constant for Fe–L^1 with respect to the one for Co–L^1. With more information on the structures of M(II)–L^1 and (ML)$_2$O$_2$ (with metal spin states), further rationalization may be invoked. It is of interest to note that myoglobin (Fe-containing) and coboglobin (Co-containing) take up molecular oxygen with almost the same second-order rate constants ($\sim$10^7 M^{-1} s^{-1}).[5] This fact is consistent with the structural features around metal ions: the iron and cobalt atoms in deoxymyoglobin and deoxycoboglobin, respectively, are both five-coordinate and the oxygen binding sites are both vacant.

The O$_2$-uptake rate constant with Fe(II)–L^1 varied with pH. Our analysis indicated that the hydroxo species FeL(OH) is a reactive form. Though there is no experimental proof, we tentatively visualize a deprotonated species FeH$_{-1}$L as an equivalent to the hydroxo species. Deprotonation of the axial amine to a conjugate imide anion may trigger the dissociation of the trans H$_2$O molecule.

In contrast to the stability constants, the second-order rate constant is about an order smaller for Co(II)–L^1 with respect to that for Co(II)–L^3. This may reflect a weaker σ donation

of the pyridyl-containing ligand L^1, which works unfavorably for the water dissociation prior to the O$_2$ attack.

Detailed characterizations of the oxygenated complexes with variously sized macrocyclic pentaamines are in progress to clarify the structure and mechanism of the interaction between O$_2$ and the intrinsic Fe(II) chelates, and moreover to correlate them with the mechanisms of the biological O$_2$-uptake systems such as hemerythrin. Structural modification of the macrocyclic pentaamines may not only give a deeper insight into the oxygenation mechanisms but also produce new synthetic O$_2$ carriers and possibly O$_2$-activating enzyme models.

Registry No. FeL$^{1\,2+}$, 79802-93-0; Cd$^{1\,2+}$, 79802-94-1; FeL$^{3\,2+}$, 79802-95-2; (FeL^1)$_2$O$_2$, 79802-96-3; (CoL^1)$_2$O$_2$, 79802-97-4; O$_2$, 7782-44-7; L^1·4HBr, 79802-91-8; L^2, 79802-92-9; diethyl pyridine-2,6-dicarboxylate, 15658-60-3; 3,7-diazanonane-1,9-diamine, 4741-99-5; L^3, 29783-72-0.

Contribution from the Istituto di Chimica Analitica, University of Turin, 10125 Turin, Italy, and the Istituto di Chimica Analitica ed Elettrochimica, University of Pisa, 56100 Pisa, Italy

Mechanism of Complex Formation: Equilibria and Kinetics of Fe^{3+} and FeOH^{2+} Interactions with Substituted Salicylic Acids

EDOARDO MENTASTI,* FERNANDO SECCO, and MARCELLA VENTURINI

The kinetics and mechanism of complex formation of reactions between Fe(III) and a series of substituted salicylic acids have been investigated with a stopped-flow technique at μ = 1.0 M (NaClO$_4$) and 25.0 °C. The reactions involve the formation of a 1:1 chelate species, at [HClO$_4$] $\geq$ 0.010 M, with release of protons from both phenolic and carboxylic groups, and the equilibrium quotients of the reactions Fe^{3+} + HL$^-$ $\rightleftharpoons$ FeL$^+$ + H$^+$ have been obtained from spectrophotometric measurements. The rates of reaction are strongly affected by acidity, and the mechanism involves Fe^{3+} and FeOH^{2+} metal species as well as H$_2$L and HL$^-$ ligand species. The ligand acidity affects the relative importance of each path, and the results are discussed with reference to the associative/dissociative character of the reaction in relation to the metal species.

Introduction

The mechanism for the formation of labile metal complexes is generally well established in the case of divalent cations,[1] and, according to the Eigen–Tamm mechanism,[2] the rate is determined by the rate of water exchange at the inner coordination sphere of the metal.

However, no clear assessment has been achieved in the case of trivalent metal ions.[3] Moreover in this case higher positive charges and low ionic radii give increased metal-coordinated water interactions with easier proton releases and strong tendencies to hydrolysis. Therefore, the number of active species, e.g., Me^{3+} and MeOH^{2+}, increase and make the mechanistic interpretation more complex.

