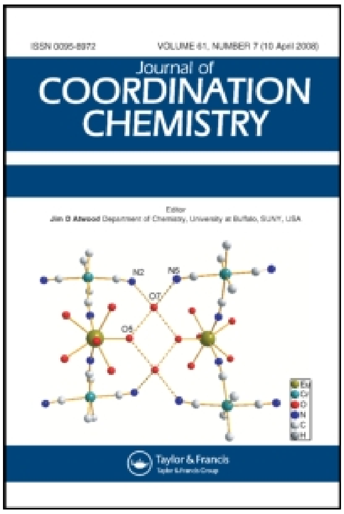

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THE KINETICS OF THE REACTION BETWEEN V(III) IONS AND SALICYLIC ACID. MECHANISM AND ACTIVATION PARAMETERS

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The kinetics of the reaction between V(III) and salicylic acid have been investigated in the temperature range between 7.5 and 45°C, at $I = 1$ M. Both kinetic and equilibrium measurements show that, at hydrogen ion concentrations between 0.015 and 0.8 M, two complexes are formed, namely, $VHSal^{2+}$ and $VSal^{+}$. The reaction proceeds by two parallel paths, involving V^{3+} and $HSal^{-}$, and V^{3+} and H_2Sal, respectively. At 27°C, the corresponding rate constants are $1.61 \times 10^3 M^{-1} s^{-1}$ and $5.9 M^{-1} s^{-1}$. No contribution of a pathway involving VOH^{2+} could be detected. This fact, together with the ligand-dependence of the rate constants, tends to confirm the S_N2 mechanism suggested by previous authors. The entropies of activation, however, are 2.2 e.u. and – within the experimental accuracy – zero, respectively. This apparent discrepancy is discussed in terms of the properties of salicylic acid. The reaction was monitored spectrophotometrically, using a stopped flow apparatus.

INTRODUCTION

The mechanism of the formation of labile complexes involving divalent cations is by now fairly well established.[1] The situation is different with respect to tervalent cations. Some of them, such as[2] Fe(III) and[3] Al(III), are usually assumed[1] to follow the dissociative Eigen mechanism of the divalent cations, whereas for others an associative interchange or S_N2 mechanism is more likely.[4–6] These reactions are further complicated by the tendency of tervalent cations to undergo hydrolysis.

Probably owing to the instability of tervalent vanadium, this cation has so far received comparatively little attention. The ligands investigated are thiocyanate,[7,8] azide,[9] oxalate,[6] chloride[6] and bromide.[6] In the case of other tervalent ions such as Fe(III) and Al(III) the hydrolyzed species reacts at a much higher rate than the unhydrolyzed ion. For the reactions of V(III) with thiocyanate, and with oxalic acid and its anions, this phenomenon was found absent. (Only for azide has the possibility of a contribution by the reaction between VOH^{2+} and N_3^- to the observed rate been envisaged.)[9] This fact, together with the large negative entropy of activation[7] has been construed[10] as evidence for an S_N2 mechanism. The case for this mechanism is further strengthened[6] by the observed ligand-dependence of the rate constants. Additional information about the kinetics of complex formation by V(III) seemed desirable. In continuation of our program of investigating the kinetics of reactions between tervalent cations and acids of moderate strength[2,3,5] we again[5] chose salicylic acid and its mono ion as ligands.

EXPERIMENTAL

Materials

a) *Tervalent vanadium* Solutions of V(III) perchlorate in perchloric acid (Merck, p.a.) were prepared by electrolytic reduction. In the first stage a suspension of V_2O_5 (Riedel de Haën, pure) in excess perchloric acid was electrolyzed with constant stirring, using platinum foil electrodes. (A mercury cathode would not be suitable at this stage since V(V) reacts directly with Hg.)[11] The process was continued until the original "muddy suspension"[12] had turned into a clear, deep-blue solution of V(IV) characterized by an absorption peak[13] at 760 nm with $\epsilon = 17.1 M^{-1} cm^{-1}$. In the second stage, an apparatus similar to that described[12] in "Inorganic Synthesis" was used. An oxygen-free atmosphere was achieved by bubbling argon through the solution. By interrupting the process at the stage where the solution has become blue-green, we were able to obtain practically pure V(III). We determined its concentration spectrophotometrically, using the values of $\epsilon = 5.6 M^{-1} cm^{-1}$ at 580 nm and $\epsilon = 8.5 M^{-1} cm^{-1}$ at 400 nm.[14] When the reduction is carried further, V(II) is obtained.[7,12] This deep-violet substance has a molar absorptivity which increases steeply above ~700 nm.[15] Its absence in our solutions, as well as the absence of V(IV), were ascertained spectrophotometrically: at wave-lengths above 750 nm the solutions were exactly as transparent as distilled water.

