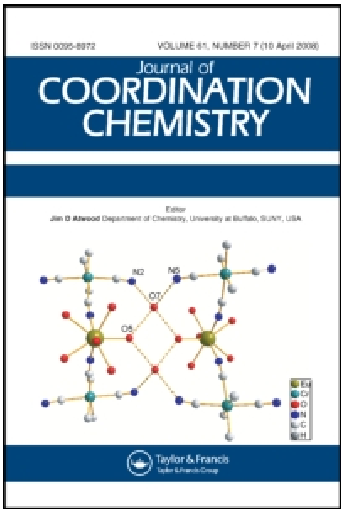

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COMPLEX FORMATION BETWEEN V(III) IONS AND 5-NITROSALICYLIC ACID. REACTION MECHANISM AND EQUILIBRIUM CONSTANTS

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INTRODUCTION

In continuation of our program of investigating the mechanism of the formation of complexes between tervalent cations and acids of moderate strength, we report in this Note the results of a study of the reaction between V(III) and 5-nitrosalicylic acid. Our aim was to compare the rate constants obtained with those reported previously for salicylic[1] and *p*-aminosalicylic[2] acids. All three ligands have identical reaction sites and differ only in their basicity.

EXPERIMENTAL

The 5-nitrosalicylic acid was Fluka "purum". Solutions of V(III) were prepared as described previously.[1,2] The kinetic results were again[1,2] obtained by the stopped flow technique, but using a Durrum apparatus. The temperature was 25°C throughout, and the ionic strength was 1M. The concentrations of the cation, *a*, ranged between 2.33×10^{-3} and 2.33×10^{-2} M, and were in excess over those of the ligand, *b*, which ranged between 1×10^{-4} and 2×10^{-4}M. All experiments were carried out at a wavelength of 365 nm, where the difference in absorption between the complex and the sum of absorptions of 5-nitrosalicylic acid and of V(III) solutions, at the same concentration and pH, was at its maximum.

RESULTS

Equilibrium Constants

We found it again[1-3] convenient to define an apparent formation constant, K_{app}, which gives the ratio between the concentrations of total complexed and total uncomplexed participants, and depends on $[H^+]$. With the aid of K_{OH}, the hydrolysis constant of V^{3+}, and K_{H1}, the first dissociation constant of 5-nitrosalicylic acid, we can write (where "Sal" stands for the salicylic acid ion)

$$K_{app} = \frac{[\text{complex}]\,[H^+]}{[V^{3+}]\,[NO_2HSal^-]} \times \frac{K_{H1}}{(K_{OH} + [H^+])(K_{H1} + [H^+])} \qquad (1)$$

(neglecting NO_2Sal^{2-} whose relative concentration is negligibly small).[4]

At two hydrogen ion concentrations, namely 0.25 and 0.35M, K_{app} was measured spectrophotometrically, and at four hydrogen ion concentrations, namely, 0.2, 0.3, 0.4 and 0.5M, it was evaluated kinetically from the concentration-dependence of k_{obsd}, the observed, psendo-first-order, rate constant; both methods are explained in our previous papers.[1-3]

Figure 1 shows a plot of $K_{app}\,(K_{OH} + [H^+])(K_{H1} + [H^+])$ as a function of $[H^+]$, with [5]$K_{OH} = 1.4 \times 10^{-3}$M and [3]$K_{H1} = 5.7 \times 10^{-3}$M. A straight line is seen to be obtained in this range, with satisfactory agreement between the kinetic and spectrophotometric results. We conclude that there are again[1] two complexes present, and Eq. (1) can be rewritten as

$$K_{app}\,(K_{OH} + [H^+])(K_{H1} + [H^+]) = K_{H1}(K_1 + K_1'\,[H^+]) \qquad (2)$$

with

$$K_1 = \frac{[VNO_2Sal^+]\,[H^+]}{[V^{3+}]\,[NO_2HSal^-]} \qquad (3)$$

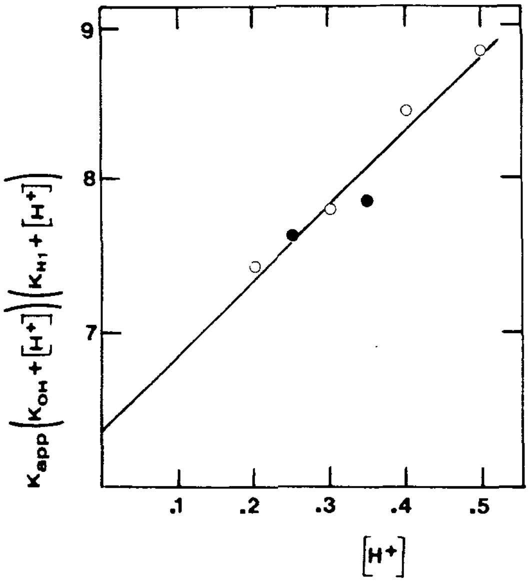

FIGURE 1 Dependence of $K_{app}(K_{OH}+[H^+])(K_{HI}+[H^+])$ on $[H^+]$ (see Eq. (2)); dots represent spectrophotometric, and open circles, kinetic results.