In fact, if the ligand species participates in acid–base equilibria, different reaction paths with the same dependence on acidity give rise to "proton ambiguities".[4] In addition the presence of the OH$^-$ ligand in several cases, even if not in general, causes increased labilities and therefore increased rates are found as in the case, for example, of Al^{3+},[5] Ga^{3+},[6] Mn^{3+},[7] or Cr^{3+}.[8] In the case of Fe(III), the OH$^-$ ligand increases by about 3 orders of magnitude the rate of water exchange of the unhydrolyzed metal and gives a dissociative character to the metal center.[9] The rate enhancement in the hydrolyzed species depresses the relative importance of the Fe^{3+} contri-

bution in reactions with several ligands of different structure and basicity; for several ligands such as, for example, α-hydroxycarboxylic acids[9,10] or phenolic and diphenolic compounds,[11,12] the FeOH^{2+} species is almost entirely the only active metal species.

For this reason few kinetic data on the unhydrolyzed species Fe^{3+} are available, and its behavior is still an object of discussion. Therefore we have undertaken a mechanistic study on the reactions of Fe(III) with a series of substituted salicylic acids, namely, 5-chloro- (Cl(SAL)), 5-nitro- (N(SAL)), 6-hydroxy- (OH(SAL)), and 3,5-dinitrosalicylic acid (DN(SAL)).

The results give information on the effect of ligand basicity on the reaction rates of the active species. In fact the sub-

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stituents have a strong effect on the ligand basicity but do not alter the detailed modes of interaction of an ortho hydroxy-carboxylic moiety. In addition the high acidity of the carboxylic groups of some of the presently investigated ligands increases (see below) the contribution of the unhydrolyzed metal species. The results are compared with previous findings on other salicylic acids of different acidity and charge.[13–15]

Experimental Section

Materials. The substituted salicylic acids, namely, 5-chloro- (supplied by E. Merck), 5-nitro- (Fluka), 6-hydroxy- (Fluka), and 3,5-dinitrosalicylic acid (Fluka) were recrystallized from water, and their stock solutions were standardized by potentiometric titrations. Fe(III) perchlorate solutions were prepared by dissolving analytical grade iron metal (C. Erba) in excess perchloric acid and further oxidation of the Fe(II) formed with H$_2$O$_2$. The excess oxidant was then removed by thermal decomposition. The concentrations of these solutions obtained from the weight of the dissolved metal were in excellent agreement with the chelometric determination (EDTA and Tiron as indicator). Typical concentrations were [Fe]$_{tot}$ = 10^{-2} M and [H$^+$] = 10^{-1} M. Perchloric acid and sodium perchlorate (both C. Erba reagent grade chemicals) were used for bringing all the solutions to the desired acidity: 0.400–0.010 M and ionic strength 1.0 M. All the measurements were performed at 25.0 °C.

Procedure and Instrumentation. Kinetic measurements were performed on a Durrum-Gibson spectrophotometer, following the procedure described elsewhere.[9] The reaction progress was monitored by following the complex formation, which for each ligand was the only absorbing species, at 525 nm for Cl(SAL), 500 nm for N(SAL), 560 nm for OH(SAL), and 520 nm for DN(SAL).

All kinetic runs were performed with the ligand in excess ((0.5–5) × 10^{-3} M) in respect to Fe(III) ((0.5–3) × 10^{-4} M)). The equilibrium quotients were obtained from spectrophotometric data obtained with a Cary 219 spectrophotometer. The hydrolysis constant for FeOH^{2+} formation (K_h) was taken to be 1.65 × 10^{-3} M at 25 °C and μ = 1.0 M.[16] The dissociation constants for the carboxylic group of the ligands (K_a) were obtained from spectrophotometric measurements for DN-(SAL), from potentiometric titrations for OH(SAL), from the literature for N(SAL),[17] and from previous measurements in our laboratory for Cl(SAL).[18]

