Contribution from the Istituto di Chimica Analitica,
Università di Torino, 10125 Torino, Italy

Equilibria and Kinetics of the Complex Formation between Iron(III) and α-Hydroxycarboxylic Acids

EDOARDO MENTASTI

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The equilibria and kinetics of the reactions of Fe(III) with glycolic, DL-lactic, DL-malic, and benzilic acids have been investigated at 25 °C and ionic strength $\mu = 1.0$ M, by using the stopped-flow method. The reactions give rise to a chelate complex and proceed mainly through interactions of $FeOH^{2+}$ with the undissociated ligands in the acidity range $0.10 \geq [HClO_4] \geq 0.010$ M. The corresponding rate constants exhibited values which agree with the Eigen mechanism of complex formation from labile aquo metal ions. The results are compared with previous findings on the formation of Fe(III) complexes and with the rate of water exchange from the hydrolyzed metal species. $FeOH^{2+}$ appears to react in a purely dissociative fashion and its characteristic water exchange rate can be obtained, as a rough estimate, from the experimental data now available, in the light of the Eigen mechanism. The equilibrium constants of the complexes have been evaluated with a spectrophotometric technique and compared with those obtained from the overall forward and reverse rate constants.

Among the first-row transition-metal ions, Fe(III) has received much attention particularly devoted to clarifying its kinetic behavior; such investigations show that some difficulties arise in the elucidation of the corresponding reaction mechanism.[1] In fact both the free metal ion and the monohydroxy species are labile toward substitution and, in the reaction of ligands that can take part in acid–base equilibria, different reactant pairs are kinetically indistinguishable and ambiguities arise in the assignment of kinetic parameters (for example, $Fe^{3+} + L^-$ or $FeOH^{2+} + HL$).

As a continuation of previous investigations of series of ligands of the same family but with different basicity and complex stability[2-6] this paper reports the results on the equilibria and kinetics of complex formation between Fe(III) and a series of α-hydroxycarboxylic acids.

Experimental Sections

Reagents. Glycolic acid (C. Erba), DL-lactic acid (BDH), DL-malic acid (C. Erba), and benzilic acid (E. Merck) were reagent grade chemicals. Stock solutions of the acids were standardized by alkali titrations. Lactic acid was dissolved in water, and the solutions were periodically warmed on a water bath, before standardization, in order to hydrolyze the esters always present in the pure compound. Solutions of reagent grade iron perchlorate and perchloric acid were used according to the described procedure.[2,4]

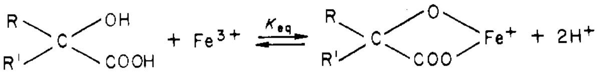
Procedure. Kinetic measurements were performed with a Durrum stopped-flow spectrophotometer. Equilibrium measurements were obtained with a Hitachi Perkin-Elmer EPS 3T spectrophotometer and with the stopped-flow machine after equilibration of the mixed solutions.

Kinetic and equilibrium measurements were performed with the ligand in excess with respect to the metal ion (at least tenfold excess) at 25 °C, $\mu = 1.0$ M ($NaClO_4$), and at $0.10 \geq [HClO_4] \geq 0.010$ M. The reactions have been monitored in the wavelength range 350–380 nm. Some equilibrium and kinetic measurements were performed in water/methanol mixtures.

The values of the first hydrolysis equilibrium constant of Fe(III), K_h, have been obtained from the data reported by Wada and Kobayashi[7] ($\mu = 1.0$, 25 °C, MeOH/H_2O 20% v/v $K_h = 3.0 \times 10^{-3}$ M, 36% v/v $K_h = 6.2 \times 10^{-3}$ M) and by Milburn[8] ($\mu = 1.0$, 25 °C, $K_h = 1.65 \times 10^{-3}$ M). The experimental data were treated with weighted least-squares methods, the uncertainties of the reported parameters are the standard deviations obtained from the scattering of the points on the computed lines.

