if there was one more ligand on the oxidized form than on the reduced form of the complex.[33] On the basis of these data and the spectrophotometric results, the electrode reactions at low pyridine concentrations can correspond to reaction 4 while that at higher pyridine concentrations can correspond to reaction 5. As long as the initial reactant is not complexed by pyridine the reaction remains reversible to quasi-reversible. However, at higher pyridine concentrations, pyridine will bind to the neutral complex and, in this case, the reaction begins to become irreversible. At very high pyridine concentrations the reaction is totally irreversible and, under these conditions, both the oxidized and the reduced forms of the complex may be bound by two pyridine molecules.

$$Rh_2(ONHCCF_3)_4(S)_2 + py \xrightleftharpoons{-e^-} [Rh_2(ONHCCF_3)_4(py)(S)]^+ + S \quad (4)$$

$$Rh_2(ONHCCF_3)_4(py)(S) \xrightleftharpoons{-e^-} [Rh_2(ONHCCF_3)_4(py)(S)]^+ \quad (5)$$

The exact cause of the irreversibility has not been identified. It is clear, however, that the lack of reverse peak is due to a chemical reaction that involves the oxidized species and that a similar reaction is observed for the oxidized rhodium(II) carboxylates in the presence of pyridine.[26] One explanation may be that the bridging ligands are partially dissociated with subsequent binding to the one or more vacant sites on the Rh_2^{4+} moiety by pyridine molecules. The new complex, whatever its stoichiometry, is electrochemically inactive in the range of potentials investigated. The complex is presently being investigated by other techniques.

In summary, we have shown in this study that electrochemical oxidation potentials for $Rh_2(ONHCCF_3)_4$ are similar to those of rhodium(II) acetate and propionate but surprisingly different from those of $Rh_2(O_2CCF_3)_4$. In our previous study of rhodium(II) carboxylates[17] it was observed that electron-withdrawing substituents help to stabilize the lower oxidation state of the metal. With a strong electron-withdrawing group like CF_3 the lower oxidation state is stabilized to such an extent that no oxidation step can be observed for $Rh_2(O_2CCF_3)_4$. The fact that $Rh_2(ONHCCF_3)_4$ is relatively easy to oxidize suggests that the substitution of nitrogen for oxygen in the bridging moiety results in a destabilization of the HOMO of the Rh–Rh bonding scheme approximately equal to the stabilization produced by the CF_3 substituent. Apparently the more basic nitrogen donor produces a greater electron density on the metal dimer than oxygen. This balancing of the two effects (change of atom in the ligand bridge and addition of an electron-withdrawing substituent) is not reflected in the reduction potentials. Contrary to the results of $Rh_2(O_2CCR)_4$ no reduction potentials are observed in any solvents except THF up to potentials of −1.9 V vs. SCE. This cathodic shift of $E_{1/2}$ suggests that the level of the LUMO is more sensitive than that of the HOMO to the change from $Rh_2(O_2CCF_3)_4$ to $Rh_2(ONHCCF_3)_4$ and that the difference between the HOMO and LUMO is greater in the latter complex than in the former. This observation qualitatively agrees with the observed spectral shift of the neutral complex toward shorter wavelengths. However, further detailed spectral and structural investigations are needed, which are presently under way.

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Equilibria and Kinetics of Complex Formation at Gallium(III). Evidence for an Associative Mode of Activation

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The kinetics and equilibria of the reaction between gallium(III) and salicylic acid (H_2SAL), 5-chlorosalicylic acid (H_2ClSAL), 5-nitrosalicylic acid (H_2NSAL), and 3,5-dinitrosalicylic acid (H_2DNSAL) have been investigated in aqueous solution within an $[H^+]$ range between 0.0075 and 0.2 M at an ionic strength 0.2 M. Two complexes, GaL^+ and $GaHL^+$, were identified with H_2SAL, H_2ClSAL, and H_2NSAL whereas only GaL^+ was detected with H_2DNSAL. Complex formation constants and acid dissociation constants, K_{A1}, for the ligands (H_2L) have been evaluated by computer analysis of spectrophotometric data. The rate constants for reactions of Ga^{3+} with HL^- are linearly dependent of K_{A1} in a dilogarithmic plot as well as rate constants for reactions involving $Ga(OH)^{2+}$ and HL^-. The activation parameters have been determined in the case of H_2DNSAL. The evidences for an associative mechanism are discussed.

Introduction

Much of the current interpretation of the kinetic behavior of metal cations in labile octahedral complex formation is based on a proposal of Eigen[1] that the S_N1 ion-pair or "dissociative-interchange" mechanism is operative. The substantial literature that has accumulated rapidly since 1965, when Eigen and Wilkins' review[2] on this topic appeared, has confirmed this interpretation chiefly as regards bivalent metal cations[3-6] whereas the kinetic features of reactions of formation of labile complexes of tervalent cations are far less clear.[5-7]

In particular, little effort has so far been devoted to the reactions of gallium(III) ion.[8-13] This is probably due to

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experimental difficulties and complications in the interpretation of kinetic results in view of the strong tendency for hydrolysis[14-16] and of the possibility of polymerization[17,18] of tervalent cations. Recent kinetic studies[11-13] of complex formation at gallium(III) seem to encourage the possibility of an S_N2_{ip} or "associative-interchange" mechanism at least as far as the unhydrolyzed form of the cation is concerned. These works include attempts to assess a possible dependence of the reaction energetics on the entering-group nature, since this provides one of the chief criteria that aid in the discrimination between associative and dissociative mechanisms,[3,7] but except for one case,[13] the compared ligands were heterogeneous and other factors such as differences in polarizability and dimensions of the ligands could invalidate such a correlation.

The present study on reactions of gallium(III) with a set of substituted salicylic acids is designed to overcome these limits, and it should throw further light on the mechanism of complex formation at tervalent cations.

Experimental Section

Materials. Salicylic acid (H_2SAL), 5-chlorosalicylic acid (H_2ClSAL), 5-nitrosalicylic acid (H_2NSAL), and 3,5-dinitrosalicylic acid (H_2DNSAL) used in this work, already available as pure chemicals, were recrystallized from water. Their stock solutions were prepared weekly and standardized by potentiometric titrations.

