thiocyanate reacts more readily than the isocyanate. Aryl isocyanide complexes of the group VI metal carbonyls are well known.[9,10,15,16] In all of the reactions described in this paper, material is lost in the form of highly-colored, polar materials, which cannot be removed from a chromatography column.

[15] W. Hieber and D. Pigenot, *Ber.*, **89**, 616 (1956).

[16] W. Hieber, W. Abeck, and H. K. Platzer, *Z. anorg. allgem. Chem.*, **280**, 252 (1955).

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A Temperature-Jump Study of the Kinetics of Complex Formation between 4,5-Dihydroxybenzene-1,3-disulfonic Acid and Nickel(II), Cobalt(II), and Magnesium(II) in Aqueous Solution[1]

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The kinetics of complexation between various charged species of the ligand 4,5-dihydroxybenzene-1,3-disulfonic acid ("tiron") and the divalent metal ions of nickel, cobalt, and magnesium have been investigated by the temperature-jump method. The complex formation rate constants for the −3 species of tiron and the divalent metal ions of nickel, cobalt, and magnesium were determined at a pH of 9.00 and at 20°. The second-order rate constants for the association of the −2 tiron species and the divalent metal ions of nickel and cobalt were determined at a pH of 4.66 and at 20°. In each case the stability of the metal complex decreases by several orders of magnitude with increasing ligand protonation; however, the association rate constant changes only by an order of magnitude. The large decrease in complex stability with increasing protonation is due to a large increase in the dissociation rate constant.

Introduction

The ligand 4,5-dihydroxybenzene-1,3-disulfonic acid forms stable complexes with transition metal ions and many other metal ions. Due to the importance of its ability to complex, and hence remove, titanium and iron when these ions interfere in an analytical procedure, Schwarzenbach[2] has named this compound "tiron"—an appellation that shall be used throughout this paper.

Kinetically, tiron complexation is of interest because the large delocalized charge on this relatively small ligand results in a high charge density. By controlling the degree of protonation on tiron, it is possible to alter the charge and thereby make direct comparisons between the rates of complex formation and dissociation for the differently charged species. Likewise, comparison of the results obtained for the three different metal ions gives some indication of the role played by electronic configuration in determining the relative importance of charge on the rates of association and dissociation.

Equilibrium Constants and Relaxation Spectra

TABLE I

STOICHIOMETRIC EQUILIBRIUM CONSTANTS[a] AT IONIC STRENGTH 0.1 *M* AND 20°

Equilibrium constant			Lit. ref.
$K_{\mathrm{H_2ti}}$	$= [\overline{\mathrm{H}}][\overline{\mathrm{Hti}}]/[\overline{\mathrm{H_2ti}}]$	$= 2.19 \times 10^{-8}$	*e*
K_{Hti}	$= [\overline{\mathrm{H}}][\overline{\mathrm{ti}}]/[\overline{\mathrm{Hti}}]$	$= 2.5 \times 10^{-13}$	*e*
K_{ROH}	$= [\overline{\mathrm{R}}][\overline{\mathrm{OH}}]/[\overline{\mathrm{ROH}}]$	$= 4.0 \times 10^{-5\,b}$	*f*
$K_{\mathrm{HIn_1}}$	$= [\overline{\mathrm{H}}][\overline{\mathrm{In_1}}]/[\overline{\mathrm{HIn_1}}]$	$= 1.1 \times 10^{-6\,c}$	*g*, *h*
$K_{\mathrm{HIn_2}}$	$= [\overline{\mathrm{H}}][\overline{\mathrm{In_2}}]/[\overline{\mathrm{HIn_2}}]$	$= 1.04 \times 10^{-5\,d}$	*g*, *h*
$K^{\mathrm{Ni}}{}_{1}$	$= [\overline{\mathrm{Niti}}]/[\overline{\mathrm{Ni}}][\overline{\mathrm{ti}}]$	$= 9.12 \times 10^{9}$	3, 4
$K^{\mathrm{Co}}{}_{1}$	$= [\overline{\mathrm{Coti}}]/[\overline{\mathrm{Co}}][\overline{\mathrm{ti}}]$	$= 3.09 \times 10^{9}$	3, 4
$K^{\mathrm{Mg}}{}_{1}$	$= [\overline{\mathrm{Mgti}}]/[\overline{\mathrm{Mg}}][\overline{\mathrm{ti}}]$	$= 7.24 \times 10^{6}$	3, 4
$K^{\mathrm{Ni}}{}_{\mathrm{NiHti}}$	$= [\overline{\mathrm{NiHti}}]/[\overline{\mathrm{Ni}}][\overline{\mathrm{Hti}}]$	$= 1.00 \times 10^{3}$	3, 4
$K^{\mathrm{Co}}{}_{\mathrm{CoHti}}$	$= [\overline{\mathrm{CoHti}}]/[\overline{\mathrm{Co}}][\overline{\mathrm{Hti}}]$	$= 1.20 \times 10^{3}$	3, 4
$K^{\mathrm{Mg}}{}_{\mathrm{MgHti}}$	$= [\overline{\mathrm{MgHti}}]/[\overline{\mathrm{Mg}}][\overline{\mathrm{Hti}}]$	$= 9.55 \times 10^{1}$	3, 4