Results and Discussion

Solutions of the investigated ligands give upon addition of Fe(III) perchlorate in acidic solution an increase of absorption in the region 500–560 nm. Spectrophotometric measurements performed on equilibrated mixtures of the reagents showed, in agreement with previous observations, the presence of the following complex formation equilibrium:[13–15]

$$Fe^{3+} + HSAL^- \rightleftarrows FeL^+ + H^+ \quad K_{eq} \quad (1)$$
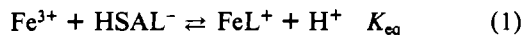
For solutions containing an excess of ligand in respect to Fe(III) and under the present conditions with FeL$^+$ as the only absorbing species, the following expression can be obtained:

$$\frac{C_{Fe}}{A} = \frac{1}{l\epsilon} + \frac{1}{l\epsilon}\frac{1}{K_{eq}}\frac{[H^+](1 + K_h[H^+]^{-1})}{C_{SAL}\alpha_{HSAL^-}} \quad (2)$$

where A is the absorbance, α_{HSAL^-} is the fraction of ligand in the form HSAL$^-$, i.e., $\alpha_{HSAL^-} = K_a/([H^+] + K_a)$, ϵ the molar absorptivity of the complex, and C_{Fe} and C_{SAL} the total metal and ligand concentration. For all ligands the phenolic group is fully protonated. The linearity of plots of C_{Fe}/A as a function of $[H^+](1 + K_h[H^+]^{-1})/(C_{SAL}\alpha_{HSAL^-})$ confirms the validity of the stoichiometry reported in eq 1. Therefore no
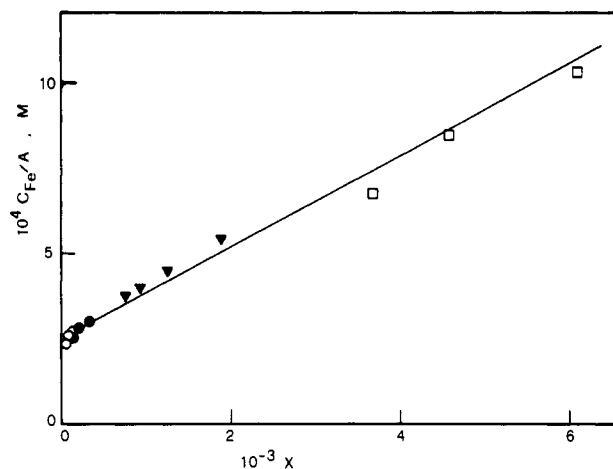
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Figure 1. Plot of C_{Fe}/A as a function of $X = [H^+](1 + K_h[H^+]^{-1})/(C_A\alpha_{HL^-})$, according to eq 2 for the reaction of Fe(III) with NSAL. The symbols refer to different acidities, namely: [HClO$_4$] = 0.020 (O), 0.040 (●), 0.100 (▼), and 0.200 M (□).
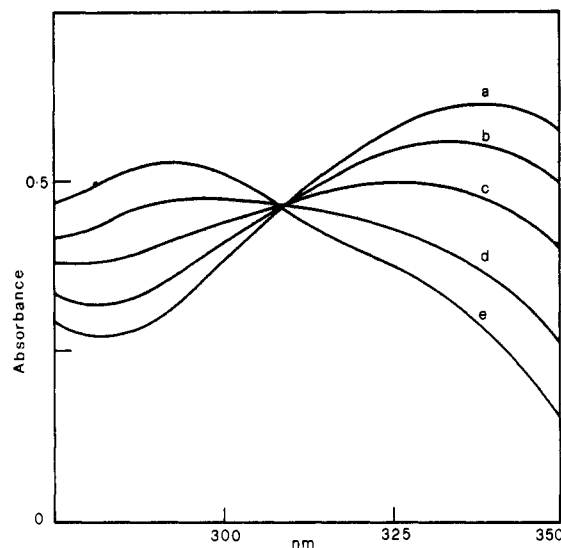

Figure 2. UV spectra of solutions of DN(SAL) at different acidities: [DN(SAL)]$_{tot}$ = 6.0 × 10^{-5} M, curve a = pH 5; curve b, [HClO$_4$] = 0.070 M, curve c = 0.20 M, curve d = 1.0 M, curve e = 6.0 M.

Table I. Equilibrium Data for the Complex Formation Reactions between Fe(III) and Salicylic Acids

ligand	K_{eq}	K_a, M	ϵ, M^{-1} cm^{-1}	λ, nm	ref
Cl(SAL)	635	0.0031^a	1640	525	this work
N(SAL)	1700	0.0057^b	2170	500	this work
OH(SAL)	223	0.10	1720	560	this work
DN(SAL)	390	0.32	1500	520	this work
SAL^c	530	0.0016	1470	530	13
SSAL^c	490	0.0050	1960	500	14
PAS^c	180	0.011	1610	500	15

^{a} From ref 18. ^{b} From ref 17. ^{c} Abbreviations: SAL = salicylic acid; SSAL = 5-SO$_3$H(SAL); PAS = 4-aminosalicylic acid.

protonated or higher complexes are formed under the present conditions. Figure 1 shows, as an example, the experimental data reported according to eq 2 for the reaction with N(SAL). Similar behavior was obtained with the other ligands. Table I collects all the K_{eq} and ϵ values obtained from these plots together with other equilibrium data for the reactions investigated.

