TABLE I: Reaction Network for the Thiocyanate–Iodate Reaction

<table>
<thead>
<tr>
<th>no.</th>
<th>reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>IO₃⁻ + SCN⁻ + H₂O → SO₄²⁻ + I⁻ + HCN + H⁺</td>
</tr>
<tr>
<td>M2</td>
<td>IO₃⁻ + 5I⁻ + 6H⁺ → 3I₂ + 3H₂O</td>
</tr>
<tr>
<td>M3</td>
<td>I₂ + CN⁻ → ICN + I⁻</td>
</tr>
<tr>
<td>M4</td>
<td>3I₂ + SCN⁻ + 4H₂O → 6I⁻ + SO₄²⁻ + HCN + 7H⁺</td>
</tr>
<tr>
<td>M5</td>
<td>I₂ + I⁻ = I₃⁻</td>
</tr>
<tr>
<td>M6</td>
<td>ICN + H⁺ + I⁻ = I₂ + HCN</td>
</tr>
<tr>
<td>M7</td>
<td>6IO₃⁻ + 5SCN⁻ + 2H₂O → 3I₂ + 5SO₄²⁻ + 6HCN + CN⁻</td>
</tr>
<tr>
<td>M8</td>
<td>7IO₃⁻ + 5SCN⁻ + 2H⁺ → I₂ + 5ICN + 5SO₄²⁻ + H₂O</td>
</tr>
<tr>
<td>M9</td>
<td>HCN = H⁺ + CN⁻</td>
</tr>
</tbody>
</table>

**Reaction Network.** Nine reactions may be identified as relevant in acidic mixtures of iodate and thiocyanate (Table I).

- **Reaction M1:** This is the stoichiometry of the reaction when thiocyanate is in excess over iodate. Its rate of reaction depends strongly on pH.
- **Reaction M2:** The well-known Dushman reaction is a standard reaction in volumetric analysis.¹⁷ Its rate is proportional to [H⁺]². In excess iodate conditions, after production of iodide in reaction M1, we would expect this reaction to take over and produce iodine.
- **Reaction M3:** This is a rapid reaction which almost instantaneously consumes all iodine produced in (M2) for as long as there is cyanide in solution (from (M1)).
- **Reaction M4:** The oxidation of thiocyanate by iodine has been studied by several workers.²⁻³ It is a very slow autoinhibitory reaction.
- **Reaction M5:** The iodine–iodide reaction is a rapid equilibrium.¹⁸
- **Reaction M6:** In high acid, ICN can regenerate I₂ and HCN.¹⁶ This is possible because HCN is such a weak acid.
- **Reaction M7:** This reaction (R3) is significant only in high acid conditions, since the cyanide ion’s affinity for acid is weaker than its affinity for iodine. The reaction as written may appear incomplete, since we still have CN⁻ and I₂ among the products. However, since the medium is highly acidic, the CN⁻ ions quickly combine with H⁺ ions of the medium to form HCN. If excess ICN has been formed, reaction M6 can regenerate iodine.
- **Reaction M8:** This reaction (R2) can be viewed as a composite of (M1), (M2), and (M3). It has a short induction period and is also catalyzed by acid.


**Discussion**

The nine reactions we have identified can explain the oligooscillatory behavior observed. In excess thiocyanate conditions (Figure 1), reaction M1 produces iodide ions before the iodate is totally consumed. Thus, for some time there is competition between SCN⁻ and I⁻ for IO₃⁻ (reactions M1 and M2), and iodine is produced by (M2). Competition ends when the iodate ions have been depleted. At this point, the solution now has iodine, thiocyanate, and reaction products of reaction M1. Reaction M4 now controls the observed depletion of iodine. Although reaction M4 is reported to be slow and autoinhibitory, this behavior is less pronounced when [SCN⁻]₀ > [I₂]₀. In fact, when thiocyanate is in sufficient (about 10-fold) excess over iodine, the reaction is quite fast, and pseudo-first-order kinetics can be observed.¹⁸ Reaction M3 is significant only after SCN⁻ is oxidized and the sulfur–carbon bond has been cleaved. Reaction M5 is necessary to achieve an accurate depiction of the iodine species present.