and

$$K_1' = \frac{[VNO_2HSal^{2+}]}{[V^{3+}][NO_2HSal^-]} \tag{4}$$

From the intercept and slope of Figure 1 we get the results for K_1 and K_1' shown in Table I. For the sake of comparison, the results for salicylic acid are included in this table.

Rate Constants

At all our values of $[H^+]$ the concentration of VOH^{2+} is very much smaller[5] than that of V^{3+}, whereas its rate constant has previously been found to be no higher[2,6-8] or even lower,[1] than that of V^{3+}. Therefore, the possible reactions contributing to the observed rate are

$$\begin{array}{lll} V^{3+} + NO_2HSal^- & \overset{k_1}{\rightleftharpoons} & VNO_2HSal^{2+} \\ & \rightleftharpoons & VNO_2Sal^+ + H^+ \quad (I) \\ V^{3+} + NO_2H_2Sal & \overset{k_2}{\rightleftharpoons} & VNO_2HSal^{2+} + H^+ \\ & \rightleftharpoons & VNO_2Sal^+ + 2H^+ \quad (II) \end{array}$$

TABLE I

Comparison of equilibrium constants for V(III) complexes

acid conjugate to ligand	$10^{-2}K_1$	$10^{-2}K_1'$, M^{-1}	10^3K_{HI}, M	[a]$10^{14}K_{H2}$, M	$10^{-13}K_1/K_{H2}$, M^{-1}
[b]salicylic	2.2	21	1.6	5.0	4.4×10^2
5-nitro-salicylic	11.3 ± 0.4	8.5 ± 1.0	[c]5.7	7.4×10^3	1.5

[a]reference 4; [b]reference 1; [c]reference 3

TABLE II

Comparision of rate constants for complex formation between V^{3+} and salicylic, and substituted salicylic, acids

ligand	[a]pK	k, M^{-1} s^{-1}	references
NO_2H_2Sal		3.5 ± 0.2	this work
H_2Sal		4.9	[b]1
$^+NH_3H_2Sal$		3.3 ± 0.1	2
NH_2H_2Sal		3.3 to 25	2
NO_2HSal^-	2.24	$(1.23 \pm 0.02) \times 10^3$	this work
$HSal^-$	2.80	1.4×10^3	[b]1
$^+NH_3HSal^-$	2.84 to 3.44	$(1.6 \text{ to } 7.0) \times 10^3$	2
NH_2HSal^-	3.60	$(7.0 \pm 1.6) \times 10^3$	2

[a]Dissociation constants of the acids conjugate to the active site;
[b]Interpolated to 25° C

Assuming all the protolytic equilibria to be again[1] rapid, and taking into account that, in all our experiments, $[H^+] \gg b$ we can write[1-3]

$$k_{obsd} = [k_1 + (k_2/K_{HI})[H^+]] \times B \tag{5}$$

where

$$B = \frac{(K_{app}\bar{a} + 1)[H^+]}{K_1 + K_1'[H^+]} \tag{6}$$

A plot of k_{obsd}/B as a function of $[H^+]$ is shown in Figure 2, for twenty-eight experiments at values of $[H^+]$ between 0.20 and 0.90M. Treating this figure as a straight line in accordance with Eq. (5), we calculated the rate constants shown in Table II. (At

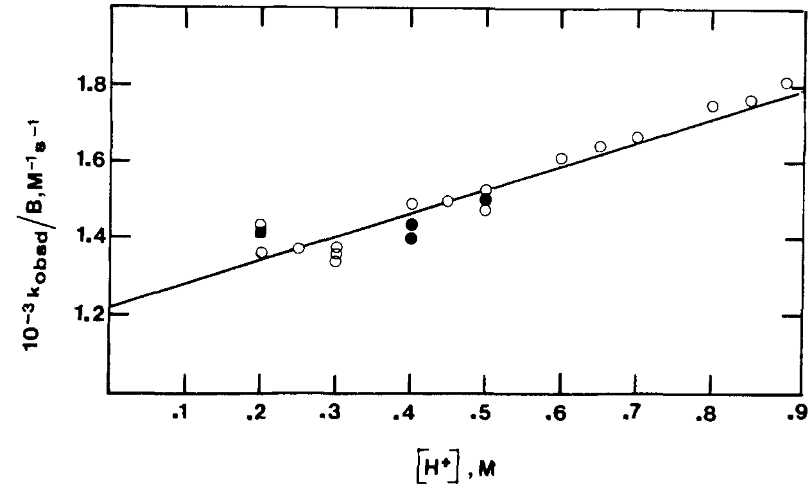

FIGURE 2 Dependence of k_{obsd}/B on $[H^+]$ (see Eq. (5)); dots represent two coinciding results, and full square represents three.

