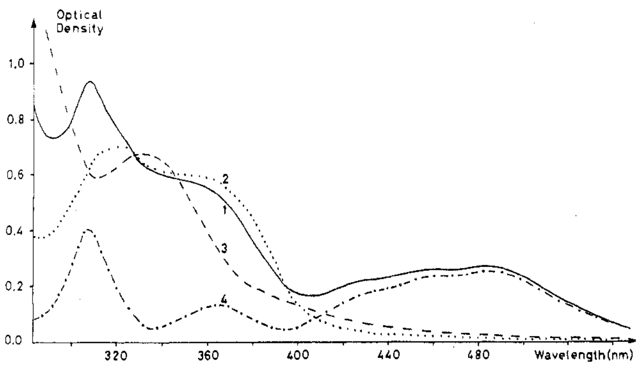

Figure 5. Spectra of (2) 1.5×10^{-4} M PH, (3) 1.5×10^{-4} M Q^-, (1) an equimolar mixture of diphenol and quinone each having a total concentration of 1.5×10^{-4} M, and (4) semiquinone alone at concentration 1.7×10^{-4} M. In each case pH was 11.79. For the determination of spectrum 4, see the text.

Figure 4 indeed shows a linear relationship over the working pH range. Therefore $K^{H}_{SQ} \ll 10^{10}$. From Figure 4 the value of K_{SQ} can be evaluated and was found to be $10^{3.2}$. Although traces of SQ were observed by ESR in the neutral pH range, the polarographic results have shown that relatively large quantities of semiquinone form only in the interval $10.8 < \text{pH} < 12.4$. Figure 5 shows the spectra of PH (curve 2) and Q^- (curve 3) at pH 11.79 as well as spectra of equimolar concentrations of PH and Q^- (curve 1) at the same pH. From the total concentrations of diphenol and of quinone which were initially added (1.5×10^{-4} M) and by using the value of K_{SQ} given above and eq 11, it is possible to calculate $[P]_T$, $[Q]_T$ and $[SQ]_T$ in the mixture. By correcting the spectrum 1 (Figure 5) to eliminate the contribution of PH and Q^-, one obtains spectrum 4 for SQ.

Conclusions

The above results seem to indicate that, from the point of view of redox properties, the PH_2/Q system is well suited for the study of the catalytic oxidation of aromatic *o*-dihydroxy compounds by dioxygen in aqueous solutions. Indeed, its normal potential is sufficiently low so that a catalytic effect of Fe(III) may arise during oxidation and that the reaction rate is sufficiently high at neutral or acidic pH value, for making measurements. This latter experimental condition allows the elimination of secondary reactions such as hydrolysis of Fe(III) or radical reactions which arise during oxidation in alkaline medium. Particularly, from the fact that the decomposition process of Q is negligible below pH 11.5 and that the formation of semiquinone is not appreciable below pH 10.8, it may be concluded that no uncatalyzed secondary reaction will take place if oxidation is performed below pH 10.

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Registry No. PH_2, 16223-99-7; Q, 2066-93-5.

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Metal Ion Catalyzed Oxidation of *o*-Dihydroxy Aromatic Compounds by Oxygen. 2. Complexes of 1,2-Dihydroxynaphthalene-4-sulfonate with Iron(III) and Iron(II)

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The interactions of Fe(II) and Fe(III) with 1,2-dihydroxynaphthalene-4-sulfonic acid (PH_2) are studied with a specially designed cell at 25.0 °C and $\mu = 0.100$ ionic strength. At pH <2 the ferric ion was found to spontaneously oxidize PH_2 to the quinone (Q). With Fe(II) ion, the complex species of importance were identified as FeP and FeP_2, and no protonated or hydrolyzed species were found to be present. With Fe(III) ion, the important complexes formed were found to be FeP, FeP_2, FeP_2H, and a "$FeP_2(OH)$" species. The hydrolyzed species is probably polynuclear. The thermodynamic stability constants for the equilibrium interconversion of these species are reported.