A stock solution of gallium(III) perchlorate was prepared by controlled-potential anodic dissolution of a weighed amount of pure metal in a measured excess of diluted perchloric acid. A plate of smooth platinum with an area of about 4 cm^2, utilized as a cathode at a distance of 2 cm from the anode, allowed the current to flow with an intensity of ca. 0.05 A. Under these conditions the Joule effect was sufficient to liquefy the metal; therefore gallium was kept in a small container immersed in the electrolytic cell, making contact with a platinum wire. Checks of the content of Ga(III) were carried out by means of EDTA titrations with PAN as an indicator.[19] Results were found to agree exactly with those derived from the weight of dissolved metal.

Other chemicals were of analytical grade, and twice-distilled water was used throughout.

Instruments. Potentiometric measurements to obtain acid dissociation constants were carried out with a digital pH meter having an accuracy of ±0.005 pH unit. The instrument was equipped with a combined glass electrode calibrated against sodium perchlorate–perchloric acid solutions of known concentration and ionic strength to give directly $-\log [H^+]$.

Spectrophotometric measurements for acid and equilibrium constants were performed with a Perkin-Elmer 200 spectrophotometer having an accuracy of ±0.002 in transmittance.

A Durrum-Gibson stopped-flow instrument was used to carry out the kinetic experiments. The data concerning the traces recorded on the oscillograph screen were immediately transferred on a pocket minicomputer, and the values of the observed rate constant, k_{obsd}, were quickly obtained by means of a WNLLSQ (weighted nonlinear least-squares) procedure. This enabled us to retain, between replicated experiments, only those whose k_{obsd} values were in agreement to within 2–3%. Without this caution mean values of k_{obsd} would be affected by an error up to 10%.

All the instruments were provided for temperature control within ±0.1 °C. The required $[H^+]$ and ionic strengths were obtained by addition of suitable amounts of perchloric acid and sodium perchlorate.

Table I. Values of the First Dissociation Constant, $10^3 K_{A1}$ (M), for Salicylic Acid (H_2SAL), 5-Chlorosalicylic Acid (H_2ClSAL), 5-Nitrosalicylic Acid (H_2NSAL), and 3,5-Dinitrosalicylic Acid (H_2DNSAL)

I	T/°C	measmt	H_2SAL	H_2ClSAL	H_2NSAL	H_2DNSAL
0.1	25	*a*	1.71 ± 0.04	3.62 ± 0.09	12.2 ± 0.4	
0.2	15	*a*				542 ± 26
0.2	25	*a*	1.91 ± 0.04	3.92 ± 0.10	13.4 ± 0.3	520 ± 25
0.2	25	*b*		3.81 ± 0.17	13.2 ± 1.0	
0.2	35	*a*				499 ± 23
0.2	45	*a*				483 ± 22
1.0	25	*a*				402 ± 15

[a] Spectrophotometric. [b] Potentiometric.

Results

Equilibrium Measurements. Since the lowest $[H^+]$ in this work is 7.5×10^{-3} M, the prevailing hydrolyzed form of the cation in equilibrium with Ga^{3+} is $Ga(OH)^{2+}$. Values of the first hydrolysis constant (K_{H1}) of Ga^{3+} are reported in the literature[16] at 25 °C and I = 0.1, 0.3, 0.5, and 1.0 M. These are surprisingly linearly arranged (with a correlation coefficient $r^2 = 0.995$) according to a graph of pK_{H1} against $I^{1/2}$, and the interpolation for I = 0.2 M gives $K_{H1} = 2.16 \times 10^{-3}$ M.

Salicylic acids under our conditions behave as monoprotic acids. Potentiometric titrations at 25 °C and I = 0.2 M were carried out in order to obtain K_{A1} values for H_2ClSAL and H_2NSAL. Solutions containing concentrations C_L of these acids and C_A of perchloric acid were titrated with sodium hydroxide of concentration C_B. The first acid dissociation constant, K_{A1}, is given by the relationship

$$K_{A1} = [H^+]([H^+] + C_B - C_A)/(C_L - ([H^+] + C_B - C_A)) \tag{1}$$

A value of K_{A1} was calculated from each data point, and the errors on the experimental variables ($\sigma_{C_L} = 0.01C_L$, $\sigma_{C_A} = 0.01C_A$, $\sigma_{C_B} = 0.01C_B$, and $\sigma_{\log [H^+]} = 0.02$) were propagated according to eq 1 to give $\sigma_{K_{A1}}$ point by point. The values of K_{A1} listed in Table I (with the label "b") for the two acids were derived from weighted means on sets of data points corresponding to a degree of dissociation ranging between ca. 0.65 and 0.9.

Spectrophotometric determinations of K_{A1} (T = 25 °C, I = 0.1 or 0.2 M) were also carried out for H_2SAL, H_2ClSAL, and H_2NSAL at λ = 315, 330, and 360 nm, respectively. Increasing amounts of perchloric acid were added by a microsyringe to a solution of the ligand directly in the spectrophotometric cell. The parameters to be determined and variables are defined in the Appendix (section B) and are related by eq A2. The weights to be assigned to the variables have been calculated by setting $\sigma_{V_0} = \sigma_{V_i} = 0.001$ mL, $\sigma_{C_L^0} = 0.005C_L^0$, $\sigma_{CA^0} = 0.005C_A^0$, and $\sigma_T = 0.002$. The resulting values of K_{A1} agree very well with those potentiometrically obtained despite the smaller accuracy of the potentiometric method in determining pK_A values lower than 3.

3,5-Dinitrosalicylic acid is almost entirely dissociated in the range of $[H^+]$ used for the K_{A1} determinations of the other acids. Nevertheless the above-mentioned procedure was successfully used to obtain K_{A1} for H_2DNSAL at I = 1 M, since we were allowed to use 1 M $HClO_4$ as a titrating agent in order to bring the degree of dissociation into a range of useful values.