hydrogen ion concentrations of 0.1M and below, the experimental points fall very significantly below the straight line drawn in Figure 2. Since we have no data on K_{app} in this range, the complex being too strong for a satisfactory determination, we decided to disregard these results for the present.)

DISCUSSION

The equilibrium data for salicylic and 5-nitrosalicylic acids presented in Table I provide additional evidence about the nature of the two complexes we have assumed in our system.

We expect the complex to be stronger the higher the basicity of the complexing ligand. This expectation is immediately borne out for VNO_2HSal^{2+}: of the two acids, salicylic acid has the lower value of K_{H1} and, correspondingly, the higher value of K'_1. At first sight, the opposite seems to be true for K_1. However, since in the formation of VNO_2Sal^+ the phenolic proton is expelled, the appropriate comparison[3] is not that between the values of K_1 on the one hand, and those of K_{H2} on the other, but rather between the values of $[VNO_2Sal^+]/[V^{3+}][NO_2Sal^{2-}] = K_1/K_{H2}$ and of K_{H2}. The two last columns in the table show that the relation between the basicity of the ligand and the stability of the complex is now in line with the expected pattern.

On the other hand, a comparison between K'_1 and K_1/K_{H2} shows that, for each ligand, the unprotonated complex is stronger than the protonated complex by a factor which is ~ 100 times higher than the effect expected from the different basicity of the ligand *alone*. This strengthens the assumption that VNO_2Sal^+ is a chelate whereas $VHNO_2Sal^{2+}$ is only a monodentate complex.

In our previous paper[2] we have already discussed not only the ligand dependence of the rate constant, but also the strong correlation between the rate constant and the basicity of the ligand which establishes V^{3+} as a hard acid.[9-11] This correlation becomes even more convincing now that we can compare ligands which have *identical* reactive sites but differ in their basicity. Such a comparison is presented in Table II, where we have summarized our data concerning salicylic and substituted salicylic acids. Our results thus further confirm the associative mechanism for V^{3+}-complex formation.[1,2,6-8]

The fact that Figure 2 does *not* curve upwards at low values of $[H^+]$ confirms the lack of reactivity of VOH^{2+}. In this respect, V(III) differs from other tervalent cations such as Al(III)[3] and Fe(III).[12] We should like to point out, however, that the lack of reactivity of the hydrolyzed species MOH^{2+} is, in itself, no proof for the associative mechanism for M^{3+}, just as we do not consider[3] the enhanced reactivity of MOH^{2+} as a proof for the dissociative mechanism for M^{3+}.

REFERENCES

1. B. Perlmutter-Hayman and E. Tapuhi, *J. Coord. Chem.*, 9, 177 (1979).

2. B. Perlmutter-Hayman and E. Tapuhi, *Inorg. Chem.*, **18**, 2872 (1979).
3. B. Perlmutter-Hayman and E. Tapuhi, *Inorg. Chem.*, **18**, 875 (1979).
4. D. V. Jahagirdar and D. Khanolkar, *J. Inorg. Nucl. Chem.*, **35**, 921 (1973).
5. L. Pajdowski, *J. Inorg. Nucl. Chem.*, **28**, 433 (1966).
6. R. C. Patel and H. Diebler, *Ber. Bunsenges.*, 76, 1035 (1972).
7. B. R. Baker, N. Sutin and T. J. Welch, *Inorg. Chem.*, **6**, 1948 (1967).
8. W. Kruse and D. Thusius, *Inorg. Chem.*, **7**, 464 (1968).
9. R. G. Pearson, *Chem. Brit.*, **3**, 103 (1967).
10. S. Ahrland, J. Chatt and N. R. Davies, *Quart. Rev. Chem. Soc.*, **12**, 265 (1958).
11. R. G. Pearson, *Science*, **151**, 172 (1966).
12. B. Perlmutter-Hayman and E. Tapuhi, *J. Coord. Chem.*, **6**, 31 (1976).