Results

Both equilibrium[9] and kinetic studies[10,11] have been devoted to reactions of Fe(III) with α-hydroxycarboxylic acids but no unequivocal conclusion has been reached whether a chelation or simply a monodentation occurs for these reactions. In order to clarify this point the effect of substituents on the coordination ability and kinetic behavior has been investigated in the reactions


(1)

Spectrophotometric measurements were performed in order to clarify the stoichiometry, dentation, and the equilibrium constants of reaction 1. If reaction 1 is assumed, from the expression for the absorbance, A, of a solution containing both Fe(III) and the ligand in excess, it can be shown by a suitable transformation that

$$\frac{C_{Fe}}{A} = \frac{1}{\epsilon l} + \frac{1}{\epsilon l K_{eq}} \frac{[H^+]^2}{C_{H_2L}}(1 + K_h[H^+]^{-1})(1 + K_a[H^+]^{-1}) \tag{2}$$

where C_{Fe} and C_{H_2L} are the stoichiometric metal and ligand concentrations and K_h and K_a are the equilibrium constants of the reactions

$$Fe^{3+} + H_2O \rightleftarrows FeOH^{2+} + H^+ \tag{3}$$

$$H_2L \rightleftarrows HL^- + H^+ \tag{4}$$

Figure 1 shows, as an example, a typical plot for benzilic acid according to eq 2; the linearity of such plots, which has been obtained for all ligands, confirms the advanced stoichiometry and shows that two protons are displaced, one from the carboxylic and one from the α-alcoholic group upon complexation. Deprotonation of an alcoholic group has been previously found for α-hydroxycarboxylic acids.[11,12] The loss of two protons could alternatively be accounted for by assuming deprotonation of the carboxylic group and dissociation of one water molecule coordinated to Fe(III). This possibility may be considered less likely because monodentate complexes with carboxylic ligands do not hydrolyze at the presently investigated acidities.[12d,13]

A linear regression analysis gave, from l/I and I/S (l = cell path length, I = intercept, and S = slope), the values of ϵ and K_{eq} which have been collected in Table I. No relevant contribution to A was observed from the metal in the case of malic and benzilic acids, whereas for glycolic and lactic acids (due to the lower stability of the complexes) the contribution due to the absorption of Fe has been taken into account and corrected in the successive iterations of eq 2 for the computation of the equilibrium data.

The variation of the equilibrium constants K_{eq} parallels the one of K_a for each ligand (see Table I). Thus the same kind of reaction must be operative for all the acids; therefore also for malic acid the interaction with the metal center is assumed through the α-hydroxycarboxylic structure, the only interaction which forms a five-membered ring with the release of two

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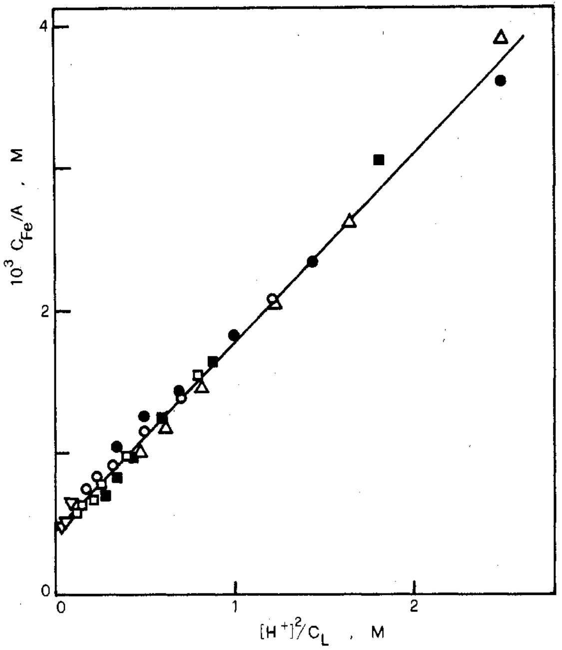

Figure 1. Equilibrium data for iron(III)-benzilic acid complex formation, reported according to eq 2, 100% water.

Table I. Summary of the Equilibrium Data for the Investigated Reactions

R	R′	ligand	pK_a[a]	10^2K_{eq}, M	ε, M^{-1} cm^{-1}
H	H	glycolic acid	3.83	2.3 ± 0.1	500 (360 nm)
H	CH_3	DL-lactic	3.86	2.6 ± 0.1	500 (360 nm)
H	CH_2COOH	DL-malic	3.46	8.7 ± 0.3	750 (350 nm)
		meth 20%		9.4 ± 0.4	
		meth 36%		10.6 ± 0.4	
C_6H_5	C_6H_5	benzilic	3.04	34 ± 1	1100 (380 nm)
		meth 20%		37 ± 1	
		meth 36%		41 ± 1	

[a] The datum for benzilic acid[13] is obtained at very low ionic strength; thus the other pK_a's are reported, for comparison purposes, also at $\mu \to 0$ ionic strength (the last term in eq 2 is always negligible for all the investigated compounds and acidities and can be set with reasonable accuracy equal to zero, i.e., $(1 + K_a[H^+]^{-1}) \simeq 1$.