The difficulties in obtaining a reliable value of K_{A1} at I = 0.2 M, when the more diluted 0.2 M $HClO_4$ is used as a titrating agent, have been overcome by working at λ = 410 nm, where $\epsilon_{H_2L} = 0$. This procedure has a number of advantages: first, the number of parameters to be determined is reduced, and second, the knowledge of the value of C_L^0 is not required (see Appendix, section B). Measurements be-

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Table II. Apparent Complex Formation Constants, K_{app}, and Molar Absorption Coefficients, ϵ_L and ϵ_C, for the Gallium(III)-Salicylate Ion Systems at Different Acidities (T = 25 °C, I = 0.2 M)

ligand	$10^2 \times [H^+]$/M	$10^{-1}K_{app}$/M^{-1}	ϵ_L/M^{-1} cm^{-1}	ϵ_C/M^{-1} cm^{-1}	λ/nm
H_2SAL	1.0	8.53 ± 0.50	130 ± 1	864 ± 25	335
	1.5	4.39 ± 0.43	129 ± 1	876 ± 52	
	2.0	2.97 ± 0.35	130 ± 1	846 ± 65	
	2.5	1.92 ± 0.46	130 ± 1	874 ± 141	
	3.0	1.60 ± 0.49	130 ± 1	844 ± 187	
H_2ClSAL	1.0	14.6 ± 0.8	84 ± 1	535 ± 12	350
	1.5	8.16 ± 0.58	84 ± 1	573 ± 20	
	2.0	5.05 ± 0.52	85 ± 1	560 ± 34	
	2.5	3.68 ± 0.49	86 ± 1	612 ± 50	
	3.0	2.62 ± 0.49	86 ± 1	650 ± 83	
H_2NSAL	1.0	130 ± 4.5	2850 ± 26	10410 ± 100	360
	2.0	48.2 ± 2.0	2390 ± 14	9800 ± 160	
	3.0	26.2 ± 1.5	2090 ± 10	9340 ± 270	
	4.0	17.2 ± 0.9	1800 ± 10	8940 ± 220	
	5.0	11.5 ± 0.8	1700 ± 9	8870 ± 340	
	6.0	8.90 ± 0.80	1620 ± 8	8670 ± 470	
	7.0	6.88 ± 0.82	1550 ± 7	8540 ± 650	
	8.0	5.95 ± 0.85	1510 ± 7	8320 ± 780	
	9.0	4.77 ± 0.92	1480 ± 7	8280 ± 990	
H_2DNSAL	1.0	249 ± 10	4260 ± 33	1740 ± 13	390
	2.0	115 ± 5	4210 ± 25	1730 ± 22	
	3.0	82.5 ± 4.5	4110 ± 25	1760 ± 30	
	5.0	46.8 ± 3.5	3920 ± 20	1720 ± 55	
	6.0	38.3 ± 3.3	3850 ± 19	1720 ± 70	
	7.0	31.5 ± 3.2	3760 ± 18	1700 ± 88	
	8.0	26.7 ± 3.2	3720 ± 18	1730 ± 110	
	9.0	21.3 ± 3.1	3660 ± 17	1680 ± 150	

Table III. Values of the Equilibrium Constants for the Gallium(III)-Salicylate Systems (T = 25 °C, I = 0.2 M)

ligand	measmt	K_1	K_2/M^{-1}	$10K_3$/M[c]
H_2SAL	*a*	5.41 ± 0.38	95 ± 19	0.57 ± 0.15
	b	4.85 ± 0.27	75 ± 17	0.65 ± 0.18
H_2ClSAL	*a*	5.86 ± 0.38	53 ± 19	1.11 ± 0.47
	b	5.52 ± 0.30	47 ± 19	1.16 ± 0.52
H_2NSAL	*a*	25.3 ± 0.8	88 ± 16	2.88 ± 0.61
	b	21.0 ± 1.4	94 ± 40	2.23 ± 1.09
H_2DNSAL	*a*	25.7 ± 1.6		
	b	25.8 ± 1.1		

[a] From equilibrium data. [b] From kinetic data. [c] Calculated as $K_3 = K_1/K_2$.

tween 15 and 45 °C show a slight change of K_{A1} with temperature (K_{A1} = 0.158 exp(355/T); H_2DNSAL, I = 0.2 M).

All the experimental values of dissociation constants are summarized in Table I.

When gallium(III) ion is added to a solution of one of the ligands, a shift of the band with λ_{max} between 300 and 335 nm is indicative of complex formation. The extent of this change, increasing from H_2SAL to H_2DNSAL, is not very large and depends on pH. Under our conditions only 1:1 complexes are formed.[11,13] As we shall see, complexation involves loss of protons.

We can define an apparent formation constant as the total complex concentration divided by the product of the total free Ga(III), Ga_f, and the total free ligand, L_f.

$$K_{app} = [\text{complex}]_T/[Ga_f][L_f] \qquad (2)$$

Spectrophotometric determinations of K_{app} were carried out

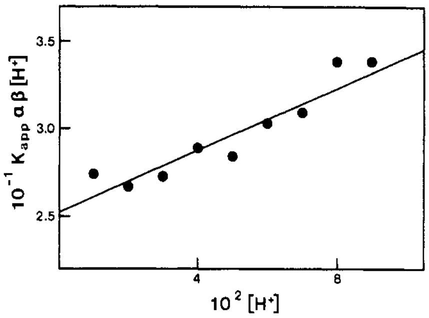


Figure 1. Plot of $K_{app}\alpha\beta[H^+]$ against $[H^+]$ (M) for the reaction between gallium(III) and H_2NSAL at 25 °C and I = 0.2 M.

by adding with a microsyringe V_i mL of $Ga(ClO_4)_3$ of concentration $C_M{}^0$ at a fixed $[H^+]$ to ligand solutions of concentration $C_L{}^0$ at the same $[H^+]$. By the application of WNLLSQ procedure to eq A12 the parameters K_{app}, ϵ_L, and ϵ_C have been calculated by setting $\sigma_{V_0} = \sigma_{V_i}$ = 0.001 mL, $\sigma_{C_M{}^0} = 0.005C_M{}^0$, $\sigma_{C_L{}^0} = 0.005C_L{}^0$, and σ_T = 0.002. Their values are summarized in Table II.

With H_2SAL, H_2ClSAL, and H_2NSAL the acidity dependence of K_{app} indicates that two complexes, $GaHL^{2+}$ and GaL^+, are formed with equilibrium constants defined by eq 3 and 4. According to eq A18 (see Appendix, section D), if

$$K_1 = [GaL^+][H^+]/[Ga^{3+}][HL^-] \qquad (3)$$

$$K_2 = [GaHL^{2+}]/[Ga^{3+}][HL^-] \qquad (4)$$

$\alpha = (1 + [H^+]/K_{A1})$ and $\beta = (1 + K_{H1}/[H^+])$, plots of $K_{app}\alpha\beta[H^+]$ against $[H^+]$ should give straight lines with intercept K_1 and slope K_2. This is shown in Figure 1 in the case of H_2NSAL.

With H_2DNSAL a zero slope is obtained within the experimental error. This does not mean that $K_2 = 0$ in this case, but only that the equilibrium (5) is shifted to the GaL^+ form

$$[GaL^+][H^+]/[GaHL^{2+}] = K_1/K_2 = K_3 \qquad (5)$$

and no appreciable amount of $Ga(H(DNSAL))^{2+}$ is detected under our conditions ($[H^+]/K_3 \ll 1$). An attempt to determine K_2 by working at higher $[H^+]$ would fail in that the extent of total compelxation is reduced to very low values.