In excess iodate conditions (Figure 2), reaction also commences with (M1) and (M2). The difference now is that thiocyanate is depleted instead of iodate. The drop in [I₂] next observed results from reaction M3. The further rise in iodine concentration at the end of the reaction is caused by (M6), which depletes ICN and yields the stoichiometric amount of iodine in highly acidic environments. Oxidation of thiocyanate goes through several intermediates¹¹ before formation of CN⁻, which will then consume the iodine formed by (M2). When iodate is in excess, the overall oxidation of thiocyanate, which produces iodide, is controlled by the [H⁺] dependence of (M2). If [H⁺] is sufficiently high, iodine is produced rapidly enough to accumulate; lower [H⁺] places (M2) at a kinetic disadvantage compared with (M1) and (M4).

The reaction network we have proposed qualitatively explains the observed oligooscillatory behavior. The mechanisms of reactions M1 and M7 (or M8) have not, however, been fully explored.

**Acknowledgment.** We acknowledge the University of Zimbabwe for granting leave of absence to R.H.S. during the summer of 1987. We thank Morningstar Manyonda and Jonathan Masere, who performed some of these experiments. This work was supported by Research Grant CHE-8800169 from the National Science Foundation and Grant 2.9999.10:2789 from the University of Zimbabwe Research Board.

**Effects of Intramolecular Hydrogen Bonding on the Rates of Complex Formation of Co²⁺ and Zn²⁺ with Substituted Salicylic Acids**

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The kinetics of the complex formation of Co²⁺ and Zn²⁺ with two substituted salicylates have been investigated and compared to those of Ni²⁺ (reported previously). The rate constants for the unprotonated salicylates are consistent with a rate-determining first substitution step at the respective aquometal ion. Because of strong intramolecular hydrogen bonding, the monoprotonated ligands are much less reactive (80-4000-fold). The metal ion dependence of the rate constants for these species leads to the conclusion that in the reactions involving Ni²⁺ and Co²⁺ ring closure is rate determining, whereas in case of the very labile Zn(II) the opening of the internal H bond in the initial complex becomes rate determining.

In a previous publication we have reported on the kinetics of complex formation of Ni²⁺ with a series of substituted salicylic acids.¹ The unprotonated form of 3,5-dinitrosalicylic acid (DNSA) reacts with Ni²⁺ with a rate constant (k₅ = 3.1 × 10⁶

0022-3654/89/20/1691-1694 © 1989 American Chemical Society
shown in Figure 1 in the form of plots of the reciprocal relaxation time, $1/\tau$ vs. the metal ion concentration. Each value of $\tau$ given is the mean of at least four individual measurements. With Co$^{2+}$ + DNSA, additional experiments were carried out at pH 4.56. In order to achieve sufficiently large amplitudes, high metal ion concentrations, e.g., $9 \times 10^{-3}$–$5 \times 10^{-4}$ M, are required at this low pH (results not included in Figure 1b). At a given pH relationships of the type

$$1/\tau = k_1[Co^{2+}] + k_2$$

are observed for both systems. This behavior is consistent with a reaction scheme of the form

$$\begin{align*}
Co^{2+} + L^{2-} & \rightarrow \frac{k_1}{k^-_1} CoL \\
Co^{2+} + HL & \rightarrow \frac{k_2}{k^-_2} CoLH^+
\end{align*}$$

where $L^{2-}$ represents a ligand species in which the carboxylate group and a hydroxy group are deprotonated. The protolytic steps may be considered as rapid pre-equilibria compared to the complex formation steps. Indeed, varying the concentration of buffer (cacoxylic acid) did not affect the observed time constant $\tau$. Then

$$k_1 = k_1K_{A2}[H^+] + k_2$$

with $K_{A2} = [H^+][L^2-]/[HL^-] \ll [H^+]$, and

$$k_6 = k_1 + k_2[H^+]/K_c$$

where $K_c$ = $[H^+][CoL]/[CoLH^+] \gg [H^+]$.