[a] In calculating the relaxation times it is often necessary to use the complex hydrolysis constant $K^{\mathrm{b}}{}_{\mathrm{MHti}} = [\overline{\mathrm{MHti}}][\overline{\mathrm{OH}}]/[\overline{\mathrm{Mti}}] = K^{\mathrm{M}}{}_{\mathrm{MHti}}K_{\mathrm{w}}/K^{\mathrm{M}}{}_{1}K_{\mathrm{Hti}}$, where K_{w} represents the ion product of water. [b] ROH is phenolphthalein. [c] $\mathrm{HIn_1}$ is chlorophenol red. [d] $\mathrm{HIn_2}$ is methyl red. [e] R. Näsänen, *Suomen Kemistilehti*, **30B**, 61 (1957). [f] A. Thiel and G. Coch, *Z. anorg. allgem. Chem.*, **217**, 353 (1934). [g] E. F. Chase and M. Kilpatrick, Jr., *J. Am. Chem. Soc.*, **54**, 2284 (1932). [h] I. M. Kolthoff, *J. Phys. Chem.*, **34**, 1466 (1930).

The relevant equilibrium constants necessary for a quantitative interpretation of the temperature-jump results are listed in Table I. The notation used in "Stability Constants" by Bjerrum, Schwarzenbach, and Sillén[3] will be followed, as far as possible. The symbol $[\overline{\ \ \ }]$ represents the equilibrium concentration. Charges have been neglected in writing the constants. The symbols ti, Hti, and $\mathrm{H_2ti}$ represent tiron in different degrees of protonation; also, M may represent Mg, Ni, or Co. No original data are available in the case of those constants for which ref. 3 has been cited as a source; however, the values for nickel(II) and cobalt(II) have been corroborated in studies by Näsänen, *et al.*,[4] to which one should refer for experimental details.

With a description of the equilibrium composition of

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[1] Presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan., 1964.

[2] G. Schwarzenbach, "Complexometric Titrations," Interscience Publishers, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 40.

[3] G. Schwarzenbach and A. Willi, "Stability Constants," Part I, J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, Ed., The Chemical Society, London, 1957.

[4] *Cf.* R. Näsänen, *Suomen Kemistilehti*, **32B**, 7 (1959).

a system, a temperature-jump (*i.e.*, relaxation spectrometric) study can be undertaken. The principle of this method is to perturb a system at equilibrium and measure the finite relaxation time required for the reestablishment of a new equilibrium. The relaxation time, τ, is a function of the concentrations and rate constants in the system. For a simple, single-step reaction, such as

$$\mathrm{M} + \mathrm{L} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML}$$

the following conditions and definitions

$$[\mathrm{X}] = [\overline{\mathrm{X}}] + \delta[\mathrm{X}];\ \delta[\mathrm{X}] \ll [\overline{\mathrm{X}}],\ [\mathrm{X}] \qquad \text{(i)}$$

$$\delta[\mathrm{M}] = \delta[\mathrm{L}] = -\delta[\mathrm{ML}] \qquad \text{(ii)}$$

$$k_1[\overline{\mathrm{M}}][\overline{\mathrm{L}}] = k_{-1}[\overline{\mathrm{ML}}];\ K_1 = k_1/k_{-1} \qquad \text{(iii)}$$

(where X represents M, L, or ML, [X] represents the instantaneous concentration, $[\overline{\mathrm{X}}]$ represents the time independent concentration, $\delta[\mathrm{X}]$ represents a small, time dependent deviation from equilibrium), applied to the rate equation for metal complex formation

$$(\mathrm{d}/\mathrm{d}t)([\mathrm{ML}]) = k_1[\mathrm{M}][\mathrm{L}] - k_{-1}[\mathrm{ML}] \qquad \text{(iv)}$$

yield, after expansion, the equation

$$(\mathrm{d}/\mathrm{d}t)(\delta[\mathrm{ML}]) = -\delta[\mathrm{ML}]/\tau \qquad \text{(v)}$$

with

$$1/\tau = k_{-1} + k_1([\overline{\mathrm{M}}] + [\overline{\mathrm{L}}]) \qquad \text{(vi)}$$

Consider now the more complicated case involving the complex formation between tiron and a divalent metal ion. Since it is possible for a metal ion, M, to combine with each of the different accessible protonated forms of tiron, the most complete mechanism for the formation of the first tiron complex is

$$\begin{tikzcd}
③ & \mathrm{M} + \mathrm{ti} \arrow[r, shift left, "k_{36}"] \arrow[d, shift left] & \mathrm{Mti} \arrow[l, shift left, "k_{36}"] \arrow[d, shift left] & ⑥ & & \\
② & \mathrm{M} + \mathrm{Hti} \arrow[u, shift left] \arrow[r, shift left, "k_{25}"] \arrow[d, shift left] & \mathrm{MHti} \arrow[u, shift left] \arrow[l, shift left, "k_{52}"] \arrow[d, shift left] & ⑤ & +\mathrm{HO} \arrow[u] & \text{(A)} \\
① & \mathrm{M} + \mathrm{H_2ti} \arrow[u, shift left] \arrow[r, shift left, "k_{14}"] & \mathrm{MH_2ti} \arrow[u, shift left] \arrow[l, shift left, "k_{41}"] & ④ & \arrow[r, "+\mathrm{M}"'] & {}
\end{tikzcd}$$

For this mechanism there are four relaxation times representative of the more rapid protolytic reactions given by the vertical steps. The fifth relaxation time is characteristic of the slower (horizontal) metal complex formation steps. Although calculable, this relaxation time is complicated, being a function of the complexation rate constants, the (rapidly established) protolytic equilibrium constants, and the concentrations of all the species present.