protons (this behavior resembles the iron(III)-citrate reaction).[12b] The possible reaction steps are as follows:

$$Fe^{3+} + H_2L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FeL^+ + 2H^+ \quad \text{(path 1)} \tag{5}$$

$$FeOH^{2+} + H_2L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} FeL^+ + H^+ \quad \text{(path 2)} \tag{6}$$

$$Fe^{3+} + HL^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} FeL^+ + H^+ \quad \text{(path 3)} \tag{7}$$

$$FeOH^{2+} + HL^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} FeL^+ \quad \text{(path 4)} \tag{8}$$

By mixing a constant Fe(III) concentration (usually (0.5-3) × 10^{-4} M) with different ligand concentrations in excess, at each acidity, one obtains an empirical dependence of the pseudo-first-order rate constant, k_{obsd}, of the form (see also Table II)

$$k_{obsd} = k_f C_{H_2L} + k_r \tag{9}$$

where

$$k_f = k_1 + (k_2K_h + k_3K_a)[H^+]^{-1} + k_4K_hK_a[H^+]^{-2} \tag{10}$$

$$k_r = k_1[H^+]^2 + (k_{-2} + k_{-3})[H^+] + k_{-4} \tag{11}$$

Table II. Forward, k_f (M^{-1} s^{-1}), and Reverse, k_r (s^{-1}), Observed Rate Constants, Computed According to Eq 9 at 25 °C, $\mu = 1.0$ M, and at Different Acidities

		[$HClO_4$], M					
ligand		0.010	0.020	0.030	0.050	0.070	0.100
glycolic	k_f	1100	550	400	240	160	
	k_r	4.0	7.5	12	20	26	
DL-lactic	k_f	650	320	160	130	80	50
	k_r	2.0	4.0	7.0	11	16	23
DL-malic	k_f	1000	500	400	190	150	95
	k_r	1.3	2.5	4.1	6.7	8.3	11.8
meth	k_f	1030	450	360	165		
20%	k_r	1.6	3.0	5.1	7.4		
meth	k_f	1620	780	580	250		
36%	k_r	2.0	4.8	6.1	9.0		
benzilic[a]	k_f	1020	480	282	140	90	60
meth	k_r	0.25	0.5	0.8	1.1	1.55	2.05
20%	k_f	1250	600	400	270		
meth	k_r	0.28	0.65	0.95	1.5		
36%	k_f	1750	950	500	350		
	k_r	0.25	0.7	1.3	1.9		

[a] k_r in 100% water and at [$HClO_4$] = 0.100 M, 2.15 s^{-1}; 0.080, 1.85; and 0.060, 1.39; these values have been determined from direct decomposition kinetic measurements (see text): each value is the mean of 4-6 runs at constant acidity; the decomposition is strictly first order (linear ln A vs. time plots for at least 90% completion).

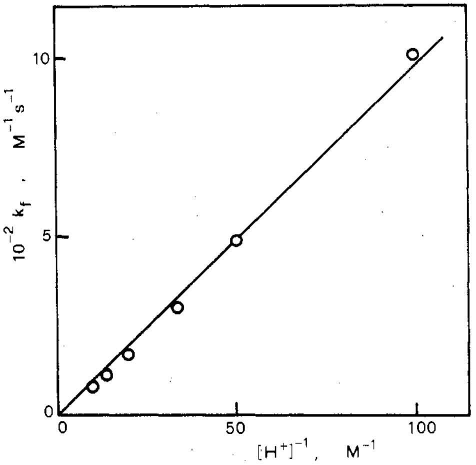

Figure 2. Inverse acidity dependence of the forward overall observed rate constant for the iron(III)-benzilic acid reaction, 100% water.