It should be noted that ϵ_L and ϵ_C are "apparent" absorption coefficients being defined as

$$\epsilon_L = (\epsilon_{HL}K_{A1} + \epsilon_{H_2L}[H^+])/(K_{A1} + [H^+])$$

$$\epsilon_C = (\epsilon_{GaL}K_1 + \epsilon_{GaHL}K_2[H^+])/(K_1 + K_2[H^+])$$

It is therefore not surprising that they can display a dependence of $[H^+]$.

A properly weighted fitting on eq A18 yielded the values of K_1 and K_2. These are listed in Table III with their quotient K_3. The weights were assessed by setting $\sigma_{[H^+]} = 0.02[H^+]$ and $\sigma_{K_{H1}} = 0.1K_{H1}$, whereas $\sigma_{K_{A1}}$ and $\sigma_{K_{app}}$ are known from the previous fittings.

Values of K_{app} were also obtained for the H_2DNSAL–Ga(III) system at 15, 35, and 45 °C and ionic strength 0.2 M. For each temperature three experiments at $[H^+]$ = 0.05, 0.07, and 0.09 M were carried out. Since the dependence of K_{H1} on the temperature is unknown, we set β = 1 in eq A18. This procedure does not introduce appreciable errors at the rather

Table IV. Forward and Reverse Rate Constants for the Gallium(III)-Salicylate Systems (T = 25 °C, I = 0.2 M)

ligand	k_1/M^{-1} s^{-1}	$10k_2$/s^{-1}	$10k_{-1}$/M^{-1} s^{-1}	10^2k_{-2}/s^{-1}
H_2SAL	392 ± 89	151 ± 8	794 ± 60	312 ± 12
H_2ClSAL	185 ± 61	92.9 ± 5.4	416 ± 69	168 ± 14
H_2NSAL	62.7 ± 9.2	44.9 ± 0.9	36.7 ± 0.8	18.9 ± 0.7
H_2DNSAL	8.00 ± 0.40	4.05 ± 0.07	3.15 ± 0.06	1.46 ± 0.08

Table V. Values of the Equilibrium Constant K_1 and the Forward and Reverse Rate Constants for the Gallium(III)–3,5-Dinitrosalicylate Ion System at Different Temperatures (I = 0.2 M)

T/°C	K_1	k_1/M^{-1} s^{-1}	$10k_2$/s^{-1}	$10k_{-1}$/M^{-1} s^{-1}	10^5k_{-2}/s^{-1}
15	18.7 ± 2.2	3.55 ± 0.15	0.87 ± 0.19	1.87 ± 0.08	0.46 ± 0.10
25	25.7 ± 1.6	8.01 ± 0.41	3.49 ± 0.51	3.14 ± 0.16	1.37 ± 0.20
35	34.6 ± 1.0	16.3 ± 1.0	14.4 ± 1.4	4.87 ± 0.31	4.29 ± 0.41
45	42.1 ± 3.5	32.9 ± 2.7	49.7 ± 3.5	7.62 ± 0.62	11.5 ± 0.8

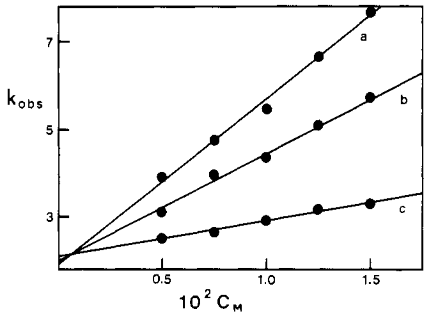


Figure 2. Plots of k_{obsd} (s^{-1}) against the gallium perchlorate concentration, C_M (M), for the reaction between gallium(III) and H_2ClSAL at 25 °C and I = 0.2 M. [H^+] = 0.0075 (a), 0.01 (b), and 0.025 M (c).

high acidities reported above. K_1 was found to be dependent on the temperature ($K_1 = 1.154 \times 10^5 \exp(-2510/T)$). The experimental values are listed in Table V.

Kinetic Measurements. Kinetic runs were carried out under pseudo-first-order conditions ($C_M \gg C_L$), over an [H^+] range between 0.0075 and 0.2 M and a C_M range between 10^{-3} and 1.5×10^{-2} M. At any given hydrogen ion concentration the observed rate constants, k_{obsd}, are independent of the initial concentrations of ligand whereas these increase linearly with C_M, as shown in Figure 2. The slopes and intercepts of the straight lines of Figure 2 represent respectively the forward and reverse rate constants for the process of complexation, which, at constant [H^+], is represented by the scheme

$$\mathrm{Ga_f} + L_f \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \text{total complex} \tag{6}$$

where

$$k_{obsd} = k_fC_M + k_d \tag{7}$$

A comparison of eq 6 with eq 2 shows that k_f/k_d must be equal to K_{app}. The kinetic values of K_{app} have been subjected to the statistical analysis based on eq A18 already performed on the spectrophotometric data, and the resulting values of K_1 and K_2 are summarized in Table III. The good agreement between the results obtained with the two different techniques can be regarded as a check of the validity of the scheme representing the equilibria.

A reaction mechanism that is compatible with the results is shown by Scheme I.

It should be noted that, owing to a proton ambiguity, paths Ia–IIa are kinetically indistinguishable from paths Ib–IIb. If the loss and addition of H^+ are assumed to be fast in comparison with complexation, the reaction scheme leads to

$$k_{obsd} = (k_1 + k_2/[H^+])C_M/\alpha\beta + (k_{-1}[H^+] + k_{-2})/(1 + [H^+]/K_3) \tag{8}$$

where

$$k_1 = k_{Ia} + k_{Ib}K_{H1}/K_{A1} \tag{9}$$

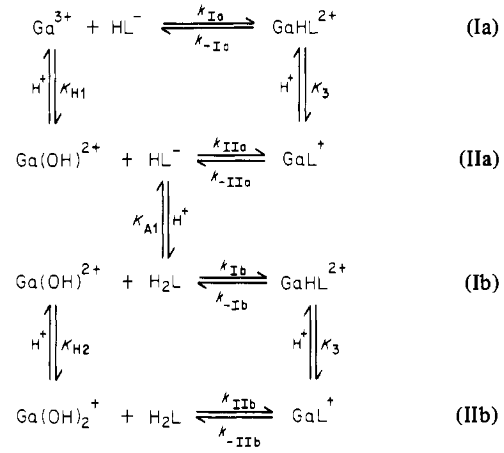
$$k_2 = K_{H1}(k_{IIa} + k_{IIb}K_{H2}/K_{A1}) \tag{10}$$

$$k_{-1} = (k_{-Ia} + k_{-Ib})/K_3 \tag{11}$$

$$k_{-2} = k_{-IIa} + k_{-IIb} \tag{12}$$

In the case of the H_2DNSAL–Ga(III) system, where no appreciable amount of $Ga(H(DNSAL))^{2+}$ is detected, steps Ia and Ib are reduced to (I'a) and (I'b), where $k_{-Ia}' = k_{-Ia}/K_3$