The table collects also the values of K_a; the value for DN-(SAL) was obtained from spectrophotometric measurements in the UV region where a consistent difference in the ab-

Table II. Pseudo-First-Order Rate Constants k_{obsd} (s^{-1}) for the Reaction of Fe(III) with OH(SAL) at Different Ligand Concentrations and Acidities
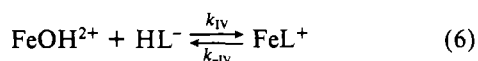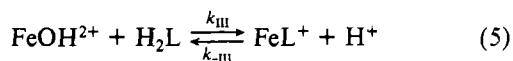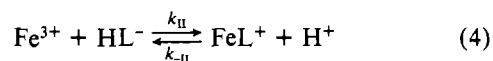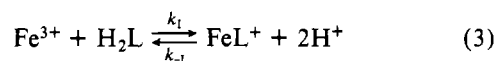
	[HClO$_4$], M				
10^3[OH(SAL)], M	0.010	0.020	0.040	0.100	0.200
1.0	1.10	0.70	0.51	0.38	0.50
2.0	2.08	1.30	0.92	0.57	0.55
3.0	2.90	1.92	1.31	0.74	0.68
4.0	3.85	2.56	1.70	0.94	0.76
5.0	4.98	3.16	2.18	1.11	0.84

Table III. Values of G (See Eq 8) as a Function of Acidity for the Reaction of Fe(III) with the Investigated Ligands

	[HClO$_4$], M					
ligand	0.010	0.020	0.040	0.100	0.200	0.400
Cl(SAL)	4500	3470	3170	3120	3320	
N(SAL)	2060	2360	1190	1080	1380	
OH(SAL)	1100	750	585	324	270	
DN(SAL)	960	470	270	160	105	65

sorption of H$_2$L and HL$^-$ occurs (see Figure 2), whereas the value for OH(SAL) was obtained from pH metric measurements by measuring the degree of protonation in solutions of the acid, upon addition of standard HClO$_4$, with a pH meter calibrated with standard HClO$_4$ solutions of comparable concentrations to those in the solutions under measurement.

Kinetic runs were performed under pseudo-first-order conditions in the same concentration range as for the equilibrium measurements. The following scheme can be advanced:

$$Fe^{3+} + H_2L \underset{k_{-I}}{\overset{k_I}{\rightleftharpoons}} FeL^+ + 2H^+ \qquad (3)$$

$$Fe^{3+} + HL^- \underset{k_{-II}}{\overset{k_{II}}{\rightleftharpoons}} FeL^+ + H^+ \qquad (4)$$

$$FeOH^{2+} + H_2L \underset{k_{-III}}{\overset{k_{III}}{\rightleftharpoons}} FeL^+ + H^+ \qquad (5)$$

$$FeOH^{2+} + HL^- \underset{k_{-IV}}{\overset{k_{IV}}{\rightleftharpoons}} FeL^+ \qquad (6)$$

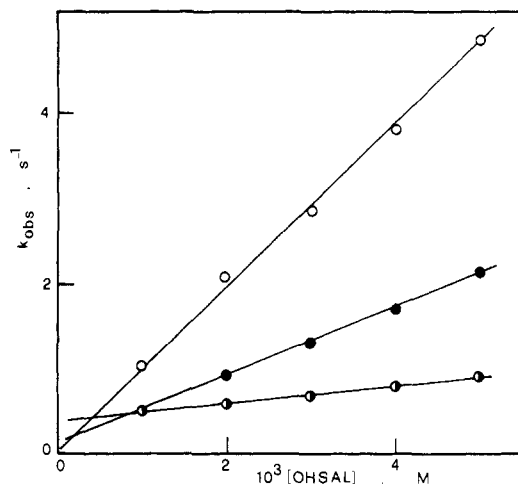For the present conditions, the following rate law can be obtained from the sequence (3)–(6):[13,14]

$$\frac{d[FeL^+]}{dt} = (k_I K_a^{-1}[H^+] + k_{II} + k_{III}K_h K_a^{-1} +$$
$$k_{IV}K_h[H^+]^{-1}) \left(\frac{C_{SAL}\alpha_{HSAL^-}}{1 + K_h[H^+]^{-1}} + [H^+]K_{eq}^{-1} \right) ([FeL^+]_{eq} -$$
$$[FeL^+]) \qquad (7)$$