For Co$^{2+}$-DHBA, the slopes of the plots of $1/\tau$ vs $[Co^{2+}]$ (Figure 1a) do not exhibit a significant variation with pH. The straight lines shown have equal slopes and have been placed such that they give a good fit to the experimental data (uncertainties in $\tau$ are $\pm 6\%$). The near-constancy of the slopes indicates that the complex formation occurs almost exclusively by reaction with HL$^-$ and gives $k_1 = k_2 = 6.6 (\pm 0.9) \times 10^3$ s$^{-1}$.

The experimental data for Co$^{2+}$ + DNSA indicate that both pathways contribute to the overall reaction. Introducing eq 4 and 5 (and simple equilibrium relationships) into the expression for $1/\tau$ (eq 2) yields

$$\begin{align*}
\frac{1}{\tau} &= (k_1K_{A2} + k_2[H^+])([Co^{2+}]/[H^+] + \frac{1}{K_{ML}K_c}) \\
\text{with } K_{ML} &= [CoL]/[Co^{2+}][L^2-] = k_1/k_2$
\end{align*}$$

Values of $k_1$, $k_2$, and $K_{ML}$ were evaluated from eq 6 by a computer-programmed least-squares fit using all 26 experiments: $k_1 = 2.3 (\pm 0.1) \times 10^4$ M$^{-1}$ s$^{-1}$, $k_2 = 7.1 (\pm 0.8) \times 10^3$ M$^{-1}$ s$^{-1}$, $K_{ML} = 2.1 (\pm 0.15) \times 10^4$ M$^{-1}$. The quality of the fit is demonstrated by a comparison of the observed and calculated values of $\tau$, Table I. The experimental errors in $\tau$ are highest at low pH and low Co$^{2+}$ concentrations (small relaxation amplitudes).

Analogous experiments were carried out for the system Zn$^{2+}$ + DNSA ([Zn$^{2+}$] = $1 \times 10^{-7}$–$7 \times 10^{-5}$ M, [DNSA] = $1 \times 10^{-4}$ M, pH 5.0–6.0, $\lambda$ = 390 nm). Again only one time constant was observed in all experiments. The kinetics, however, appear to be more complicated than in the reactions with Co$^{2+}$. The measured time constant ($\tau = 11–54 \mu$s) depends also on the concentration of buffer ($2 \times 10^{-3}$–$10 \times 10^{-3}$ M cacoxylic acid), and under

$$\begin{align*}
\text{(4) A referee has pointed out (and we had noticed before) that a better fit can be obtained if the condition } K_c \gg [H^+] \text{ (line after eq 5) is abandoned.} \\
\text{The last term of eq 6 has then to be multiplied by } K_c/(K_c + [H^+]). \text{ Using this equation, a best fit is obtained with } K_c = 1.6 \times 10^7 \\text{M}^{-1} \text{s}^{-1}, k_2 = 2.0 \times 10^4 \text{M}^{-1} \text{s}^{-1}, \text{ and } K_{ML} = 1.9 \times 10^4 \text{M}^{-1}. \text{ We consider this improvement of the fit to be fortuitous since all other evidence indicates that } K_c \text{ is much larger than } 1.6 \times 10^7 \text{M}^{-1}. \text{ The results of our equilibrium studies for } Ni^{2+}-\text{DNSA and } Co^{2+}-\text{DNSA (ref 1 and this paper) indicate } K_c \geq 4 \times 10^4 \text{M for } Ni^{2+}-\text{DNSA. A similar value should be expected for } Co^{2+}-\text{DNSA.}$
most conditions $\tau$ increases with increasing metal ion concentration. Complex formation reactions of Zn$^{2+}$ proceed much faster than those of Ni$^{2+}$ and Co$^{2+}$, and apparently the protonation/deprotonation steps (scheme 3) are no longer rapid pre-equilibria compared with the reaction steps with Zn$^{2+}$. Only one reaction effect is observed since L$^2$ and ZnLH$^+$ may to a good approximation be considered as steady states under our conditions. Thus we are left with the overall reaction

