acid, both of which have the same chelate ring in the same position relative to the 4-hydroxy group. In the case of the 4,8-dihydroxy compound the effect is uniformly smaller. Although it is likely that the greater part of the change in the order of magnitude of the acid strengthening effect is due to the change in the nature of the chelate ring, the role played by the change in the location of the dissociating hydroxy group relative to the chelate ring as well as possible differences in the tautomeric equilibrium constants of the ligands must not be overlooked. Further work is underway to evaluate these separate effects.

Acknowledgment.—The authors are grateful to the National Institutes of Health for financial assistance.

CONTRIBUTION FROM THE U. S. NAVAL ORDNANCE LABORATORY, CORONA, CALIFORNIA

Preparation of Linear Phosphonitrilic Derivatives

BY K. L. PACIOREK

Received April 29, 1963

Reaction of diphenylphosphinyl azide with diphenylchlorophosphine afforded the compound $(C_6H_5)_2P(O)-[N{=}P(C_6H_5)_2]_3Cl$ (VIII) as the main product. Various mechanisms are considered for this process. Azido, triphenylphosphine, phenoxy, and phosphinyl terminated chains were prepared from compound VIII. Infrared and ultraviolet spectra of several of these phosphonitrilic derivatives were determined and are discussed.

Syntheses and Mechanism Discussion

Trivalent phosphorus compounds are readily oxidized by azides such as diphenylphosphinyl azide,[1] triphenylsilyl azide,[2] or phenyl azide,[3] forming phosphonitrilic linkages. Mono-, bis-, and trishalogenophosphines are also reported to give phosphonitriles[4] when treated with alkali metal azides. This reaction proceeds most probably *via* the trivalent phosphorus azide intermediate, inasmuch as bis(trifluoromethyl)azidophosphine (prepared from bis(trifluoromethyl)chlorophosphine and lithium azide) decomposed thermally into polymeric bis(trifluoromethyl)phosphonitrile.[5] Based on the facts outlined above a stepwise synthesis of linear phosphonitrilic derivatives, initiated by an oxidative attack of pentavalent phosphorus azide upon a trivalent phosphorus halide, appeared feasible. Accordingly, the reaction of diphenylphosphinyl azide[6] with an equimolar quantity of diphenylchlorophosphine should afford $(C_6H_5)_2P(O)-N{=}P(C_6H_5)_2Cl$, wherein chlorine is attached to a pentavalent phosphorus atom, allowing chain extension *via* an exchange with an azido group (supplied by an alkali metal azide), followed by treatment with a trivalent phosphorus compound. Since the interaction products do not contain trivalent phos-

(1) R. A. Baldwin and R. M. Washburn, *J. Am. Chem. Soc.*, **83**, 4466 (1961).
(2) N. Wiberg, F. Raschig, and R. Sustmann, *Angew. Chem. Intern. Ed. Engl.*, **1**, 551 (1962).
(3) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 61 (1921).
(4) D. L. Herring, *Chem. Ind.* (London), 717 (1960).
(5) G. Tesi, C. P. Haber, and C. M. Douglas, *Proc. Chem. Soc.*, 219 (1960).

(6) Diphenylphosphinyl azide was first prepared by Baldwin and Washburn[1] from diphenylphosphinyl chloride and sodium azide in boiling pyridine. Interestingly, treatment of diphenylphosphinyl chloride with lithium azide in acetonitrile at room temperature resulted in the formation of a 1:1 complex of diphenylphosphinyl azide and lithium chloride, which when heated above 73°, the melting point of the complex, decomposed into its constituents. The assignment of structure $(C_6H_5)_2P(O)N_3{\cdot}LiCl$ to the complex is based on its infrared spectrum, which is almost identical with that of diphenylphosphinyl azide and differs from that exhibited by diphenylphosphinyl chloride. The failure of Baldwin and Washburn[1] to isolate the sodium analog of the complex can be ascribed to the relatively high temperatures employed in their reaction.