Plots of k_{obsd} against C_{H_2L} at different acidities were linear with significant intercept (k_r) and slope (k_f). Figure 2 shows the dependence of k_f vs. $[H^+]^{-1}$, for benzilic acid as an example; this behavior suggests that the active paths could be 2 + 3 and by comparison of the reactivities of $FeOH^{2+}$ and Fe^{3+} (K_a is always lower than K_h,[12d,13] and $FeOH^{2+}$ is orders of magnitude more reactive than Fe^{3+} [1,2,4]), path 3 can be ruled out and the reaction proceeds kinetically through reaction 6. If one would assume that the observed rate k_f is due mainly to reaction 3, values of (1-5) × 10^4 M^{-1} s^{-1} are obtained for k_2 which are too high with respect to the rate of water exchange on Fe^{3+} (~10^3 times). Figure 3 reports the dependence of the reverse reaction rate with $[H^+]$, for benzilic acid as an example; as can be seen the reaction is $[H^+]$ dependent and this result has been obtained also from direct measurements of k_r (open circles of the figure) by reacting a mixture of Fe(III) and excess ligand at low acidity with excess perchloric acid and by following the decomposition. The behavior, in accordance with the microscopic reversibility principle, is in agreement with the observed forward active path (compare eq 11 and 10). The kinetic measurements on both forward and reverse reactions make possible the kinetic evaluation of the equilibrium constant of reaction 6 and these values can be compared with

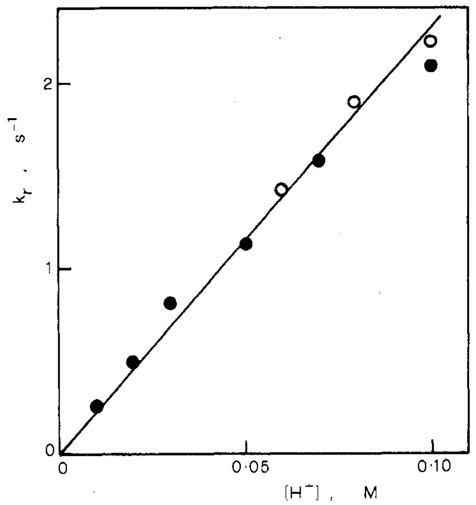

Figure 3. Direct acidity dependence of the reverse overall observed rate constant for the iron(III)–benzilic acid reaction, 100% water.

Table III. Kinetic Parameters for the Investigated Reactions

ligand	$10^{-3}k_3$, M^{-1} s^{-1}	k_{-3}, M^{-1} s^{-1}	$K_3 = k_3/k_{-3}$	$K_3 = K_{eq}/K_h$
glycolic acid	5.5 ± 0.4	380 ± 30	14.5 ± 2	13.9
DL-lactic acid	3.6 ± 0.3	220 ± 20	16.4 ± 2	15.7
DL-malic acid	6.0 ± 0.4	120 ± 16	50 ± 5	52.7
meth 20%	3.3 ± 0.3	160 ± 20	21 ± 2	31
meth 36%	2.7 ± 0.3	200 ± 20	14 ± 2	17
benzilic acid	6.1 ± 0.5	22 ± 2	277 ± 25	206
meth 20%	4.1 ± 0.4	30 ± 4	137 ± 15	123
meth 36%	3.0 ± 0.4	35 ± 4	85 ± 8	67

those obtained from equilibrium data: $K_2 = K_{eq}K_h^{-1}$ (see Table III). Additional kinetic runs have been performed in water/methanol mixtures and all the derived parameters are reported in Table III.

There has been some discussion as to whether Fe^{3+} and $FeOH^{2+}$ exhibit rate constants which are "normal" in the sense of the Eigen mechanism or whether a dependence on the basic strength of the ligand is present.[14,15] Recently it has been demonstrated without proton ambiguity[14,20] that Fe^{3+} shows rate constants which are ligand dependent in the series chloro-, dichloro-, trichloroacetic acids.[15a] On the other hand we can compare the present results for $FeOH^{2+}$ ion with previously published data (see Table IV). According to the Eigen mechanism,[25] the observed rate constant equals K_0k^*, where K_0 is an outer-sphere association constant and k^* the first-order constant for the rate at which the entering ligand exchanges water molecules in the inner-coordination sphere of the metal ion. K_0 values can be estimated to be ca. 0.2 M^{-1} for ion-molecule dipolar interactions[26] and can be computed with the Fuoss equation[27] in the case when both reactants are charged. On the assumption of d = 5 Å as the closest approach between reactants, the computed values of K_0 for charge products −2, −4, and −6 are respectively ∼2, ∼15, and ∼100 at μ = 1.0–0.1 M (it is assumed that the effect of ionic strength within this range is insignificant compared with other uncertainties in the computation, e.g., the value of d and approximations such as the assumption that the ligands are spherical entities). The closeness of the k^* values obtained for a series of ligands of quite different structure, binding sites, and basicity (see Table IV) allows one to conclude that $FeOH^{2+}$ species can be regarded as a "normal" cation.[25] In other words $Fe(H_2O)_5OH^{2+}$ behaves like other bivalent metal ions such as Co^{2+} and Ni^{2+}, whose dissociative behavior has been so clearly assessed.[1,25] For H_4EDTA and H_3EDTA^- species, as for reactions with other aminopolycarboxylic acids,[3] it is not easy to obtain a clear k^* value; in fact these ligand species, which show overall 0 and −1 charges, exist in a zwitterionic form (for example, H_4EDTA has two unprotonated carboxylate groups, a total −2 charge, and two protonated N atoms). The ligand penetration starts from the free carboxylate groups and then the true charge that the metal sees on the ligand is intermediate between −2 and 0 (extreme values on which the interval in the second column of Table IV has been computed). If, for example, H_4EDTA is thought to be seen by the metal, in the outer-sphere complex, as a −1 charged species, k^* would be ca. 1.5 × 10^4 s^{-1}.