If higher order complexing occurs, additional linearized rate equations similar to (v) can be written, and the relaxation times calculated. Then the slower relaxation time will also, in addition to the previously mentioned parameters, depend upon the equilibrium quotient for the more rapid complexation process.

A thorough discussion of multiple-step equilibria and relaxation spectrometry is given by Eigen and DeMaeyer.[5] Hammes and Steinfeld[6] also give a complete discussion of multiple-step reactions with specific reference to metal–complex formation.

The equations which appear in later sections of this paper were derived by following steps (i)–(vi). The conservation equations (ii) in the actual examples include all protolytic forms of the ligand and complex and any indicators used. It will be shown that a simplification may be obtained by adjusting the pH so that one or more of the protolytic species in (A) may be omitted in writing the rate equation.

Experimental

The temperature-jump apparatus is essentially the same as that described by Czerlinski and Eigen.[7] The apparatus was modified to use the single-beam method.[6] The temperature-jump cell was maintained at 10 ± 0.5°; 30 kv. was discharged through the solution in a few microseconds to bring the temperature of the solution to the reference temperature of 20 ± 1°. An acid–base indicator was coupled to the metal–tiron system so that the relaxation could be followed spectrophotometrically.

Each solution was prepared in a 100-ml. volumetric flask. Weighed amounts of metal(II) nitrate and tiron, pipetted amounts of stock solutions of indicator and potassium nitrate, and sufficient boiled, distilled water were used. The nickel(II) nitrate, cobalt(II) nitrate, magnesium(II) nitrate, and potassium nitrate were Fisher reagent grade. The tiron was Eastman White Label. The indicators phenolphthalein, chlorophenol red, and methyl red were also from Eastman. The water was boiled, distilled, and kept in a nitrogen atmosphere. The ionic strength (μ) was adjusted to 0.1 *M* throughout by adding potassium nitrate. The pH of the solution was set by adding small amounts of nitric acid and sodium hydroxide, as necessary. The solution was cooled to approximately 10° in an ice bath, and nitrogen was passed through the solution. The solution was then placed in the thermostated temperature-jump cell. The relaxation time for each solution was measured within 45 min. of the original mixing of the reagents to minimize the transition of tiron to another, possibly quinone-like, form. It has been reported that the quinone form is favored at high pH and high excess of reagent in an oxygenated solution.[8,9] Passing nitrogen into the solution stabilized the tiron, although decomposition over a time long in comparison to the experiment was observed.

Blank solutions containing only nickel ion–indicator and only tiron–indicator at ionic strength 0.1 *M* were examined. These solutions were found to be free of any observable relaxation effect in the time range covered.

In the pH range from 7 to 10, the insolubility of nickel or cobalt hydroxide made it impossible to carry out experiments involving large nickel or cobalt excesses. At a pH of 9.00, the metal–tiron complex was stable for a period of several hours, whereas at a higher pH the complex was less stable and the relative error in the rate constant was larger. The pH range studied was from 3.5 to 10.

The relative error of individual rate constants for nickel and cobalt at a pH of 4.66 and a pH of 9.00 did not exceed ±10%, depending upon the size of the effect. For magnesium, the relative error in the rate constants is about ±25% in each case.

Two representative oscillographs of the nickel–tiron system are shown in Fig. 1, (a) and (b). Similar results were obtained for the other metal–tiron systems.

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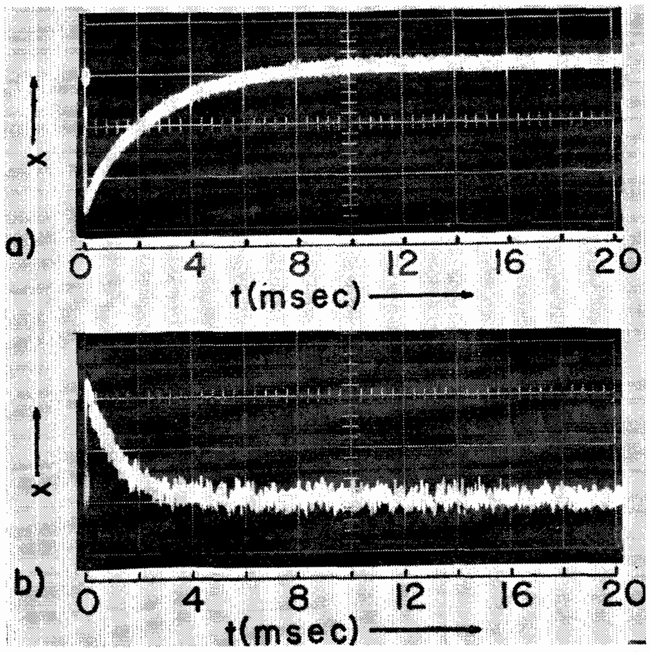