Plots of ln $(A_{eq} - A)$ vs. time were always linear, and from the slopes the observed first-order rate constants k_{obsd} were obtained. Table II reports as an example the data for OH-(SAL).

Figure 3. Variation of k_{obsd} as a function of [H$_2$L]$_{tot}$ at different acidities for the reaction of Fe(III) with OH(SAL).
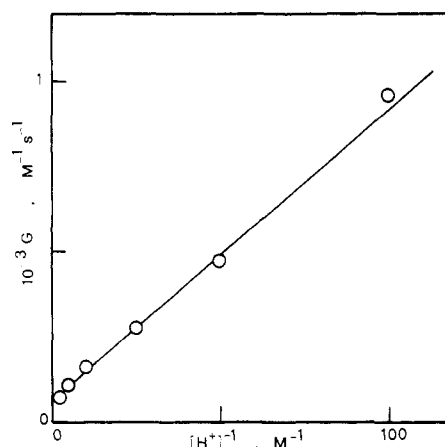
Figure 4. Variation of G as a function of [H$^+$]$^{-1}$ for the reaction of Fe(III) with DN(SAL).

Plots of k_{obsd} as a function of $C_{SAL}\alpha_{HSAL^-}/(1 + K_h[H^+]^{-1})$ at constant acidity were linear according to eq 7 (see, for example, Figure 3), and from their slopes the quantity G could be evaluated.

$$G = k_I K_a^{-1}[H^+] + k_{II} + k_{III}K_h K_a^{-1} + k_{IV}K_h[H^+]^{-1} \qquad (8)$$

Therefore the variation of G as a function of acidity can give information on the occurrence of the separate pathways of the scheme which contribute to the expression 8.

Table III collects the values of G at different acidities for the reactions investigated. Plots of G as a function of [H$^+$]$^{-1}$ show a linear behavior for OH(SAL) and DN(SAL) (see, for example, Figure 4), and from intercept and slope of the above plots $k_{II} + k_{III}K_h K_a^{-1}$ and $k_{IV}K_h$, respectively, can be obtained.
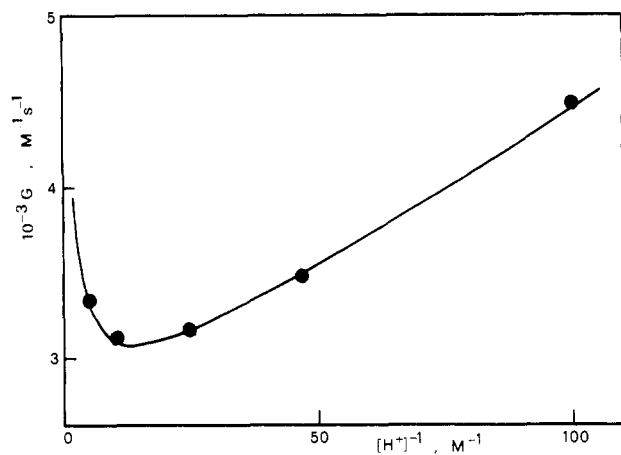
Table IV. Kinetic Parameters for the Reactions of Fe(III) with Substituted Salicylic Acids

ligand	$K_h K_a^{-1}$	$k_I K_a^{-1}$, M^{-1} s^{-1}	k_I, M^{-1} s^{-1}	$k_{II} + k_{III}K_h K_a^{-1}$, M^{-1} s^{-1}	$k_{IV}K_h$, s^{-1}	$10^{-4}k_{IV}$, M^{-1} s^{-1}	$k_{III}K_h K_a^{-1}$,[a] M^{-1} s^{-1}	k_{II}, M^{-1} s^{-1}	$10^{-3}k^*_{H_2O}$ (FeOH^{2+}),[b] s^{-1}	$k^*_{H_2O}$ (Fe^{3+}),[c] s^{-1}	ref
Cl(SAL)	0.53	3200	10	2600	18	1.3			6.5	50	this work
N(SAL)	0.29	4000	23	600	15	0.9			5.5	115	this work
OH(SAL)	0.017			200	13	0.8	70	135	4	27	this work
DN(SAL)	0.0052			60	8.65	0.52	20	40	3	8	this work
SAL[d]	1			5500	23	1.4			7		13
S(SAL)[d]	0.33	300	1.5	1800	20	1.2			6	8	14
PAS[d]	0.15			525	12.2	0.74			4		15