$$\text{Zn}^{2+} + \text{LH}^- \rightleftharpoons \text{ZnL} + \text{H}^+$$  \hspace{1cm} (7)

which may proceed by two pathways, via L$^2$ or via ZnLH$^+$ (scheme 3). Which [Zn$^{2+}$] $\gg$ [DNSA] and the steady-state approximations for [L$^2$] and [ZnLH$^+$], the reciprocal relaxation time is now given by

$$\frac{1}{\tau} = \frac{k_1 k_{2} [\text{Zn}^{2+}] + k_{2} k_{p} L}{k_1 [\text{Zn}^{2+}] + k_{p} L} + \frac{k_{2} k_{c} [\text{Zn}^{2+}] + k_{2} k_{p} C}{k_{c} C + k_{-2}}$$  \hspace{1cm} (8)

where $k_{p}$ and $k_{c}$ are the rate constants for the protonation and deprotonation of the ligand (uncatalyzed and buffer-catalyzed, i.e., $k_{p} = k_{p} [\text{H}^+] + k_{p} [\text{Ca}^+][\text{H}^+]$, $k_{c} = k_{c} + k_{c} [\text{ca}^-]$, where $\text{H}^+ + \text{L}^2 \rightleftharpoons \text{LH}^- + \text{ca}^-$) and $k_{c} C$ and $k_{c} C$ are the rate constants for protonation and deprotonation of the complex. The rate constants $k_{p}$ and $k_{c}$ (i.e., $k_{p} k_{p} k_{p} L$, and $k_{c} C$) have been determined experimentally, whereas values for $k_{c} C$ and $k_{c} C$ can only be estimated. Then the rate constants $k_{1}, k_{2}, k_{3},$ and $k_{4}$ may be evaluated (from 31 experiments) by a fitting procedure based on eq. 8. The evaluation clearly showed that $k_{3} C > k_{3} C$. This condition allows a simplification of the expression for 1/1 (and with equilibrium relationships) a reduction in the number of parameters which have to be fitted (now 3):

$$\frac{1}{\tau} = \frac{k_1 k_{2} [\text{Zn}^{2+}] + k_{2} k_{p} L}{k_1 [\text{Zn}^{2+}] + k_{p} L} + \frac{k_1 [\text{H}^+] + k_2 k_{c} [\text{Zn}^{2+}]}{k_1 k_{2} C}$$  \hspace{1cm} (9)

In addition, this modification eliminates the quantities $k_{2} C$ and $k_{3} C$ for which only estimated values are available. A fitting program based on eq. 9 yielded $k_1 = 5.6 \pm (1.4) \times 10^{3} \text{ M}^{-1} \text{s}^{-1}$.

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(2) and (5) is not fulfilled: In M–LH⁺ the metal ion is bound to the carboxylic group whereas in M–L it may be bound preferentially to the phenolic O– atom.

Which conclusions can be drawn from the magnitude of the observed rate constants?

The values of k₁ for the reactions with DNSA²⁻ are in line with those of other ligands of simple structures reacting with these three metal ions; i.e., they are of the magnitude as expected for a rate-determining first substitution step at the aquometal ions. In the case of the strongly basic DHBA²⁻, only upper limits of k₁ could be evaluated. Presumably the true values are about the same as those for DNSA²⁻.

By contrast, the rate constants k₂ for the reactions with HL⁻ of DNSA and DHBA are by 2–3 orders of magnitude lower than the corresponding values of k₁. Electrostatic effects will contribute not more than a factor 5 to these differences. Obviously the first substitution step cannot be rate determining in the reactions with HL⁻. As demonstrated previously, the monoprotonated forms of DHBA and DNSA are characterized by strong intramolecular hydrogen bonding. The low rates of the reactions Ni²⁺ + HL⁻ were rationalized in terms of scheme 1, shown above, with the second step (k₆) or the third step (k₃) being rate determining. The new data presented here allow a distinction between these two possibilities. The data of Table III reveal that the values of k₆ are much higher in the case of Co²⁺ than for Ni²⁺. A similar difference has been reported also for unsubstituted salicylic acid.