Fig. 1.—Oscillograms of temperature-jump relaxation experiments for the nickel–tiron system: (a) pH 9.00, $[Ni]^0 = 2.00 \times 10^{-3}$ *M*, $[ti]^0 = 2.50 \times 10^{-3}$ *M*, $[ROH]^0 = 2.56 \times 10^{-5}$ *M*, $\tau = 2.92$ msec.; (b) pH 4.66, $[Ni]^0 = 2.00 \times 10^{-3}$ *M*, $[ti]^0 = 3.00 \times 10^{-3}$ *M*, $[HIn_1]^0 = 8.0 \times 10^{-5}$ *M*, $\tau = 1.20$ msec. The ordinate in both (a) and (b) represents a change in light absorption due to a concentration change of the appropriate indicator, which is coupled to the metal–complex reaction through the more rapid protolytic steps.

Results

Since magnesium hydroxide is relatively soluble, no special precaution was taken with regard to exceeding the solubility product. The concentration of the free magnesium ion varied between 2.9×10^{-4} and 6.4×10^{-4} *M*, and the concentration of free Hti varied between 1.09×10^{-3} and 3.07×10^{-3} *M*. Both the nickel and cobalt hydroxides are insoluble enough to preclude high pH studies in the presence of appreciable amounts of either metal ion. By utilizing an excess of tiron (3×10^{-4} to 6×10^{-3} *M*), however, it was possible to reduce sufficiently the concentration of free metal ion (to about 10^{-6} *M*) in order to study the kinetics of complex formation. In selecting the proper pH, attention was paid to the instability of tiron at higher pH values. At a pH of 9.00 the solutions were stable; also $[Hti] \cong 22[H_2ti] \cong 4 \times 10^3[ti]$, which leads to a simplification of mechanism (A) by neglecting the kinetically insignificant species. As the pH is lowered from a pH of 10, the observed relaxation process diminishes in magnitude, until at pH values between 7 and 6 essentially no effect is observed. Starting with a pH around 5, further reduction in pH results in a single measurable effect which diminishes in magnitude below a pH of 4. The best effects in the low pH range were obtained at a pH of 4.66, where $[H_2ti] \cong 10^3[Hti] \cong 8.7 \times 10^{10}[ti]$, which likewise leads to a simplification of (A). No low pH effect could be detected for magnesium. The relaxation times measured and calculated for the dipositive ions of nickel, magnesium, and cobalt with tiron under varying conditions of pH and ligand concentration are given in Table II. (See section on Mechanisms and Rate Constants for calculation of τ.) Each experiment in Table II represents an average of three oscillographic determinations. Studies at pH values other than those listed gave relaxation times which are consistent with those given in Table II.

Table II

Results for M(II)–Tiron Solutions

Expt. no.	M	$[ti]^0$, *M*	pH	τ (sec.) measd.	τ (sec.) calcd.
1	Mg	2.5×10^{-3}	9.00	4.5×10^{-5}	4.0×10^{-5}
2	Mg	3.0×10^{-3}	9.00	4.5×10^{-5}	4.1×10^{-5}
3	Mg	4.0×10^{-3}	9.00	4.0×10^{-5}	4.1×10^{-5}
4	Mg	5.0×10^{-3}	9.00	3.9×10^{-5}	3.9×10^{-5}
5	Ni	2.30×10^{-3}	9.00	3.52×10^{-3}	3.62×10^{-3}
6	Ni	2.50×10^{-3}	9.00	3.04×10^{-3}	2.92×10^{-3}
7	Ni	3.00×10^{-3}	9.00	2.22×10^{-3}	2.16×10^{-3}
8	Ni	3.50×10^{-3}	9.00	1.73×10^{-3}	1.74×10^{-3}
9	Ni	4.00×10^{-3}	9.00	1.41×10^{-3}	1.44×10^{-3}
10	Co	2.25×10^{-3}	9.00	3.23×10^{-4}	3.22×10^{-4}
11	Co	2.50×10^{-3}	9.00	2.60×10^{-4}	2.49×10^{-4}
12	Co	3.00×10^{-3}	9.00	1.50×10^{-4}	1.70×10^{-4}
13	Co	3.50×10^{-3}	9.00	1.28×10^{-4}	1.28×10^{-4}
14	Ni	3.50×10^{-3}	5.00	1.10×10^{-3}	
15	Ni	2.50×10^{-3}	4.66	1.25×10^{-3}	
16	Ni	3.00×10^{-3}	4.66	1.20×10^{-3}	
17	Ni	5.00×10^{-3}	4.66	1.00×10^{-3}	
18	Ni	1.00×10^{-2}	4.66	7.20×10^{-4}	
19	Co	1.50×10^{-3}	4.66	1.55×10^{-4}	
20	Co	3.00×10^{-3}	4.66	1.00×10^{-4}	
21	Co	8.00×10^{-3}	4.66	6.10×10^{-5}	
22	Co	1.60×10^{-2}	4.66	3.90×10^{-5}	

The indicators used were: 2.2×10^{-4} *M* phenolphthalein for expt. 1–4, 4×10^{-5} *M* for expt. 5–9, and 3.1×10^{-4} *M* for expt. 10–13; 4×10^{-5} to 8×10^{-5} *M* chlorophenol red for expt. 15–22; and 3.6×10^{-5} *M* methyl red for expt. 14. The initial metal ion concentration was 2.00×10^{-3} *M* for expt. 1–18, 20, and 21, 1×10^{-3} *M* for expt. 19, and 4×10^{-3} *M* for expt. 22.