Assuming an S_N1 IP mechanism, one can calculate, as a rough and indirect estimate, the first-order water exchange rate to be $k_{H_2O} \simeq (2\text{–}4) \times 10^4$ s^{-1}. In fact k^* and k_{H_2O} are statistically related:[15a] the exchange rate of a single water molecule is $^1/_6k_{H_2O}$, whereas the ligand penetration competes with water in the outer coordination and its chance is lowered by a factor of 8 (eight faces of the octahedral structure, where the approach of the competing ligand molecules occurs); thus $k^* = 0.75k_{H_2O}$. Then $k_{H_2O} \simeq (2\text{–}4) \times 10^4$ s^{-1} which is in good agreement with previous findings.[14,15,18] The purely dissociative behavior advanced for $FeOH^{2+}$ does not have, however, any implication on the behavior of Fe^{3+}, and, from a kinetic point of view, these species must be regarded as two independent ions even if related by a protolytic equilibrium.

The effect of methanol in the reaction rates is very small and in the direction of the lowering of the rate with increasing methanol concentration; this finding strengthens the assignment of the reactive path to the reaction of $FeOH^{2+}$ with a neutral species. In fact if the Fe^{3+} and HL^- species were active a strong increase of the specific rate constant with increasing methanol fraction would be expected.

Table IV. Specific Complex Formation Rate Constants for $FeOH^{2+}$ + Ligand Reactions, 25 °C, and Computed Water Exchange Rates from the Corresponding Outer-Sphere Complexes

ligand	$10^{-3}k_{ov}$, M^{-1} s^{-1}	$10^{-4}k^*$, s^{-1}	ligand	$10^{-3}k_{ov}$, M^{-1} s^{-1}	$10^{-4}k^*$, s^{-1}
HF[16]	3.1	2	$CH_2ClCOOH$[14,19]	8.3	4
HN_3[17]	6.1	3	$CHCl_2COOH$[15a,19]	8.3	4
HSO_4^- [18]	50	2	CCl_3COOH[15a,19]	8.3	4
CH_3COOH[19]	5.3	3	CH_2ClCOO^- [15a]	41	2
H_3PO_2[20]	21	8	$CHCl_2COO^-$ [15a]	19	1
C_6H_5OH[21]	1.5	0.8	CCl_3COO^- [15a]	7.8	1
$HSal^-$ [22]	14	0.7	salicylamide[23]	2.9	1
H_4EDTA[2]	30	0.2–15	salicylaldehyde[23]	1.4	0.7
H_3EDTA^- [2]	110	0.1–6	2-hydroxyacetophenone[23]	1.8	0.9
3-Py-OH[6]	3.1	2	2-methoxyphenol[23]	1.0	0.5
2-Py-OH[6]	6.6	3	dibutylphosphinepropionic acid[11]	1.44	0.7
2,3-Py(OH)$_2$[6]	9.2	5	substituted hydroxamic acids[24]	1–6	0.5–3
Catechol[4]	3.1	2	glycolic acid	5.5	2
L-Dopa[5]	2.5	1	DL-lactic acid	3.6	2
adrenaline[5]	2.4	1	DL-malic acid	6.0	3
Tiron[5]	2.1	1	benzilic acid	6.1	3

The first reaction step is the penetration of the carboxylic group (in agreement with the much higher affinity of Fe(III) for carboxylic than for alcoholic groups) and then the chelation step occurs: the alcoholic oxygen coordinates the metal center and this link labilizes the alcoholic proton which is subsequently released. The chelation ring closure must be fast and not rate limiting as can be concluded by comparing the present results with those for monodentate carboxylic ligands (see for example the data for $FeOH^{2+}$–acetic acids reactions in Table IV).