The acid concentration was determined by passing the solution through a cation-exchange column in its hydrogen form under an atmosphere of argon, titrating the eluate with sodium hydroxide solution, and taking into account the three moles of hydrogen ion per mole of V(III)-ion exchanged with the column.[7]

The V(III)-solutions were kept under argon for not more than one week from the time of preparation, although even after *two* weeks, they contained only ~4% V(IV). This confirms a previous finding[15] according to which the reaction between V(III) and perchlorate to yield VO^{2+} and Cl^- – although thermodynamically favorable – is very slow. On the other hand, the oxidation of V(III) by oxygen was found to be quite rapid.

b) *Other solutions* Stock solutions of 5 x 10^{-3} *M* salicylic acid (Baker's Analyzed) were protected from daylight and kept for no more than two weeks, because they are liable to undergo photochemical decomposition.[16] Their concentration was determined by titration with carbon dioxide-free NaOH-solutions. The hydrogen ion concentration was regulated by the addition of perchloric acid solutions, and the ionic strength (1 *M* throughout) by the addition of sodium perchlorate (Fluka puriss.) solutions.

All solutions were prepared in triple-distilled water.

Apparatus

Spectra were scanned in a Cary Model 14 Spectrophotometer. Measurements at constant wavelength were carried out in a Hilger-Gilford spectrophotometer.

Kinetic measurements were carried out in an Aminco-Morrow stopped flow apparatus.

Temperatures were measured with a copper-constantan thermocouple connected to a digital millivoltmeter. The temperature was constant within the accuracy of the instrument, namely 0.01 mV, corresponding to 0.25°C.

RESULTS

Spectrophotometric Measurements

In the presence of V(III) in acid solution the absorption peak[16] of salicylic acid at 303 nm was lowered and a broad shoulder appeared around 380 nm. The molar absorptivity of V(III) is much too low to account for this phenomenon. We therefore ascribe it to complex formation, and carried out the spectrophotometric determination of the formation constants, as well as all kinetic measurements, at this wavelength.

When the absorbance of a solution containing V(III) and salicylic acid was compared with the *sum* of the two *separate* components (at the same H^+-concentration), a sharp peak at 330 nm, together with the shoulder at ~380 nm, were obtained. Both decreased with increasing hydrogen ion concentration, but the latter more so than the former.

In the determination of the formation constant, we varied *a*, the stoichiometric concentration of V(III), between 4.5 x 10^{-3} and 4.6 x 10^{-2} *M*; it was thus always much higher than *b*, the concentration of salicylic acid, which was between 3.4 x 10^{-4} and 7.5 x 10^{-4} *M*. Measurements were carried out at three to six hydrogen ion concentrations, between 0.05 and 0.25 M. Under these conditions, the relative concentration of the fully deprotonated ion Sal^{2-} is negligible.[16]

We again (see, for instance, Ref. 3) found it convenient to define an apparent formation constant K_{app}, which depends on $[H^+]$, namely:

$$K_{app} = \frac{\text{total complex concentration}}{[V(III)]([H_2Sal] + [HSal^-])}$$

$$= \frac{\text{total complex concentration x } [H^+] \text{ x } K_c}{[V^{3+}][HSal^-]([H^+] + K_{OH})([H^+] + K_c)} \tag{1}$$

where $[V(III)]' = [V^{3+}] + [VOH^{2+}]$, K_c is the first dissociation constant of salicylic acid, and [14]K_{OH} = 1.4 x 10^{-3}*M* is the hydrolysis constant of vanadium, that is to say $K_{OH} = [VOH^{2+}][H^+]/[V^{3+}]$.