[a] Computed from the extrapolated k_{III} value (see text and Figure 6). [b] Computed from k_{IV} by assuming $K_{os} = 2$ M^{-1}. [c] Computed from k_I with $K_{os} = 0.2$ and from k_{II} with $K_{os} = 5$ M^{-1}. [d] Abbreviations: SAL = salicylic acid; S(SAL) = 5-SO$_3$H(SAL); PAS = 4-aminosalicylic acid.

Figure 5. Variation of G as a function of $[H^+]^{-1}$ for the reaction of Fe(III) with Cl(SAL). The line represents the behavior calculated with the data in Table IV.

Figure 6. Plot of $\log F$ ($F = k + kK_hK_a^{-1}$) as a function of $\log (K_h/K_a)$ for the reactions of Fe(III) with the investigated salicylic acids. The line represents slope = 1.

For the other ligands, namely, N(SAL) and Cl(SAL) (see, for example, Figure 5), the plots go through a minimum, and at higher acidities the contribution of reaction 3 results in an increase in G which should be minimum at $dG/d[H^+] = 0$, i.e., at $[H^+] = (k_{IV}K_hK_a/k_1)^{1/2}$. The quantity $k_{IV}K_h/k_1$ for reactions of Fe(III) is ~ 10; therefore, the minimum value for G should be at $[H^+] \simeq (10K_a)^{1/2}$. This accounts for the observed minimum for Cl(SAL) and N(SAL) around $[H^+] \simeq 0.1$ M, as well as for the absence of any contribution from reaction 3 for OH(SAL) and DN(SAL). In fact these reactions should become relevant at acidities higher than $(10K_a)^{1/2}$, i.e., $[H^+] \geq 1$ M, where the conditional stability constants of DN(SAL) and OH(SAL) complexes is so low that no significant concentration of complexes is formed in the concentration ranges investigated.

Table IV collects all the experimental rate constants together with previous findings for other substituted salicylic acids reactions. As it can be seen from eq 8, the variation of G as a function of acidity makes possible the evaluation of K_I, when present, and k_{IV}, whereas for reactions 2 and 3, which show a common and kinetically indistinguishable behavior, the sum of their contributions is derived: $k_{II} + k_{III}K_hK_a^{-1}$. The evaluation of their single contribution is, however, important since it is on the occurrence of reactions 4 and 5 and on the magnitude of their rate constants that interpretations of the dissociative or associative character of Fe³⁺ (reaction 4 and of FeOH²⁺ (reaction 5) are advanced. The dissociative behavior of FeOH²⁺ seems to be clearly assessed,[9] whereas no definitive conclusion for Fe³⁺ has been achieved. If reaction 6, which is not involved in any proton ambiguity, is now taken into account, the value of its specific rate constant k_{IV} should be related, according to the Eigen–Tamm scheme,[2] to the outer-sphere equilibrium constant k_{os} and the rate of water exchange in the coordination sphere of FeOH²⁺, i.e., $k_{IV} = k_{os}k^*_{H_2O}$.[19] The outer-sphere association constant K_{os} can be estimated with the Fuoss equation[20] for various charge types to be $K_{os} \simeq 0.2$, 2, and 5, respectively, for the product of charges $(z_a z_b) = 0$, −2, and −3,[20,21] with 5 Å as the distance of closest approach between the reactants and $\mu = 0.1$ M. These values are assumed to hold as rough estimates up to ionic strength 1.0 M. This assumption seems to be less approximate than the applicability of the Debye–Hükel interionic potential, which is a part of the Fuoss equation, up to $\mu = 1.0$ M.[4,19]
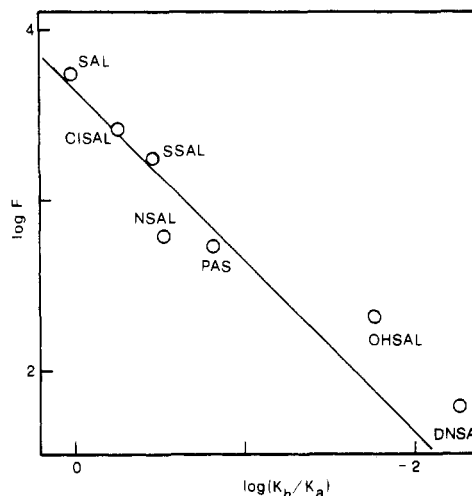
Therefore $k^*_{H_2O}$ can be computed from k_{IV} values to lie in the range $(4–7) \times 10^3$ L mol⁻¹ s⁻¹ for all the reactions investigated, in agreement with previous findings[9] (see Table IV). After consideration of the sum of the contributions of $k_{II} + k_{III}K_hK_a^{-1}$, a clear assessment of the relative importance of the term k_{II} and $k_{III}K_hK_a^{-1}$ cannot be made.