Mechanisms and Rate Constants

In this section the mechanism at the two main pH values (9.00 and 4.66) will be treated separately. In addition the treatment for pH 9.00 is divided into two parts, one for magnesium and the other for cobalt and nickel, since these two groups of ions differ considerably. The rate constants for pH 9.00 given in this section were those which gave the best agreement between the measured and calculated values of τ. The rate constants for pH 4.66 were determined by a graphical method.

pH 9.00. Magnesium.—One relaxation time is observed for magnesium at pH 9.00. The main metal–ligand reaction is

$$\overset{\textcircled{2}}{\mathrm{Mg + Hti}} \underset{k_{52}}{\overset{k_{25}}{\rightleftharpoons}} \overset{\textcircled{5}}{\mathrm{MgHti}} \qquad \mathrm{(I)}$$

At this pH, the reactions of state ③ cannot compete with ② since $[ti] = 2.5 \times 10^{-4}[Hti]$ and k_{36} will at most not be more than 2 to 5 times larger than k_{25}.

The step ① $\rightleftharpoons$ ④ also makes a negligible contribution to the rate, since [Hti] > [H_2ti] and $k_{14} \cong k_{25}$ (see below). Nevertheless, the conservation equations will be affected by the rapid equilibrations between states ① and ②, ⑤ and ⑥, and the rapidly established indicator equilibration (state ④ does not contribute at this pH). To calculate the relaxation time, the following reactions must therefore be added to (I)

$$\mathrm{H_2ti} + \mathrm{OH^-} \rightleftharpoons \mathrm{Hti}$$

$$\mathrm{MgHti} + \mathrm{OH^-} \rightleftharpoons \mathrm{Mgti}$$

$$\mathrm{R} + \mathrm{OH} \rightleftharpoons \mathrm{ROH}$$

(ROH = phenolphthalein)

Following the derivation previously outlined, and omitting the bar since $[\ \ ] \cong [\overline{\ \ }]$ (a procedure to be followed hereinafter) yields

$$1/\tau_{\mathrm{I}} = k_{25}([\mathrm{Mg}]\alpha_1 + [\mathrm{Hti}]) + k_{52}\beta_1 \qquad (1)$$

$$\alpha_1 = \frac{[\mathrm{OH}] + [\mathrm{H_2ti}]a_1}{[\mathrm{OH}] + K^{\mathrm{b}}{}_{\mathrm{Hti}}}$$

$$\beta_1 = \frac{K_{\mathrm{MgHti}} - [\mathrm{MgHti}]a_1}{K_{\mathrm{MgHti}} + [\mathrm{OH}]}$$

and

$$a_1 = \left[\frac{[\mathrm{OH}] + 2K^{\mathrm{b}}{}_{\mathrm{Hti}}}{[\mathrm{OH}] + K^{\mathrm{b}}{}_{\mathrm{Hti}}} - \frac{K^{\mathrm{b}}{}_{\mathrm{MgHti}}}{[\mathrm{OH}] + K^{\mathrm{b}}{}_{\mathrm{MgHti}}}\right] \Big/ \left[\frac{[\mathrm{H}]}{[\mathrm{OH}]} + \frac{[\mathrm{MgHti}]}{[\mathrm{OH}] + K^{\mathrm{b}}{}_{\mathrm{MgHti}}} + \frac{[\mathrm{H_2ti}]}{[\mathrm{OH}] + K^{\mathrm{b}}{}_{\mathrm{Hti}}} + \frac{[\mathrm{ROH}]}{[\mathrm{OH}] + K^{\mathrm{b}}{}_{\mathrm{ROH}}}\right]$$

Each of the terms [Mg], α_1, [Hti], and β_1 in eq. 1 can be calculated explicitly. The rate constants and the stability constants obtained from the quotient of the rate constants are given in Table III. The deviation in the stability constant for magnesium from that given in Table I is 23%, which is within the experimental error for this system.