The expression for the absorbance *A* was again[3] transformed to give:

$$\frac{ab}{A - \bar{\epsilon}_V a} = \frac{a}{\bar{\epsilon}_c - \bar{\epsilon}_V} - \frac{1}{\bar{\epsilon}_c - \bar{\epsilon}_V}\,\frac{1}{K_{app}} \tag{2}$$

Here $\bar{\epsilon}_V$ and $\bar{\epsilon}_c$ are weighted molar absorptivities of V(III) and complex, respectively, and depend on pH.

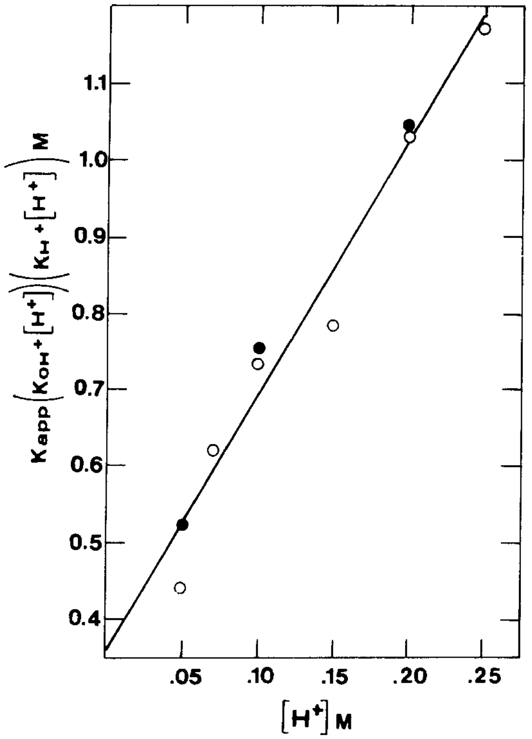

FIGURE 1 Dependence of $K_{app}([H^+]+K_{OH})([H^+]+K_H)$ on hydrogen ion concentration (see Eq. (5)). Open circles, equilibrium measurements; full circles, kinetic results.

The values of $\bar{\epsilon}_V$ were determined experimentally. Eq. (2) predicts that, at constant hydrogen ion concentration, a plot of the left hand side as a function of a should be a straight line; this was indeed found to be the case. The ratio of the slope over the intercept yields K_{app}. As expected, the values obtained were found to decrease strongly with increasing $[H^+]$.

The fact that not only the height, but also the shape of our difference spectrum depends on $[H^+]$ suggests the existence of two complexes, their apparent formation constants differing in their $[H^+]$-dependence. If we assume these complexes to be $VSal^+$ and $VHSal^{2+}$ and define the formation constants:

$$K_1 = [VSal^+][H^+]/[V^{3+}][HSal^-] \quad (3)$$

and

$$K_1' = [VHSal^{2+}]/[V^{3+}][HSal^-] \quad (4)$$

then we can rearrange Eq. (1) to give:

$$K_{app}([H^+]+K_{OH})([H^+]+K_c) = K_c(K_1 + K_1'[H^+]) \quad (5)$$

In order to calculate the left hand side of this equation we need the values of K_c and K_{OH}. The value of the former was found[17] by potentiometric titration to be 1.6×10^{-3} M at 20, 25 and 30°C, and our ionic strength. This constancy with temperature is not surprising, since the heat of dissociation of carboxylic acids is usually very nearly equal to zero.[18] We therefore assumed K_c to be constant over our whole temperature range. No data on the temperature dependence of K_{OH} are available; however, since $K_{OH} \ll [H^+]$, no appreciable error is introduced if we use the 25°C-value throughout.

Figure 1, which refers to 27°C, shows the left hand side of Eq. (5) as a function of $[H^+]$ (open circles). A straight line is seen to be obtained. This confirms our assumption about the nature of our complexes, and about K_c.

From the intercept and slope we get K_1 and K_1', respectively. The results at five temperatures between 7.5 and 45°C are shown in Table I. From the data in this Table we calculate $\Delta H_1^0 = -(1.4 \pm 0.2)$ Kcal/mole and $\Delta H_1^{0\prime} = (4.1 \pm 0.2)$ Kcal/mole.