Introduction

Recent studies on the oxidation of ascorbic acid[1] and *o*-dihydroxy aromatic compounds[2,3] by oxygen in the presence of a metal catalyst have demonstrated complex formation between the metal ion and these organic substrates. Before attempting the study of the catalytic oxidation of 1,2-naphthalenediol-4-sulfonate (PH_2) in the presence of Fe(III) it was found necessary to quantitatively determine the

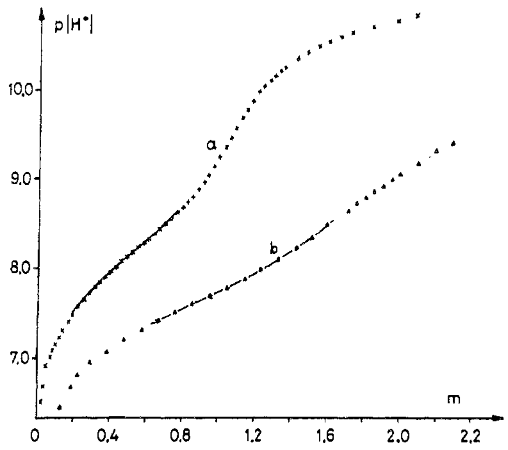

Figure 1. Potentiometric equilibrium curves for (a) PH_2 alone (6.08×10^{-4} M) and (b) Fe^{II}–PH_2 (1:2) solution (7.0×10^{-4} M Fe(II)): ▲ and ×, experimental points; —, adjusted curves using constants cited in the text. m is moles of base added per mole of PH_2 present.

equilibria which would be established between Fe(III), Fe(II), and the system PH_2/Q (Q is the corresponding quinone). Indeed no literature information is available regarding these equilibria.

Experimental Section

The essential experimental condition for the study of complex formation of PH_2 with Fe(II) or Fe(III) is the complete exclusion of oxygen. Fe(III) actively catalyzes the oxidation of PH_2 by oxygen[4] and also Fe(II) itself is oxidized very readily in the medium employed. This study of the complex formation between Fe(II) or Fe(III) with 1,2-dihydroxynaphthalene-4-sulfonic acid and its quinone over a wide pH range was carried out through the use of the apparatus and experimental conditions described earlier.[5]

Results

Complexation of Fe(II) with PH_2. The potentiometric equilibrium curve for a mixture of PH_2–Fe^{II} (2:1) is shown in Figure 1. If it assumed that complexes FePH, FeP_2H, FeP, and FeP_2 are formed, the complex formation constants are given by

$$\beta^{II}_{1H} = \frac{[FePH]}{[Fe^{2+}][P][H^+]}$$

$$\beta^{II}_{2H} = \frac{[FeP_2H]}{[Fe^{2+}][P]^2[H^+]}$$

$$\beta^{II}_{1} = \frac{[FeP]}{[Fe^{2+}][P]}$$

$$\beta^{II}_{2} = \frac{[FeP_2]}{[Fe^{2+}][P]^2}$$

Charges of complexes are omitted.

Through the use of charge and mass balance equations, and the acid dissociation constants of the ligand,[5] values of [P] and $[Fe^{2+}]$ were computed for various values of pH. The formation constants were then calculated by the equation

$$[H^+] - C_A + C_B = [OH^-] + [P](2 + K^H_1[H^+]) + [Fe^{2+}][P][(\beta^{II}_{1H}[H^+] + 2\beta^{II}_1) + (3\beta^{II}_{2H}[H^+] + 4\beta^{II}_2)[P]] = F(\beta^{II}_{1H}, \beta^{II}_{2H}, \beta^{II}_1, \beta^{II}_2)$$