TABLE III

Results at pH 9.00

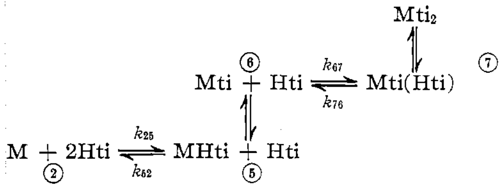
	$K^{\mathrm{M}}{}_{\mathrm{MHL}}$, M^{-1}	k_{25}, M^{-1} sec.$^{-1}$	k_{52}, sec.$^{-1}$
Mg^{2+}	1.2×10^2	3.5×10^6	3.0×10^4
Co^{2+}	1.01×10^3	4.20×10^6	4.15×10^3
Ni^{2+}	1.04×10^3	2.85×10^5	2.75×10^2

Results at pH 4.66

		k_{14}, M^{-1} sec.$^{-1}$	k_{41}, sec.$^{-1}$
Ni^{2+}	...	8.15×10^4	$k_{41} \geq k_{52}$
Co^{2+}	...	1.04×10^6	$k_{41} \geq k_{52}$

Nickel and Cobalt.—The important feature in deriving the mechanism for the nickel and cobalt data is that the data could not be interpreted consistently on the basis of formation of only one complex. The following inconsistencies were evident. (a) A single set of rate constants k_{25} and k_{52} which would fit the data within experimental error over the concentration range studied could not be found. (b) The best set of such rate constants for steps ② $\rightleftharpoons$ ⑤ resulted in an equilibrium quotient differing from the thermodynamically determined equilibrium quotient by approximately a factor of 2. (c) At approximately twofold stoichiometric excesses of tiron and higher, the observed relaxation times showed deviations from simple exponential behavior, indicating the presence of coupled relaxation processes. It was not possible to separate these processes, since higher excesses of tiron eventually coincide with smaller observable effects.

Since it is well known that tiron forms higher order complexes with other transition metal ions,[10–15] it has been assumed that a second complex of the type $\mathrm{Mti_2}$ or Mti(Hti) is formed in these solutions. Moreover, since [Niti] $\cong 2.5 \times 10^3$[NiHti] and [Coti] = 6.1×10^2[CoHti], the reaction between Hti and either NiHti or CoHti will be negligible in comparison to that with the unprotonated tiron complex. Thus, the mechanism used is



(II)

In mechanism II the vertical and horizontal arrows have the same meaning as before, M = Ni or Co, and state ⑦ represents the rapidly established equilibrium between Mti(Hti) and $\mathrm{Mti_2}$. The equilibration between ⑥ and ⑦ is also assumed to be rapid with respect to that between ② and ⑤ Under these assumptions the relaxation time for (II) is

$$1/\tau_{\mathrm{II}} = k_{25}[\mathrm{Hti}] + k_{52}\left(\frac{2[\mathrm{MHti}]}{[\mathrm{OH}]}\right) \times \left(\frac{K^{\mathrm{b}}{}_{\mathrm{ROH}} + [\mathrm{OH}]}{[\mathrm{ROH}]}\right)\left[1 + {}^3/_2\left(\frac{2[\mathrm{Mti}] + K_2{}^{-1}\alpha_2}{[\mathrm{Mti}] + [\mathrm{Hti}]}\right)\right] \qquad (2)$$

where

$$\alpha_2 = \frac{K^{\mathrm{b}}{}_{\mathrm{Mti(Hti)}}}{K^{\mathrm{b}}{}_{\mathrm{Mti(Hti)}} + [\mathrm{OH}]}\left[1 - 4\left(\frac{K^{\mathrm{b}}{}_{\mathrm{ROH}} + [\mathrm{OH}]}{[\mathrm{ROH}]}\right) \times \left(\frac{[\mathrm{MHti}]}{[\mathrm{OH}]} - \frac{[\mathrm{Mti(Hti)}]}{K^{\mathrm{b}}{}_{\mathrm{Mti(Hti)}}}\right)\right]$$

$$K_2 = \frac{[\mathrm{Mti(Hti)}]}{[\mathrm{Mti}][\mathrm{Hti}]} = \frac{k_{67}}{k_{76}}$$

$$K^{\mathrm{b}}{}_{\mathrm{Mti(Hti)}} = \frac{[\mathrm{Mti(Hti)}][\mathrm{OH}]}{[\mathrm{Mti_2}]}$$

In deriving eq. 2 use was made of the following approximations: $k_{67}, k_{76} >> k_{25}, k_{52}$; $[\mathrm{OH}] >> [\mathrm{Mti(Hti)}]$; $[\mathrm{OH}] >> K^{\mathrm{b}}{}_{\mathrm{Mti(Hti)}}$; $1 >> [\mathrm{H}]/[\mathrm{OH}]$. The reactions of $\mathrm{H_2ti}$, MHti, and $\mathrm{R^+}$ with $\mathrm{OH^-}$ were included, as in the case of magnesium.

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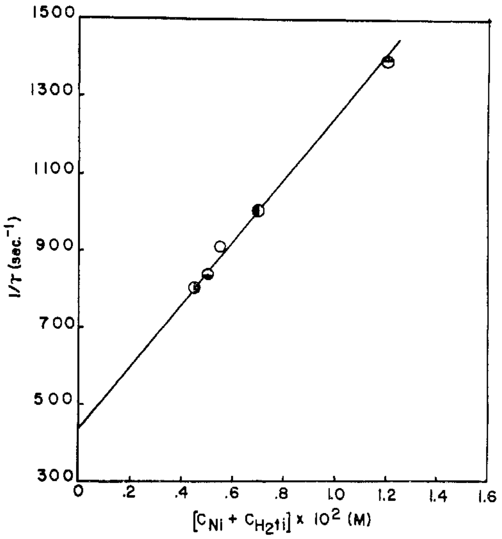

Fig. 2.—Concentration dependence of the nickel–tiron system at low pH, $\mu = 0.1$ *M*, and 20°. For concentrations see experiments in Table II. ◑, expt. 15; ◒, expt. 16; ○, expt. 14; ◐, expt. 17; ◓, expt. 18.