Scheme I



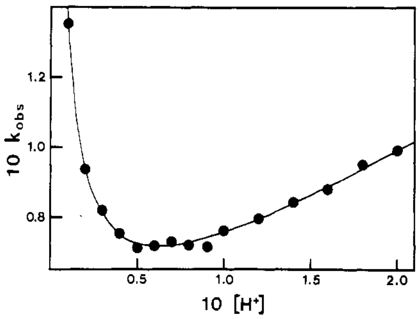
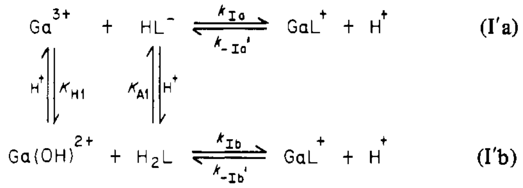


Figure 3. Plot of k_{obsd} (s^{-1}) against [H^+] (M) for the reaction between gallium(III) and H_2DNSAL at 25 °C and I = 0.2 M.



and $k_{-Ib}' = k_{-Ib}/K_3$ so that eq 11 is still valid. In this case the term $(1 + [H^+]/K_3)$ can be set equal to unity without serious error. In other cases it contributes to k_d to an appreciable extent at the highest [H^+]. Plots of k_{obsd} against [H^+] at constant C_M, as shown in Figure 3 for the H_2DNSAL–Ga(III) system, are consistent with eq 8. The curves show no upward trend at the highest values of [H^+]. This indicates that a reaction path involving Ga^{3+} and H_2L is not operative.

By use of the appropriate values of K_{A1}, K_{H1}, and K_3, eq 8 can be treated as a linear equation with four independent parameters, k_1, k_2, k_{-1}, and k_{-2}. These have been obtained by performing a statistical analysis over 30 accurately determined data for each acid. Their values are listed in Table IV. The percent standard deviations were within 3% in any case.

An inspection of the reaction scheme shows that the quotients k_1/k_{-1} and k_2/k_{-2} must both be equal to K_1. Since this is verified within the experimental errors, it constitutes a check

Table VI. Values of the Activation Parameters for the Gallium(III)–3,5-Dinitrosalicylate Ion System ($I = 0.2$ M)

path	$10^{-3}(\Delta H^{\ddagger})$/ J M^{-1}	$\Delta S^{\ddagger}$/ M^{-1} K^{-1}	path	$10^{-3}(\Delta H^{\ddagger})$/ J M^{-1}	$\Delta S^{\ddagger}$/ M^{-1} K^{-1}
k_1	54.0 ± 2.0	−47 ± 7	k_{-1}	33.1 ± 2.0	−144 ± 7
k_2	100.9 ± 4.5	85 ± 15	k_{-2}	80.0 ± 4.5	−12 ± 15

of the validity of our kinetic model.

In order to obtain the activation parameters, we also investigated the decomposition of the complex at 15, 25, 35, and 45 °C and $I = 0.2$ M for the H_2DNSAL–Ga(III) system. The complex was formed by mixing equal, small amounts (10^{-4} M) of the reactants at pH $\simeq 3.3$ and decomposed at [H^+] between 0.08 and 0.2 M. Under these conditions Ga_f is negligibly small and eq 7 is reduced to $k_{obsd} = k_d$. Plots of k_{obsd} against [H^+] gives straight lines with positive intercepts (k_{-2}) and slopes (k_{-1}), meaning that paths of zero and first order with respect to [H^+] are operative in the reverse reaction. Since no downward trend is observed at the highest acidities, it follows that the term $1 + [H^+]/K_3$ in eq 8 is close to unity and therefore K_3 is expected to be higher than 2 M. This confirms the conclusion drawn from the equilibrium experiments that the protonated complex is present in negligible amounts in the gallium(III)–H_2DNSAL system.

Values of k_1 and k_2 can be obtained from k_{-1} and k_{-2} in conjunction with the K_1 values at the above-mentioned temperatures. The results are given in Table V.

The activation parameters were calculated from the temperature dependence of the rate constants by setting $\sigma_T = 0.1$ °C whereas σ_{k_i} was known for each value of k_i. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are listed in Table VI.

Discussion

Equilibria. The values of K_{A1} presented in this work can be compared with the values reported in the literature. For H_2SAL $K_{A1} = 1.55 \times 10^{-3}$ M is reported[20] at 25 °C and $I = 0.1$ M. From the K_{A1} values of H_2ClSAL and H_2NSAL at $I = 0$[20] the values of 3.75×10^{-3} and 1.35×10^{-2} M, respectively, have been derived at $I = 0.1$ M with the aid of the Davies equation[21] ($B = 0.3$). A great deal of confusion exists in the published data as far as K_{A1} of H_2DNSAL is concerned. Potentiometric K_{A1} values of 4.9×10^{-2} M at $I = 0.1$ M and 31 °C[22] and of 5.6×10^{-3} M at $I = 0.1$ M and 25 °C[20,25] are quoted. On the other hand, spectrophotometric measurements, which are in our opinion more reliable with acids of this strength, show that H_2DNSAL is, as expected, far more dissociated than H_2NSAL. The values of K_{A1} at 25 °C that have been obtained by spectrophotometry are 0.54 M ($I = 1$ M), 0.56 M ($I = 0.1$ M),[23] and 0.32 M ($I = 1$ M).[24]