A plot of $\log (k_{II} + k_{III}K_hK_a^{-1})$ as a function of $\log (K_hK_a^{-1})$ is reported in Figure 6 for this series of ligands with the same structure but with various values of the factor $K_hK_a^{-1}$. If the single term $k_{III}K_hK_a^{-1}$ were present a linear behavior with slope 1 would be expected (in fact k_{III} refers to the species of FeOH²⁺, which is dissociative in kind, with the same H_2L species) as shown by the line which has been drawn in Figure 6 with slope 1.

For ligands with a favorable K_h/K_a value, the term k_{II} (if present) is small in respect to $k_{III}k_h/K_a$ so that, within experimental uncertainties, no deviation from the line occurs. For OH(SAL) and DN(SAL), which have the lowest K_h/K_a values, the points in Figure 6 are higher than expected if the single reaction (5) were present. This is confirmed by the following observation: if one calculates the value to be assigned to k_{III} when path 4 is considered absent, then a rate constant higher than the one found for the reaction of the same cation, namely, FeOH²⁺, with a less protonated species (compare the upper value of k_{III} with k_{IV}) would be obtained. Then a reasonable value for k_{II} can be obtained according to the following procedure: the extrapolation of the plot to $\log (K_hK_a^{-1}) = 0$ gives a value for $k_{III} = 4 \times 10^3$ L mol⁻¹ s⁻¹, from which is obtained $k^*_{H_2O} \simeq 2 \times 10^4$ L mol⁻¹/s⁻¹, which is in excellent agreement with previous findings from a series of ligands of different structure and basicity.[9] With this averaged k_{III} value, the single contribution from the k_{III} term to the quantity $A = k_{II} + k_{III}K_hK_a^{-1}$ can be computed and, as a difference, the contribution of the single reaction 4, namely, k_{II}, can be derived (see Table IV). In other words k_{III} can be calculated as a mean value for the results for SAL, Cl(SAL), and SC(SAL) where the contribution of k_{II} can be neglected; for the stronger acids OH(SAL) and DN(SAL), k_{II} follows from the excess value.

The data obtained for FeOH²⁺ do not need further comment as they again confirm the dissociative character of this metal species. The values of $k^*_{H_2O}$ for reactions 3 and 4, which can be computed from the appropriate K_{os} values (see Table IV), can give information on the behavior of Fe³⁺ species. The constancy of this parameter and its closeness with the experimentally evaluated water exchange rate is a clear proof for a purely dissociative character; on the contrary, the present

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values seem to show too a high scatter so that an independence of the ligand basicity cannot be assumed. In particular the data show a tendency to enhanced reactivity with decreasing the strength of the carboxylic group of the ligands, i.e., the basicity of their conjugated base; therefore our results provide

additional evidence that a departure from a dissociative behavior is present for Fe^{3+} ion.[3,9,10]

Steric and Conformational Effects on the Kinetics of Ligand Substitution in Bis(salicylaldiminato)nickel(II) Complexes