In evaluating the data for these systems, we begin with the terms comprising the coefficient of k_{52} in eq. 2. Of these quantities, $k_2^{-1}\alpha_2$ is not calculable. However, since the higher order complex manifests itself at all—and analogously to other known second-order tiron complexation constants—K_2 must be large with respect to unity. Further, since in the majority of protonated complexes the ratio of unprotonated to protonated favors the former, it is concluded that $K^{\mathrm{b}}_{\mathrm{Mti(Hti)}}$ and [Mti(Hti)] are small with respect to [OH]. Thus $K_2^{-1}\alpha_2 <<$ [Mti]. Then, if we let the remaining terms in the coefficient of k_{52} be represented by the symbol y, we have

$$1/\tau_{\mathrm{II}} = k_{25}[\mathrm{Hti}] + k_{52}y \tag{3}$$

where

$$y = 2\left(\frac{[\mathrm{MHti}]}{[\mathrm{OH}]}\right)\left(\frac{K^{\mathrm{b}}_{\mathrm{ROH}} + [\mathrm{OH}]}{[\mathrm{ROH}]}\right) \times \left(1 + \frac{3[\mathrm{Mti}]}{[\mathrm{Mti}] + [\mathrm{Hti}]}\right)$$

The rate constants and the equilibrium constants calculated from these rate constants are given in Table III. The deviations in the stability constants from the constants in Table I are 3.6% for nickel and −18% for cobalt.

pH 4.66.—At the lower pH values, results were obtained only for nickel and cobalt. Since the concentration of ti is so small at this pH, we need consider only

$$\begin{tikzcd} ② \quad \mathrm{M} + \mathrm{Hti} \arrow[r, shift left, "K_{25}"] \arrow[d, shift left] & \mathrm{MHti} \quad ⑤ \arrow[l, shift left, "K_{52}"] \arrow[d, shift left] \\ ① \quad \mathrm{M} + \mathrm{H_2ti} \arrow[r, shift left, "k_{14}"] \arrow[u, shift left] & \mathrm{MH_2ti} \quad ④ \arrow[l, shift left, "k_{41}"] \arrow[u, shift left] \end{tikzcd} \tag{III}$$

To this mechanism the indicator equilibrium must be added, namely

$$\mathrm{HIn} \rightleftharpoons \mathrm{H^+} + \mathrm{In^-}$$
(HIn = chlorophenol red or methyl red)

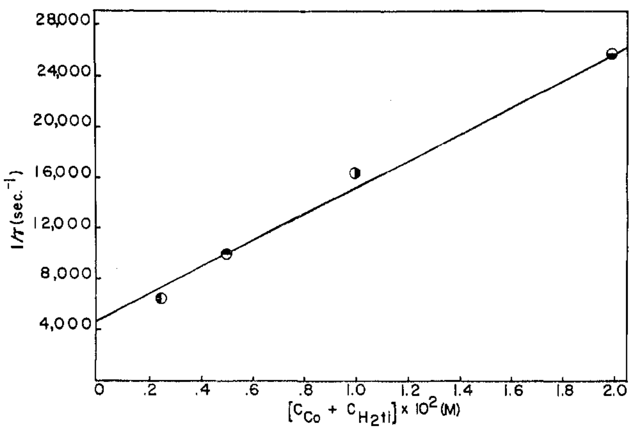

Fig. 3.—Concentration dependence of the cobalt–tiron system at pH 4.66, $\mu = 0.1$ *M*, and 20°. For concentrations see experiments in Table II. ◐, expt. 19; ◓, expt. 20; ◑, expt. 21; ◒, expt. 22.

In obtaining a solution for this mechanism we do not distinguish *a priori* between the paths ① ⇌ ④ ⇌ ⑤ and ① ⇌ ② ⇌ ⑤. However, the over-all second-order rate constant for the pathway involving Hti (state ②) is

$$\frac{K_{\mathrm{H_2ti}}}{[\mathrm{H}]}k_{25} = \frac{2.2 \times 10^{-8}}{2.2 \times 10^{-5}}k_{25} = 10^{-3}k_{25}$$

Since $[\mathrm{H_2ti}] >> [\mathrm{Hti}]$ and k_{14} is roughly of the same order of magnitude as k_{25}, the k_{25} term is negligible in comparison with k_{14}, so that steps ① ⇌ ④ ⇌ ⑤ are the most significant at this pH. Using this approximation and the fact that $[\mathrm{H_2ti}] >> [\mathrm{Hti}]$ leads to the following expression for the relaxation time

$$1/\tau_{\mathrm{III}} = k_{14}([\mathrm{M}] + [\mathrm{H_2ti}]) + k_{52} \times \left[\left(\frac{K_{\mathrm{MH_2ti}} - [\mathrm{MHti}]a_2}{K_{\mathrm{MH_2ti}} + [\mathrm{H}]}\right) + [\mathrm{MHti}]a_2\right] + k_{41}\left(\frac{[\mathrm{H}] + [\mathrm{MHti}]a_2}{[\mathrm{H}] + K_{\mathrm{MH_2ti}}}\right) \tag{4}$$

where M = Co or Ni, and

$$a_2 = \left(\frac{1}{K_{\mathrm{MH_2ti}} + [\mathrm{H}]}\right)\left[\frac{K_{\mathrm{MH_2ti}}}{\dfrac{[\mathrm{MHti}]}{K_{\mathrm{MH_2ti}} + [\mathrm{H}]}\,\dfrac{[\mathrm{In}]}{K_{\mathrm{HIn}} + \mathrm{H}} + 1}\right]$$