Higher values of the equilibrium and kinetic constants were obtained in a previous study on the Ga(III)–H_2NSAL system.[13] The disagreement is due in part to the difference in ionic strength but mainly to the different value of K_{A1} (5.7×10^{-3} M) used in calculating results. In fact, if we use $K_{A1} = 1.22 \times 10^{-2}$ M and make the appropriate corrections for the ionic strength, the results substantially agree with the present ones. The differences between the present and previous values of the equilibrium and kinetic constants for the Ga(III)–H_2SAL system[11] cannot be explained only by the difference in ionic strength. The present work has been carried out at pH ≤ 2.1, where the value of β is not far from unity, whereas in the previous work K_{app} values were determined at $2 \leq \text{pH} \leq 3.2$, where the term β has a considerable weight. We ascribe the difference in the results to the uncertainties of the composition of solution at pH >2.5, where amounts of several monomeric and polymeric hydrolyzed forms of the cation can be present.[14–18]

Table VII. Values of the Second Dissociation Constant, K_{A2}, and the Equilibrium Constant, K_4, for the Gallium(III)–Salicylate Ion Systems ($T = 25$ °C)

ligand	pK_{A2}[a]	K_{A2}/M[d]	K_4/M^{-1} [e]
H_2SAL	13.4[b]	4.8×10^{-14}	1.1×10^{14}
H_2ClSAL	12.95[b]	3.6×10^{-13}	1.6×10^{13}
H_2NSAL	10.11[b]	9.3×10^{-11}	2.7×10^{11}
H_2DNSAL	7.22[b]	7.2×10^{-8}	3.6×10^{8}

[a] From ref 20. [b] $I = 0.1$ M. [c] $I = 0$. [d] Corrected for $I = 0.2$ M with the aid of the Davies equation ($B = 0.3$).[21] (e) Obtained as $K_4 = K_1/K_{A2}$.

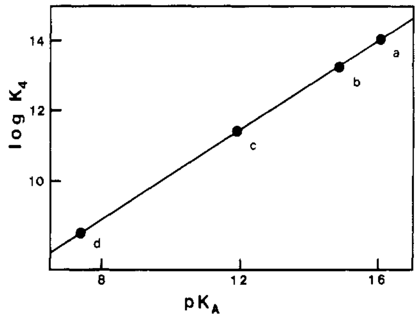


Figure 4. Plot of log $K_4 \equiv \log K_1 + pK_{A2}$ against $pK_A \equiv pK_{A1} + pK_{A2}$ for the gallium(III) and H_2SAL (a), H_2ClSAL (b), H_2NSAL (c), and H_2DNSAL (d) systems at 25 °C and $I = 0.2$ M.

The trend of K_1 values (the lower the value, the more basic the ligand) can be regarded as a consequence of the different labilities of the phenolic proton. The more appropriate equilibrium constant for the consideration of the relative stabilities of the complexes is given by eq 13. By the correction of the values of K_{A2}, the second dissociation constant

$$K_4 = [\text{GaL}^+]/[\text{Ga}^{3+}][\text{L}^{2-}] = K_1/K_{A2} \qquad (13)$$

of the salicylic acids, reported in the literature[20] at $I = 0.2$ M, with the aid of the Davies equation[22] ($B = 0.3$), the K_4 values listed in Table VII were obtained. It can be seen that the real stability of the chelated complexes increases from GaDNSAL$^+$ to GaSAL$^+$.

The changes in partial molar free energies of the cation-ligand and the proton-ligand complexes are proportional, since the values of K_4 are linearly arranged (with a correlation coefficient $r^2 = 0.9997$) according to a graph of log K_4 against $pK_A \equiv pK_{A1} + pK_{A2}$. This is shown in Figure 4. By means of the values of the slope and the intercept, equal to 0.6335 and 3.858, respectively, values of K_1 can be calculated at 25 °C and $I = 0.2$ M for complexation of gallium(III) by every substituted salicylic acid of known K_{A1} and K_{A2}.

The trend of K_2 values is not easily explainable, even when possible considerable errors are taken into account. We are driven to think that some interactions between the cation and the phenolic oxygen are present in the GaHL^{2+} complex that modify its stability.

Kinetics. The occurrence of ion pairs in solution has been demonstrated extensively, and it has found a widespread acceptance. Whereas this does not necessarily mean that the substitution pathway proceeds through ion pairs,[26] or "outer-sphere complexes", such a mechanism is an attractive possibility since the aquo ion and the ligand are held in close

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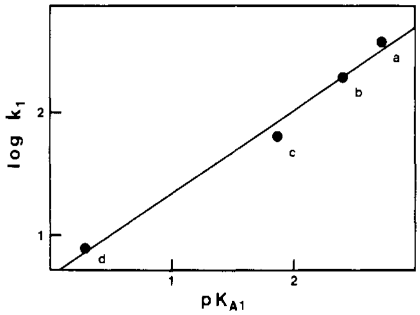

Figure 5. Plot of the logarithm of the first-order rate constant for the reaction of substitution at Ga^{3+}, k_1, as a function of pK_{A1} of the following entering groups: $H(SAL)^-$ (a), $H(ClSAL)^-$ (b), $H(NSAL)^-$ (c), $H(DNSAL)^-$ (d). $T = 25$ °C, $I = 0.2$ M.

proximity. We shall regard the reaction between gallium(III) and salicylic acids as a process of conversion of the outer-sphere complex into the corresponding inner-sphere complex. The first, rate-determining step is the formation of unidentate carboxylato complex, whereas a subsequent step involves deprotonation and ring closure.

We have assumed equilibrium 14 to be fast in comparison

$$GaHL^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} GaL^+ + H^+ \qquad (14)$$

with formation and decomposition of the unidentate complex. If step 14 were rate determining, the kinetic expression (8) should be replaced by (15), the dependence of k_{obsd} upon C_M

$$k_{obsd} = (k_3K_2 + k_2/[H^+])C_M/(\alpha\beta + K_2C_M) + k_{-3}[H^+] + k_{-2} \qquad (15)$$

at constant $[H^+]$ would not be linear at higher C_M values, and plots such as that in Figure 2 would display a curvature with a downward concavity. This has never been observed in this work.

Reaction paths involving L^{2-} have been ruled out because of the extremely low relative concentrations of these species at pH ≤ 2 ($pK_{DNSAL^{2-}} = 7.2$,[23] the lowest in the series) as well as reaction paths involving Ga^{3+} with H_2L (see the Kinetic Measurements part of the Results section) and $Ga(OH)_2^+$ with HL^- because the observed pH dependence provides no evidence for such reactions. This is not in contrast with previous investigations on Ga(III)–H_2SAL[11] and Ga(III)–H_2NSAL[13] systems, where a reaction between $Ga(OH)^{2+}$ and HL^- was detected at $[H^+]$ values lower than 10^{-2} M, because of the limited pH range considered here.