where C_A is the excess of acid initially present and C_B is the concentration of base added. The constants β^{II}_{1H}, β^{II}_1, β^{II}_{2H}, and β^{II}_2 were evaluated by least-squares calculations utilizing the MALIK computer program described previously.[5] The values of the constants thus calculated were found to be log $\beta^{II}_1 = 8.99 \pm 0.05$ and log $\beta^{II}_2 = 16.49 \pm 0.09$. This method also indicated that insufficient concentrations of the protonated species were present to allow calculation of the constants β^{II}_{1H} and β^{II}_{2H}. Furthermore this result was confirmed by the UV–visible spectra measured during the course of the potentiometric experiments (Figure 2). A comparison of these spectra with those obtained for PH_2, PH, and P (ref 5) along with the well-defined isosbestic points of Figure 2 indicates that only unprotonated complexes of Fe(II) with PH_2 (i.e., FeP and FeP_2) are formed. The theoretical curve indicated by a solid line in Figure 1 (b) was calculated by using the values of constants determined previously and shows good agreement with the experimentally observed values.

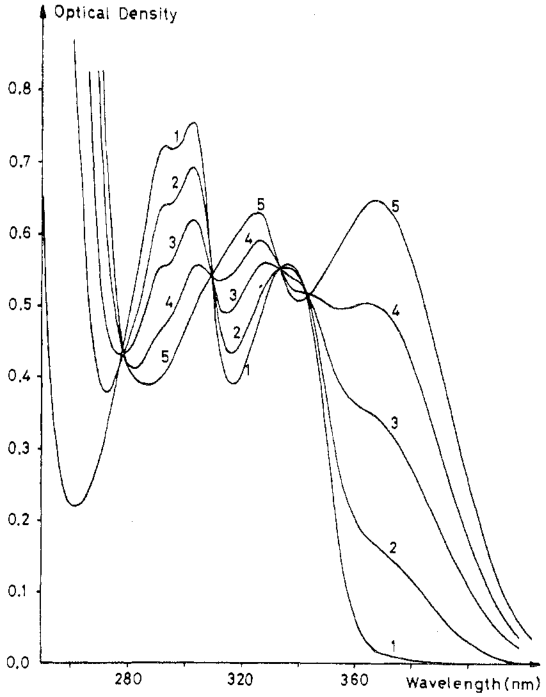

Figure 2. UV spectra of Fe^{II}–PH_2 (1:2) solutions (7.0×10^{-4} M Fe(II)). p[H^+] values: 1, 4.94; 2, 7.06; 3, 7.51; 4, 7.88; 5, 8.34. Cell path length = 0.100 cm.

Reactions of Fe(III) and PH_2 in Acidic Media. Spectrophotometric measurements show that, when Fe(III) and PH_2 are mixed in acidic medium (pH <2), an instantaneous stoichiometric oxidation reaction (eq 1) of PH_2 is observed.

$$Fe(III) + {}^1/_2PH_2 \rightarrow {}^1/_2Q + Fe(II) + H^+ \qquad (1)$$

An isosbestic point appears at 348 nm when the Fe(III):PH_2 ratio is increased from 0 to 2.

Complexation Reaction of Fe(III) with PH_2. The acidimetric titration curves of PH_2 in the presence of Fe(III), for different values of total concentration of naphthalenediol and Fe(III) are shown in Figure 3. In all these cases with increase in pH the following changes are observed. A buffer region between pH 3 and 4 corresponding to the H^+ liberated by reaction 1 indicates neutralization of 1 equiv of H^+ with respect to Fe(III). The UV and visible spectra obtained during the course of the potentiometric determination also show the presence of quinone up to the pH inflection (Figures 4 and 5).