As eq. 4 indicates, the relaxation time (τ_{III}) is dependent upon both reverse rate constants k_{52} and k_{41} multiplied by their respective coefficients. Since $K_{\mathrm{MH_2ti}}$ is not known, it is not possible to evaluate these two terms separately. A plot of the reciprocal relaxation time *vs.* the sum of the concentrations of metal ion and $\mathrm{H_2ti}$ is shown in Fig. 2 and 3 for nickel and cobalt, respectively. There are two points to be noted. First, each curve is a straight line, within experimental error, indicating that the relaxation time is not sensitive to [H] or [MHti]. The slope is equal to the rate constant k_{14}, which is given in Table III. Second, the value of the intercept is consistent with the data at high pH since this value (435 sec.$^{-1}$) is greater than k_{52}. If it were less, there could possibly be an inconsistency. Therefore, only the lower limit for k_{41} could be determined. This quantity is also shown in Table III.

Discussion

Metal ion substitution reactions may be controlled by a first-order process and thereby independent of the incoming ligand, or controlled by a second-order process and thus ligand dependent. In the case of substitution reactions controlled by a first-order process, the mechanism has at least two well-defined steps. First, there is the rapid, diffusion-controlled formation of an ion pair. The equilibrium quotient for this step may be estimated from an equation derived independently by Eigen[16] and Fuoss.[17] In the second, rate-determining step a water molecule is dissociated from the aquated metal complex and ligand substitution can consequently occur.

By using the sound absorption method it has, in some cases, been possible to detect and measure the rate of each step separately.[18-20] Temperature-jump studies, in which a bimolecular rate constant is experimentally measured, may be used to obtain the value of the unimolecular substitution rate constant if the experimentally determined rate constant is divided by the ion-pair equilibrium quotient. Unimolecular substitution rate constants determined in this way may be compared with the results obtained from n.m.r. studies of the lifetime of water molecules in the inner coordination sphere of paramagnetic ions. Connick and Swift[21] reported the first-order rate of water exchange for a number of divalent transition metal ions. The results of the n.m.r. and relaxation experiments are in good agreement with regard to the mechanism of substitution and the rate of substitution. Thus, the substitution rate constants for Ni^{2+}, Co^{2+}, and Mg^{2+} are about 1×10^4, 2.5×10^5, and 1×10^5 sec.$^{-1}$, respectively. These values are correct to within a factor of 2 or 3, depending upon the uncertainty in the ion-pair formation constant.[22]

If the effective charge at the binding site at a pH of 9.00 is approximately -2, the ion-pair formation constant is on the order of 10 M^{-1}.[6] For a pH of 4.66, the observed rate constant is only slightly lower, thus the ion-pair formation constant is also lower by about the same factor. The unimolecular substitution rate constants obtained by correcting for the rapid ion-pair equilibration are therefore consistent with the previously cited rate constants.

It may consequently be concluded that protonation does not act to reduce the charge density at the binding site as drastically as, for example, F^- *vs.* HF; *i.e.*, F^- substitutes more than 100 times faster than HF.[23] The very large differences in stability of Mti with respect to MHti are therefore due to the difference in the dissociation rate constant, an effect which has been observed by Melson and Wilkins[24] in a slightly different context for nitrogen-containing unidentate ligands. The effect is approximately the same for the nickel(II) and cobalt(II) ions. Moreover the (estimated) values for k_{41} and the lack of an observed effect for magnesium at the low pH (where [MgH_2ti] would be expected to be highest) indicate that the MH_2ti complex would have a much smaller stability constant than the MHti complex. These results, which conclusively point to the existence of NiHti and CoHti complexes in agreement with the thermodynamic data,[3,4] raise some questions about the structure of these species with regard to the position of the proton.

Bidentate bonding with Hti would take place either between the sulfonate group and the adjacent hydroxyl group or between the two hydroxyl groups since complexation by any other pair of sites would result in a ring of unreasonable strain. The single dissociable proton in Hti is probably located in a hydrogen bond between the sulfonate group and the adjacent hydroxyl group with the metal ion bonding between the two phenolic hydroxyl groups, as is the case for other dihydroxy ligands.[25]

The pK values of the protons associated with the two sulfonate groups are too low to be measured. Protonation of the complex MHti must therefore introduce a positively charged species directly into the metal–chelate ring system. The binding is thereby rendered unstable, causing increased dissociation of the complex. The intramolecular hydrogen bonding increases the stability of the protonated complex by providing a mechanism for the withdrawal of excess repulsive charge (that of the proton) from the metal–ligand bond.

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