KINETIC MEASUREMENTS

Kinetic Evaluation of Formation Constants

The concentration of V(III), a, was always at least 15 times higher than that of salicylic acid, b. We therefore can write an observed pseudo-first order rate constant.

$$k_{obs} = k_f\bar{a} + k_b \quad (6)$$

where $\bar{a}$ is a value suitably weighted between initial and equilibrium concentrations, the difference between a and $\bar{a}$ being negligible except at the lowest values of $[H^+]$, and k_f and k_b are the second order,

TABLE I
Formation constants of $VSal^+$ (K_1) and of $VHSal^{2+}$ (K_1'), at five different temperatures

T°K	280.65	290.65	300.15	308.15	318.15
$10^{-2}\ K_1$	2.4 ± 0.6	2.3 ± 0.2	2.2 ± 0.2	1.9 ± 0.9	1.8 ± 0.4
$10^{-3}\ K_1'$	1.3 ± 0.3	1.6 ± 0.1	2.1 ± 0.2	2.4 ± 0.5	3.1 ± 0.2

and pseudo-first order, overall rate constants of the forward and back reactions respectively, and depend on $[H^+]$. At one temperature, namely 27°C, the linear dependence of k_{obs} on $\bar{a}$ was verified at three values of $[H^+]$. The ratios $k_f/k_b = K_{app}$ for these three values are shown as full circles in Figure 1 and are seen to be in good agreement with the spectrophotometrically determined values.

Reaction Mechanism

Possible formation reactions for our complexes are:

$$HSal^- + V^{3+} \rightleftharpoons VHSal^{2+} \rightleftharpoons VSal^+ + H^+ \qquad (I)$$

$$H_2Sal + V^{3+} \rightleftharpoons VHSal^{2+} + H^+ \rightleftharpoons VSal^+ + 2H^+ \qquad (II)$$

$$HSal^- + VOH^{2+} \rightleftharpoons VSal^+ + H_2O \qquad (III)$$

where we have omitted coordinated water molecules. If we assume all protolytic equilibria to be maintained while complexation proceeds, and if we take into account the fact that in all our experiments $[H^+] \gg a$, $[VSal^+]$, $[VHSal^{2+}]$, we can write:[19,20]

$$k_{obs} = (k_1 + [H^+]k_2/K_c + k_3K_{OH}/[H^+])B \qquad (7)$$

where (see, for instance, Ref. 5):

$$B = \frac{(K_{app}\bar{a} + 1)\,[H^+]}{K_1 + K_1'\,[H^+]} \qquad (8)$$

and k denotes the rate constant of the respective forward reaction. Figure 2 shows k_{obs}/B as a function of $[H^+]$, at five different temperatures.

At 27°C, twenty-two experiments were carried out at values of $[H^+]$ varying between 0.015 and 0.8 *M*, values of *a* varying between 2.2×10^{-3} and $2.5 \times$