Registry No. Glycolic acid, 79-14-1; DL-lactic acid, 598-82-3; DL-malic acid, 617-48-1; benzilic acid, 76-93-7; Fe(III), 20074-52-6.

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Contribution from the Department of Chemistry,
Aligarh Muslim University, Aligarh-202001, India

Composition and Kinetics of the Complex Formed by the Interaction of Chromium(III) with *p*-Hydroxybenzoic Acid

SURESH CHAND TYAGI and A. AZIZ KHAN*

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The composition of the complex formed by the interaction of solutions of chromium(III) and *p*-hydroxybenzoic acid was determined by using Job's method of continuous variations in aqueous ethanolic medium. The reaction was found to be slow, and the kinetic studies were carried out under varying conditions of temperature, hydrogen ion concentration, solvent composition, and ligand concentration. The pseudo-first-order rate constants (k_{obsd}) were found to follow the equation $k_{obsd} = k_{an}K_IK_a[AH]_T/([H^+] + K_a + K_IK_a[AH]_T)$. A possible mechanism of the associative interchange (I_a) type was proposed. The activation parameters are $\Delta H^*_{an} = 105 \pm 1$ kJ mol^{-1} and $\Delta S^*_{an} = 25 \pm 3$ J K^{-1} mol^{-1} for anation and $\Delta H^\circ_{IP} = -52 \pm 8$ kJ mol^{-1} and $\Delta S^\circ_{IP} = -159 \pm 25$ J K^{-1} mol^{-1} for ion pairing.

Swaddle and King[1,2] have discussed the proton ambiguity involved in the substitution reactions of chromium(III) for the aquation of CrF^{2+} and CrN_3^{2+} complexes. Espenson[3] has reported the same type of ambiguity for the anation reactions of hexaaquochromium(III) with various weak and strong acids and concluded that kinetic studies will not differentiate between the two pathways, since they correspond to transition states of the same composition. Later Thusius[4] studied the rate of formation of monosubstituted chromium(III) complexes and supported the conclusion reached by Espenson[3] on the basis of activation parameters and the ratios of the rate constants for the anation and the water-exchange reactions. Swaddle[5] has reviewed many possibilities of proton participation in the substitution reactions of hexaaquochromium(III). In continuation of our studies on the anation reactions of chromium(III) with oxygen- and nitrogen-containing organic ligands, the work on the interaction of hexaaquochromium(III) with *p*-hydroxybenzoic acid in aqueous ethanolic medium is reported here.

Experimental Section

Stock solutions of chromium nitrate, sodium nitrate, sodium hydroxide, and nitric acid were prepared from AR grade reagents. *p*-Hydroxybenzoic acid (Riedel-De Haenag, Seelze-Hannover) was used as such. Absolute ethanol was prepared as described by Vogel.[6] Chromium nitrate solution was standardized by the ion-exchange method.[7] All the solutions were prepared in aqueous ethanol (mole fractions of ethanol = 0.09, 0.23, and 0.48).

The composition of the complex formed by the interaction of chromium(III) and *p*-hydroxybenzoic acid was determined by Job's method of continuous variations. The optical density measurements were made at 580 nm with a Bausch and Lomb Spectronic-20. The pH measurements were made with a Titrierautomat, Type AT-2, by a suitable correction for solvent composition.[8]

The kinetic measurements for the reaction of *p*-hydroxybenzoic acid with chromium(III) were carried out by mixing the solutions in a two-necked flask fitted with a double-walled condenser. The reaction flask was kept in a thermostat-controlled bath at the desired temperature within ±0.1 °C. The final concentration of chromium nitrate in the reaction vessel was 4.0×10^{-3} M and that of *p*-hydroxybenzoic acid was varied from 0.04 to 0.16 M. Nitrogen gas was bubbled through the reaction mixture for stirring and in order to maintain an inert atmosphere. The ionic strength of the reaction mixture was adjusted with sodium nitrate solution. The progress of reaction was followed spectrophotometrically at 580 nm. The pseudo-first-order rate constants (k_{obsd}) and other parameters were calculated by using an IBM 1130 computer.

Results and Discussion

It was found by Job's method of continuous variations that 1 mol of *p*-hydroxybenzoic acid reacts with 1 mol of chromium(III). The composition of the complex was not affected

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