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Stopped-flow spectrophotometry has been used to study the kinetics of ligand substitution in bis(N-R-salicylaldiminato)nickel(II) complexes I (R = Et, i-Pr, t-Bu) by bidentate ligands HB (acetylacetone, benzoylacetone, dibenzoylmethane, trifluoroacetylacetone, 8-hydroxyquinoline, N-ethylsalicylaldimine) in methanol, 2-propanol, and toluene. A two-term rate law, rate = $(k_S + k_{HB}[HB])$[complex], has been found. The substitution of the first ligand in I is rate determining. Rate constant k_S, describing the solvent path, and the corresponding activation parameters ΔH^* and ΔS^* do not depend on the nature of the entering ligand for I with R = t-Bu studied in methanol. Rate constant k_{HB} is strongly dependent on the nature of the entering ligand HB. The relative contributions of the two pathways to the overall rate are governed by the conformational equilibrium planar $\rightleftharpoons$ tetrahedral of complexes I: the planar isomer favors the ligand-dependent path k_{HB} and the tetrahedral one the solvent path k_S. For both pathways mechanisms are derived, which have in common the rate-determining rupture of the Ni—O bond. They differ in that the solvent path is initiated by the attack of an alcohol molecule at the donor oxygen of a coordinated ligand through hydrogen bonding, whereas ligand attack occurs at the metal. The factors influencing the ligand path are the donor ability, acid strength, and stereochemical properties of the entering ligand as well as the Lewis acidity of the substrate. The discussion focuses on a comparison of the nickel system studied with corresponding copper(II) systems and with ligand substitution in square-planar d^8 complexes. Additional kinetic information is presented from studies carried out in the solvent mixtures toluene/methanol and toluene/pyridine. The equilibrium constant for the addition of pyridine to complexes I (R = Et, n-Pr, i-Pr, allyl, n-Bu, i-Bu, t-Bu, phenyl) has been determined spectrophotometrically in toluene at 298 K. The individual equilibrium constants for the formation of the mono- (K_1) and bis(pyridine) (K_2) adduct were calculated ($K_1 << K_2$). The effect of the conformational equilibrium and of self-association on K_1 and K_2 is discussed.

Introduction

The kinetics of ligand substitution in square-planar platinum(II) and palladium(II) complexes according to

$$ML_3X + Y \rightleftharpoons ML_3Y + X$$
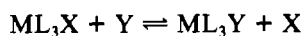
appears to be a matter well understood.[1] There is general agreement that the mechanism of substitution is associative in character for both the solvent path k_S and the reagent path $k_Y[Y]$, forming the observed rate law

$$k_{obsd} = k_S + k_Y[Y]$$

It is generally assumed that this is also true for other d^8 systems although there is much less experimental evidence for metal centers such as Ni(II), Ir(I), or Au(III).

As pointed out by Billo[2] and recently by Fayyaz and Grant,[3] in the case of nickel(II) the choice of suitable square-planar complexes is strongly restricted. As a consequence, the relatively few kinetic studies on ligand substitution in planar nickel(II) complexes have been concerned with S_4 and N_4 chelate complexes of types A–C. The kinetics of ligand substitution in bis(dithiolato) complexes of type A[4] and in type B complexes[2] were studied in aqueous solution, bidentate or monodentate nucleophiles serving as entering ligands. Studies

A   B

C   D
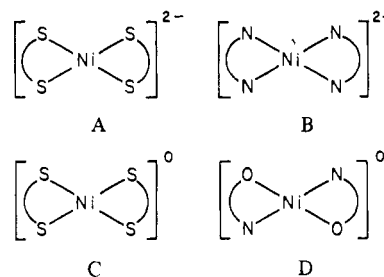
with neutral bis(dithiophosphato) and bis(dithiocarbamato) complexes of type C were carried out in methanol[5] and acetone.[3] The ligand substitution in complexes A, B, and C proceeds exclusively through a reagent path, clearly associative in character. So, in contrast to the intensely studied Pt(II) substrates these complexes seem not to allow a solvent pathway.

In this paper we present further information on the kinetic behavior of neutral four-coordinate nickel(II) bis-chelate species in chelate ligand substitution reactions carried out in organic media. In contrast to the neutral S_4 complexes of type C the complexes studied here are of the *trans*-N_2O_2 type D with N-alkylsalicylaldimines ($\equiv$HSA$\Longrightarrow$$N$-R) serving as ligands.

The X-ray structures of the complexes Ib and Ic have been determined. Ic exhibits a coordination geometry that is essentially planar (so-called stepped structure[6b]). In Ib the

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