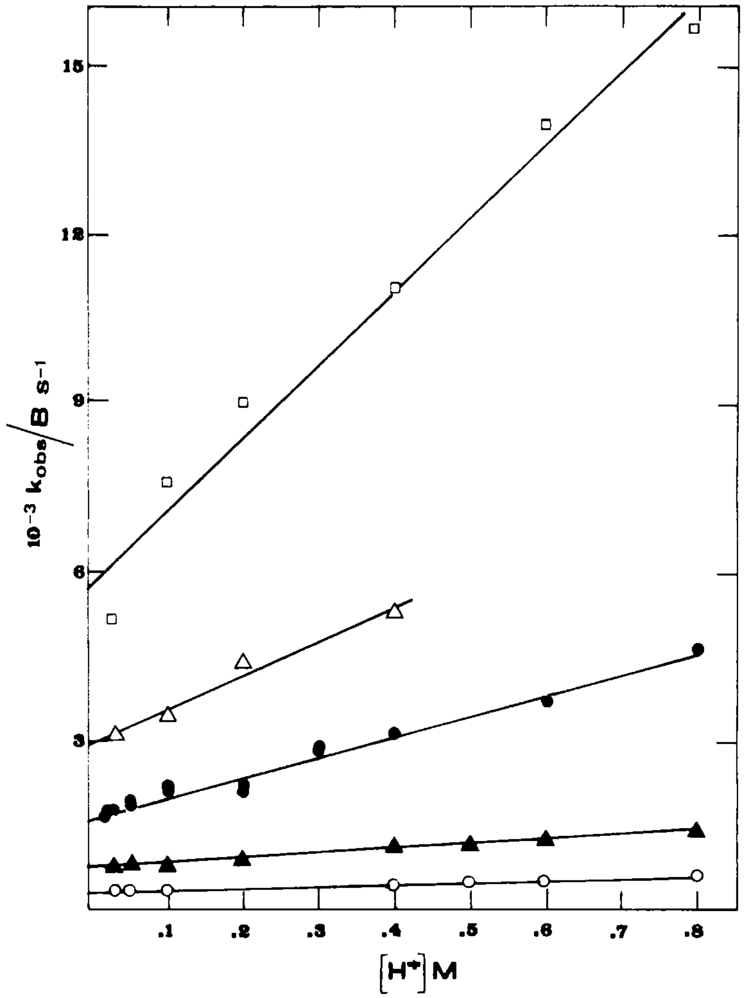

FIGURE 2 Dependence of k_{obs}/B on hydrogen ion concentration (where B is defined by Eq. (7)). ○, 7.5°C; ▲, 17.5°C; ●, 27°C; △, 35°C; □, 45°C.

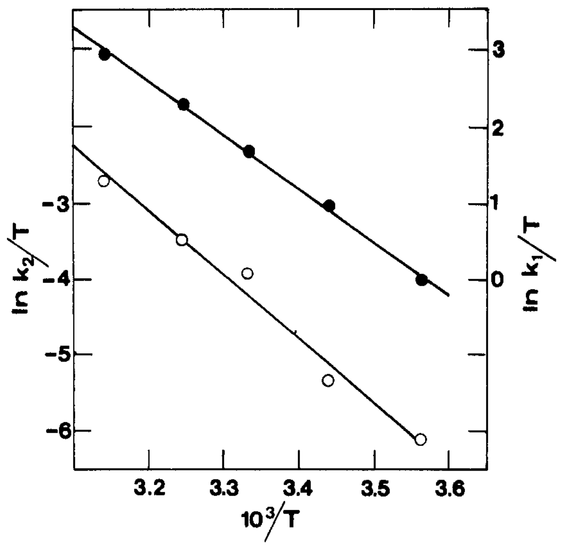

FIGURE 3 Eyring plots of ln (k/T); full circles, k_1 ; open circles, k_2.

10^{-2} M, and values of b varying between 8.5 x 10^{-5} and 7.7 x $10^{-4}M$, the higher reactant concentrations corresponding to experiments at higher values of [H^+] where the complex becomes very weak. A straight line is seen to be obtained showing no sign of bending upward at the lowest values of [H^+]. This shows that reaction III makes no discernable contribution to our observed rate. (In an attempt to investigate this point still further, we carried out some experiments at even lower values of [H^+], namely, 0.008 and 0.010 M. We obtained a slight *downward* trend which we ascribe to the presence of non-negligible amounts[14] of VOH_2^+ and $V_2(OH)_2^{4+}$ which seem to be kinetically inactive. This subject is outside the scope of the present paper. We have therefore not included these results in Figure 2.)

Activation Parameters

At the four additional temperatures, namely 7.5, 17.5, 35 and 45°C, the values of [H^+] ranged between 0.03 and 0.8 M, and those of a between 4.7 x 10^{-3} and 2.4 x 10^{-2} M; those of b were again much lower (by a factor of at least fifteen). Figure 2 shows that, at each temperature, k_{obs}/B as a function of [H^+] is again a straight line. From the intercepts and slopes, respectively, we calculated k_1 and k_2, for all five temperatures. The results are shown in Table II. In order to obtain the activation parameters, we plotted ln(k/T) as a function of 1/T, as shown in Figure 3. The results are:

$\Delta H_1^\ddagger$ =13.8 ± 0.4 Kcal mol^{-1} ; $\Delta S_1^\ddagger$ = 2.2 ± 1.4 e.u.

$\Delta H_2^\ddagger$ =16.7 ± 1.1 Kcal mol^{-1} ; $\Delta S_2^\ddagger$ = -0.1 ± 4.3 e.u.