The rate constant, k^*, for the process of conversion of the outer-sphere into the inner-sphere complex is obtained by dividing the experimental rate constant by K_{os}, the stability constant of the outer-sphere complex. After calculating K_{os} for the path Ia at 25 °C and $I = 0.2$ M with the Fuoss equation,[27] we have obtained upper limits for the values of k^*. These are considerably different among themselves and *all lower* than the value of $0.75k_{H_2O}$,[28] where $k_{H_2O} = 7.6 \times 10^2$ s^{-1} (or 1.8×10^3 s^{-1}) is the rate constant for the process of water exchange at Ga^{3+} as determined by NMR measurements.[8,29] This result lessens the change that a S_N1_{ip} mechanism could be operative in the reactions of the tripositive Ga^{3+} ion.

Further argument against the dissociative character of reaction Ia is offered by the low value of $\Delta S^{\ddagger}$ obtained in the case of H_2DNSAL. The negative value of $\Delta S^{\ddagger}$ for path k_1 embodies the ΔS° for ion-pair formation involving a 3:1 electrolyte. This can be evaluated to be ca. 20 J M^{-1} K^{-1} at 25 °C and $I = 0.2$ M by using the Fuoss equation[27] for $a = 5$ Å. Therefore for the path of conversion of the outer-sphere into the inner-sphere complex one obtains $\Delta S^{\ddagger *} = -67$ J M^{-1} K^{-1}. It is worth mentioning that the available values of $\Delta S^{\ddagger}$ for water exchange are so different (+42 J M^{-1} K^{-1} [29] and −92 J M^{-1} K^{-1} [8]) that it is impossible to draw any conclusion about the mechanism of solvent exchange from these data.

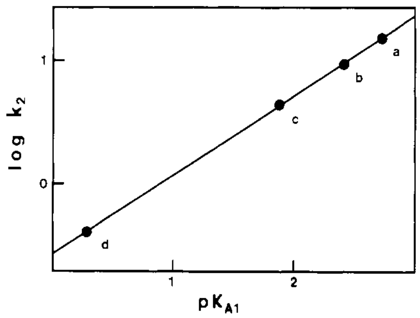

Figure 6. Plot of the logarithm of the first-order rate constant for the reaction of substitution at $Ga(OH)^{2+}$, k_2, as a function of pK_{A1} of the following entering groups: $H(SAL)^-$ (a), $H(ClSAL)^-$ (b), $H(NSAL)^-$ (c), $H(DNSAL)^-$ (d). $T = 25$ °C, $I = 0.2$ M.

Figures 5 and 6 show the linear dependence of log k_1 (slope = 0.67) and log k_2 (slope = 0.64), respectively, on the pK_{A1} of the salicylic acids. Both rate constants increase with the basicity of the ligand, and this behavior is often assumed as a proof for an associative mechanism. It should be noted however that the rates should depend on K_{A1} also in the case of a dissociative mechanism, provided that paths Ia and IIa make a negligible contribution to the reaction (see eq 9 and 10). In this case however the slope of the dilogarithmic plot should be unity, contrary to experiment. The second limiting case (dissociative mechanism with negligible contribution of paths Ib and IIb) must be ruled out since in this case both k_{Ia} and k_{IIa} should be ligand independent. In any intermediate case (dissociative mechanism with significant contributions of both path "a" and path "b") the dilogarithmic plots of Figures 5 and 6 should give curves with an upward concavity. The extent of this curvature would be evident and can be calculated (see Appendix, section E). We conclude therefore that the experimental results shown in Figures 5 and 6 reflect a dependence of k_{Ia} and k_{IIa} on the ligand basicity. On this basis we suggest an associative mode of activation (S_N2_{ip}) not only for the reactions of Ga^{3+} but also for those of $Ga(OH)^{2+}$ with this kind of ligand, although the latter possibility could be, at first, somewhat surprising in view of the reduced charge density at the metal ion.

Acknowledgment. This work has been partially supported by the "CNR", Italy.

Appendix

(A) Whenever not otherwise specified, WNLLSQ (weighted nonlinear least-squares) procedures were carried out to fit experimental data. Some details will be given here, but for a more extensive treatment on this matter we refer to a paper by Wentworth.[30]

Let us suppose the n observations of the m variables X_J verify a function F (in the form equated to zero) of the l parameters P_k, within the experimental errors. The least-squares problem can be stated mathematically as a desire to obtain a minimization of the sum of the squares of the weighted residuals

$$S = \sum_{i=1}^{n} \sum_{J=1}^{m} (W(X_{J_i}))(X_{J_i} - \bar{X}_{J_i})^2 = \min$$

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under the restriction that the condition equations

$$F_i(X_{1_i}, ..., X_{m_i}, P_1, ..., P_l) = 0 \qquad i = 1, ..., n$$

be satisfied. The weights $W(X_{J_i})$ are defined as a quantity inversely proportional to the variance

$$W(X_{J_i}) = \sigma_0^2/\sigma^2(X_{J_i})$$

where σ_0 is an arbitrary constant. Furthermore let us define

$$L_i = \sum_{J=1}^{m} F'^2(X_{J_i})/W(X_{J_i})$$

where $F'(X_{J_i})$ is the partial derivative of F with respect to X_J, calculated in the ith point. The notation $F'(P_{k_i})$ has a similar meaning. The values of $\sigma(X_J)$ are assigned as well as approximate initial values of the parameters (P_k^0) and the procedure is accomplished by solving the system

$$\begin{pmatrix} \Sigma\dfrac{(F'(P_{1_i}))(F'(P_{1_i}))}{L_i} & \cdots & \Sigma\dfrac{(F'(P_{1_i}))(F'(P_{l_i}))}{L_i} \\ \vdots & & \vdots \\ \Sigma\dfrac{(F'(P_{l_i}))(F'(P_{1_i}))}{L_i} & \cdots & \Sigma\dfrac{(F'(P_{l_i}))(F'(P_{l_i}))}{L_i} \end{pmatrix} \begin{pmatrix} \Delta P_1 \\ \vdots \\ \Delta P_l \end{pmatrix} = \begin{pmatrix} \Sigma\dfrac{(F'(P_{1_i}))F_i}{L_i} \\ \vdots \\ \Sigma\dfrac{(F'(P_{l_i}))F_i}{L_i} \end{pmatrix}$$

for $\Delta P_1, ..., \Delta P_l$. New, better values of P_k are obtained as $P_k = P_k^0 - \Delta P_k$, and the process is protracted until convergence is reached. The variances of the parameters are given by the diagonal elements of the covariance matrix.