If the second step, the opening of the intramolecular H bond, were rate determining, then k₂ = (k₆/k₃)k₆. Now, the stability constant for the binding of Co²⁺ to a given ligand is usually somewhat lower than that for the binding of Ni²⁺, in accordance with the Irving–Williams rule, and the same is expected for k₆/k₃. Furthermore, the rate of opening the intramolecular H bond, k₆, will not depend very much on whether the bound metal ion is Co²⁺ or Ni²⁺. Therefore, if k₆ were rate determining, k₂ should be slightly lower for Co²⁺ than for Ni²⁺, contrary to our observations. If, however, ring closure were rate determining, i.e., k₂ = (k₁k₆/k₆k₃)k₆, then the higher values of k₂ in case of Co²⁺ are easily rationalized by the differences in k₆. This rate constant for ring closure, i.e., for the second substitution step at the metal center, is much higher in case of Co(II) than in the case of Ni(II).

The evaluations of the kinetics for the reaction Zn²⁺ + DNSA yield a value of k₁ which is about 200-fold larger than the one for Co²⁺ + DNSA. Differences in rate by about a factor 100 have also been reported for the complex formation reactions of several other ligands with these two metal ions. The rate constant k₂, however, is only 20-fold higher for Zn²⁺ + HL⁻ as compared to Co²⁺ + HL⁻. As discussed before, the reaction with HL⁻ includes a pathway in which the ligand’s hydrogen bond is closed (k₃H) and one in which it is open (k₃), k₂ = k₃H + 10⁴k₃o, where the factor 10⁴ denotes the fraction with the open structure. The reaction with the open form is expected to show normal behavior, the first substitution step being rate determining. For Zn²⁺ + HL⁻ (open) the value of k₂ will be near 1 × 10⁸ M⁻¹ s⁻¹. Thus the pathway with the “open” ligand contributes heavily to k₂ (contrary to the systems Ni²⁺–DNSA and Co²⁺–DNSA), and k₃H is below 1 × 10⁷ M⁻¹ s⁻¹, i.e., it is not much higher than in case of Co²⁺. This relatively small variation in k₃H may well be indicative of a change in the rate-determining step (scheme 1): Presumably the rate of the second binding step, k₃, is so high in the case of Zn²⁺ that now k₂ > k₃o, i.e., the second step of scheme 1 becomes rate determining, k₄H = (k₆/k₃)k₆. Such a change in the rate-determining step would be expected if k₃o is near 10⁷ s⁻¹, since then k₄H/k₄o < k₃o, but k₃ > k₃o.

The kinetic data reported here also provide some information on the complex stabilities. The [H⁺] dependence of the apparent stability constant kₐpp = k₁/k₃ enables the determination of individual stability constants; see eq 4 of ref 1. For Co²⁺–DHBA results KML = [ML]/[M²⁺][L²⁻] = k₁/k₃ = 6.4 × 10⁴ M⁻¹ (Ni²⁺–DHBA²⁻ 2.0 × 10⁸). For Co²⁺–DNSA²⁻ the computer evaluation (see above) yields directly KML = 2.1 × 10⁸ M⁻¹ (Ni²⁺–DNSA²⁻, 6 × 10⁴). Potentiometric titrations (applying a procedure described earlier) and spectrophotometric titrations yielded a somewhat higher value for the stability constant of Co²⁺–DNSA²⁻: KML = 2.7 (±0.2) × 10¹⁰ M⁻¹. Evidence for the formation of appreciable amounts of protonated complex, CoLH⁺, at pH values ≥5.0 could not be derived from these studies. The relative stabilities of the Ni²⁺ and Co²⁺ complexes confirm what was stated above. Finally, the ratio k₁/k₃ for Zn²⁺–DNSA (see above) gives KML = 4 × 10³ M⁻¹.


(8) Taylor, R. S.; Diebler, H. Bioinorg. Chem. 1976, 6, 246.