DISCUSSION

Formation Constants

From our values of K_1 and K_1' at 27°C we calculate that at our lowest value of [H^+] the species $VHSal^{2+}$ constitutes only ~13% of the total complex, whereas at the highest value, it constitutes ~88%. It is not surprising that at values of pH which are by ten to twelve units[16] lower than its pK the proton should be only partly dislodged on complex formation, despite the additional stability of the complex which is gained when the proton leaves and a chelate complex is formed. Other cases of a similar nature have recently been reported (see Ref. 21 and literature quoted therein).

Reaction Mechanism

a) *Discussion of an alternative mechanism* Since the reaction:

$$VHSal^{2+} \rightleftharpoons VSal^+ + H^+ \qquad \text{(Ia)}$$

is in fact not a simple proton transfer but probably involves the process: ring opening ⇌ ring closure, the assumption that this reaction is rapid in comparison with the rate of complexation must be checked. For every run, k_{obs} was found time-independent up to 80% reaction. In analogy with relaxation experiments we can say that we see only *one* "normal mode," the

TABLE II
Rate constants for the reaction between V^{3+} and $HSal^-$(k_1) and between V^{3+} and H_2Sal (k_2), at five different temperatures

T°K	280.65	290.65	300.15	308.15	318.15
10^{-3} k_1	0.27 ± 0.02	0.76 ± 0.01	1.61 ± 0.03	3.0 ± 0.1	5.8 ± 0.5
k_2	0.62 ± 0.06	1.39 ± 0.04	5.9 ± 0.2	9.5 ± 1.0	21 ± 2

other being too fast to be observed. Let us therefore examine the possibility that deprotonation is slow in comparison with the rate of formation of VHSal^{2+} from the reactants. This would lead to:

$$k_{\mathrm{obs}} = k_{1\mathrm{a}} \frac{K_{\mathrm{c}}K_1{}'}{K_{\mathrm{c}} + [\mathrm{H}^+] + K_{\mathrm{c}}K_1{}'\bar{a}}\, \bar{a} + k_{-1\mathrm{a}}[\mathrm{H}^+] \qquad (9)$$

to very good approximation. This expression fits neither our [H$^+$]- nor our a-dependence. Furthermore, k_f/k_b would not be equal to the spectrophotometrically determined value of K_{app}. This mechanism can therefore be ruled out.

b) *Discussion of rate constants* Although our results do not enable us to determine $\mathbf{k}_3$, we can at least estimate a lower limit. Eq. (7) predicts that k_{obs}/B should show a minimum at $[\mathrm{H}^+] = (\mathbf{k}_3 K_{\mathrm{OH}} \cdot K_{\mathrm{c}}/\mathbf{k}_2)^{1/2}$. Figure 2 shows that this minimum obviously has not been reached; we conclude that at 27°C:

$$\mathbf{k}_3 < [\mathbf{k}_2(0.015)^2/K_{\mathrm{OH}}K_{\mathrm{c}}] = 5.9 \times 10^2\ \mathrm{M}^{-1}\mathrm{s}^{-1}$$

Comparison with Table II shows that VOH^{2+} reacts with HSal$^-$ more *slowly* than does V^{3+}. For this reason, we have not included in our reaction scheme the reaction between VOH^{2+} and H$_2$Sal which has the same dependence on [H$^+$] as reaction I, but whose contribution to the observed rate is even smaller than that of reaction III. This means that our system does not exhibit proton ambiguity.[22]

As a warning against rash conclusions it might be mentioned in this context that Eq. (7) predicts that, at constant a, the observed rate constant, k_{obs}, *does* pass through a minimum even when $\mathbf{k}_3$ equals zero. This is a consequence of K_{app} decreasing, and $\mathbf{k}_2\,[\mathrm{H}^+]$ increasing with increasing [H$^+$]. This rather intriguing effect was indeed observed at low values of [H$^+$] at all four temperatures, as it was in the system Al^{3+}-sulfosalicylic acid.[3]

The rate constant for HSal$^-$ is almost 200 times higher than that for H$_2$Sal. This factor is rather higher than can be ascribed to the charge effect alone. When we compare our results at 27°C with those at 25°C summarized by Patel and Diebler[6] we find that our rate constant for undissociated salicylic acid is very similar to those[6] of the very weak bases Cl$^-$ and Br$^-$, whereas the rate constant for the monoanion HSal$^-$ resembles that[6] of HC$_2$O$_4^-$. This confirms[6] the dependence of the rate constant on the basicity of the ligand, and strongly argues in favor of an S$_{\mathrm{N}}$2 mechanism.