(B) With the assumption that Beer's law is obeyed

$$A = \epsilon_{HL}[HL^-] + \epsilon_{H_2L}[H_2L] \qquad (A1)$$

the expression of the first acid dissociation constant, K_{A1}, and the mass conservation yield

$$A/C_L - (\epsilon_{HL}K_{A1} + \epsilon_{H_2L}[H^+])/(K_{A1} + [H^+]) = 0 \qquad (A2)$$

where the cell path is set equal to unity, A is the absorbance, and ϵ_{HL} and ϵ_{H_2L} are the molar absorption coefficients of HL^- and H_2L, respectively. If V_0 mL of the ligand of concentration C_L^0 are titrated by adding V_i mL of $HClO_4$ of concentration C_A^0, we have

$$C_L = C_L^0V_0/(V_0 + V_i) \qquad (A3)$$

and, provided that the contribution of the ligand dissociation to the total acidity is negligible

$$[H^+] = C_A^0V_i/(V_0 + V_i) \qquad (A4)$$

By propagating the errors, one obtains

$$\sigma_{C_L} = C_L(\sigma_{C_L^0}/C_L^0) + (\sigma_{V_0}V_i/V_0 + \sigma_{V_i})/(V_0 + V_i) \qquad (A5)$$

$$\sigma_{[H^+]} = [H^+](\sigma_{C_A^0}/C_A^0) + (\sigma_{V_i}V_0/V_i + \sigma_{V_0})/(V_0 + V_i) \qquad (A6)$$

$$\sigma_A = (10^{-A}/\ln 10)\sigma_T \qquad (A7)$$

If $\sigma_{C_L^0}$, $\sigma_{C_A^0}$, σ_{V_0}, σ_{V_i}, and σ_T (transmittance) are assigned, the WNLLSQ procedure can be carried out on eq A2 to obtain values of the parameters K_{A1}, ϵ_{HL}, and ϵ_{H_2L} by considering A, C_L, and $[H^+]$ as variables.

If ϵ_{H_2L} is equal to zero, by means of (A3) and (A4) eq A2 is converted to

$$A(1 + (1 + C_A^0/K_{A1})V_i/V_0) - C_L^0\epsilon_{HL} = 0 \qquad (A8)$$

in which the parameters to be determined are only K_{A1} and ($C_L^0\epsilon_{HL}$). A further advantage of eq A8 is that the knowledge of the value of C_L^0 is not required in order to obtain K_{A1}. Equation A8 can be fitted with the WNLLSQ method, provided that $\sigma_{C_A^0}$, σ_{V_i}, σ_{V_0}, and σ_T are assigned.

(C) By setting

$$[Ga_f] = C_M - [complex]_T \qquad (A9)$$

and

$$[L_f] = C_L - [complex]_T \qquad (A10)$$

(where C_M and C_L are the analytical concentrations of gallium(III) and ligand) eq 2, together with Beer's law

$$A = [L_f]\epsilon_L + [complex]_T\epsilon_C \qquad (A11)$$

yields the equation

$$C_M/(\epsilon_LC_L - A) + 1/(\epsilon_C - \epsilon_L) + 1/K_{app}(C_L\epsilon_C - A) = 0 \qquad (A12)$$

The WNLLSQ procedure allows the data to be treated according to equation A12, nonlinear in the parameters K_{app}, ϵ_L, and ϵ_C. The involved variables are A, C_M, and C_L, and their errors have been defined in section B except for σ_{C_M}. This can be derived from

$$C_M = C_M^0V_i/(V_0 + V_i) \qquad (A13)$$

and is given by

$$\sigma_{C_M} = C_M(\sigma_{C_M^0}/C_M^0) + (\sigma_{V_i}V_0/V_i + \sigma_{V_0})/(V_0 + V_i) \qquad (A14)$$

(D) Since

$$[GaL^+] + [GaHL^{2+}] = [complex]_T \qquad (A15)$$

$$[Ga_f] = [Ga^{3+}] + [Ga(OH)^{2+}] = [Ga^{3+}](1 + K_{H1}/[H^+]) = [Ga^{3+}]\beta \qquad (A16)$$

$$[L_f] = [HL^-] + [H_2L] = [HL^-](1 + [H^+]/K_{A1}) = [HL^-]\alpha \qquad (A17)$$

by means of eq 2–4 we can write

$$K_{app}\alpha\beta[H^+] - K_1 - K_2[H^+] = 0 \qquad (A18)$$

Equation A18 can be treated with the WNLLSQ method as a function of two parameters, K_1 and K_2, and four variables, K_{app}, $[H^+]$, K_{H1}, and K_{A1}, provided that $\sigma_{K_{app}}$, $\sigma_{[H^+]}$, $\sigma_{K_{H1}}$, and $\sigma_{K_{A1}}$ are assigned.

(E) The dilogarithmic form of eq 9 is given by (A19). If

$$\log k_1 = \log(k_{Ia} + 10^{pK_{A1}}k_{Ib}K_{H1}) \qquad (A19)$$

the mechanism S_N1 is supposed to be operative, k_{Ia} and k_{Ib} remain constant as pK_{A1} changes and eq A20 can be derived.

$$y' = d(\log k_1)/d(pK_{A1}) = 1/(1 + 10^{-pK_{A1}}k_{Ia}/k_{Ib}K_{H1}) \qquad (A20)$$

Equation A20 shows that the slope of the line obtained by plotting log k_1 against pK_{A1}, as in Figure 5, must increase with increasing pK_{A1}. In order to calculate the extent of the hypothetical curvature of the line, we can reasonably assume that the slope of its central portion, i.e., at $pK_{A1} = 1.5$, is equal to the experimental slope of 0.67. Under this assumption one obtains a value of 15.6 for the ratio $k_{Ia}/k_{Ib}K_{H1}$. With this value one can calculate $y' = 0.06$ at $pK_{A1} = 0$ and $y' = 0.98$ at $pK_{A1} = 3$. Similar considerations, in the case of Figure 6, where eq 10 is involved, yield $y' = 0.05$ at $pK_{A1} = 0$ and $y' = 0.98$ at $pK_{A1} = 3$ if $y' = 0.64$ is assumed at $pK_{A1} = 1.5$.

Registry No. Ga, 7440-55-3; H_2ClSAL, 321-14-2; H_2SAL, 69-72-7; H_2DNSAL, 609-99-4; H_2NSAL, 96-97-9.