The rate of exchange of a water molecule in the inner coordination shell fits very well into this framework. The corresponding *bimolecular* rate constant[23] is $(10^4/6) \times 6/55 = 180\ \mathrm{M}^{-1}\mathrm{s}^{-1}$; thus, just as the basic strength of H$_2$O falls between those of Cl$^-$, Br$^-$ and H$_2$Sal on the one hand, and of HSal$^-$ and HC$_2$O$_4^-$ on the other, so does the rate constant.

Bimolecular reactions are usually characterized by a large negative entropy of activation; this was indeed found[7] for the reaction of V^{3+} with NCS$^-$ and with water.[23] The present entropies of activation, however, are slightly positive and – within the limits of accuracy – zero, for paths I and II, respectively. Let us examine the possibility that this seeming discrepancy might be connected with the presence of an internal hydrogen bond in HSal$^-$ and possibly, though to a lesser extent, in H$_2$Sal.[24]

The presence of a hydrogen bond is known[25] to reduce the rate of formation of very labile complexes to values for below those considered "normal" for the participating cations.[21,26-29] Sometimes this reduction is so drastic as to lead to the conclusion that only the small non-hydrogen bonded fraction is able to react at all.[28] When the reduction in rate is less pronounced, it *must* be assumed[21,27] that the metal can directly attack the hydrogen bond. For substitution-labile cations this attack may become rate determining, and the deceleration is satisfactorily explained. In the present case, however, the hydrogen-bonded ligands react at rates which are almost entirely in line with their basicity. Therefore, firstly, the possibility that only the non-hydrogen-bonded form should react can be excluded without doubt. Secondly, we must assume that for this comparatively slow reaction the overall free energy of activation is only little affected by the necessity of breaking the hydrogen bond. This situation is analogous to that encountered with[3] Al^{3+}, [5] Ga^{3+} and,[17] possibly,[†] Fe^{3+}.

This does not mean, however, that $\Delta H^\ddagger$ and $\Delta S^\ddagger$ necessarily remain unaffected. We have recently found[30] that the opening of the internal hydrogen bond in tropaeolin O has a very high positive activation entropy. If the same is true for the hydrogen bond in salicylic acid, and if its breakage occurs in the same rate-determining step in which the seven-coordinated intermediate is formed, then the positive

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[†] The authors interpret their results in terms of the reaction between FeOH^{2+} and H$_2$Sal *only*, disregarding the proton-ambiguous path involving Fe^{3+} and HSal$^-$. However, if we assign to the former reaction a rate constant "normal" for FeOH^{2+} we find that the latter reaction can contribute with a rate constant which is rather higher than that usually considered "normal" for Fe^{3+}.

entropy of activation of this process could completely mask the negative value associated with the bimolecular reaction.

Further insight into the mechanism may be gained from the fact that VOH^{2+} does not react faster than V^{3+}; it even reacts more slowly, possibly considerably so. In the case of[3] Al(III), [5]Ga(III) and [1]Fe(III), the hydrolyzed species react very much faster than the aquo ions. Since OH^- exerts a labilizing effect on the remaining water molecules in the inner coordination sphere, this behavior is in line with the dissociative mechanism according to which water loss is the rate determining step. We should like to point out, however, that this does not *prove* the dissociative mechanism for the aquo ion; a closer inspection of the results obtained, for example, for Fe^{3+}-complexation shows that an S_N2 mechanism for this ion cannot be excluded. On the other hand, if the hydrolyzed species does not react faster than the aquo ion, this can be considered a strong argument in favor of an S_N2 mechanism.[10] As pointed out by Espenson and Pladziewicz,[9] if water loss is not the rate-determining process, then a possible labilizing effect of OH^- is no longer relevant. The results concerning the lack of reactivity of VOH^{2+} thus confirm the conclusion drawn from the ligand dependence of the rate constants.

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