Although the solution is yellow (due to the presence of Q) up to the first inflection, it turns green toward the end of the inflection, and at higher pH values (4.5 < pH < 7), it turns rapidly intensely blue. Moreover the UV spectra (Figure 4) show that in this pH range quinone is reduced back to the naphthol. The intense coloration and the values of redox potentials of the two couples[5] suggest that a charge-transfer

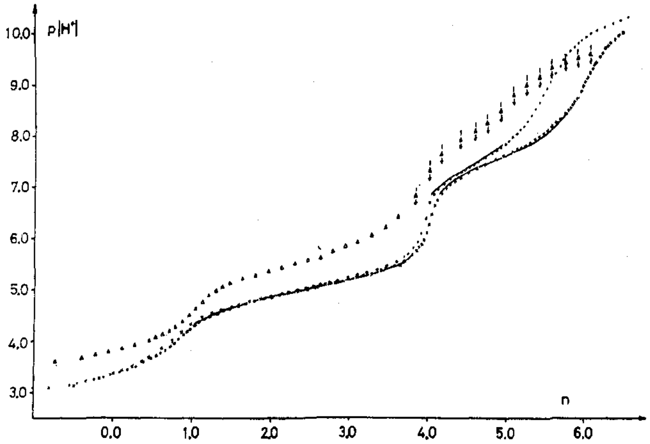

Figure 3. Potentiometric titration curves for Fe^{III}–PH_2 solutions. $[P]_T/[Fe]_T$ values: ×, 3/1; ●, 2.57/1; ▲, 2/1. $[Fe]_T$: ×, 4.87×10^{-4} M; ●, 5.18×10^{-4} M; ▲, 1.44×10^{-4} M. ×, ●, and ▲ are experimental points; the curves are adjusted using constants cited in the text; ↓ indicates that the equilibrium is attained very slowly (pH decreases); × and ● points are from back-titration; ▲ points are from direct titration. n is moles of base added per mole of Fe(III) present.

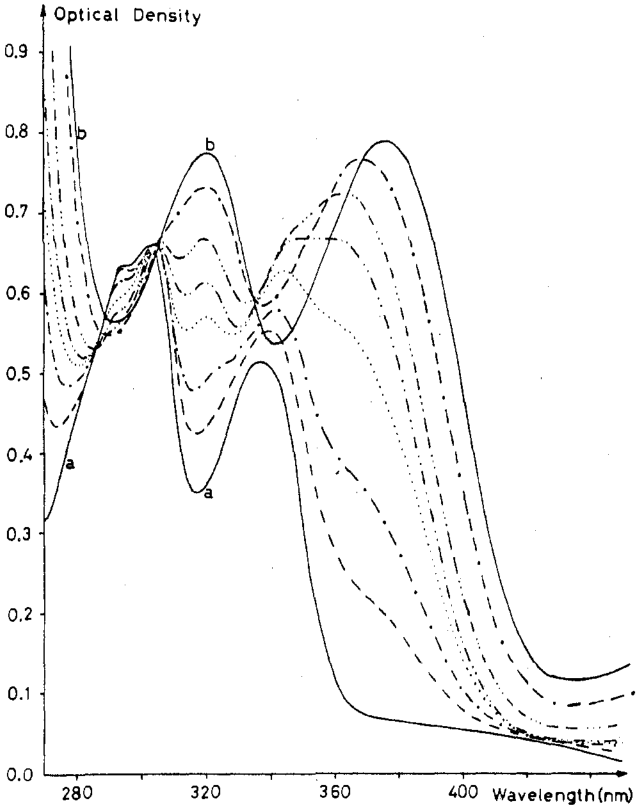

Figure 4. UV spectra for Fe^{III}–PH_2 (1:3) solutions (4.87×10^{-4} M Fe(III)). p[H^+] values: curve b, 8.91; —·—·—·, 7.84; ···—···—, 7.30; —··—··, 6.10; ·······, 5.40; —·—, 5.03; ----, 4.79; curve a, 2.94.

complex forms between Fe(III) and naphthol. The formation of this complex with PH_2 is confirmed by the observed shift in the UV absorption band toward longer wavelengths. This bathochromic shift indicates deprotonation, as can be seen by comparing Figure 4 with UV spectra of P, PH, and PH_2.

The second inflection in the potentiometric equilibrium curves (Figure 3) is observed around pH 6–7 and corresponds to 4 equiv of H^+. Since the ratio $[P]_T/[Fe]_T$ does not affect the position of the inflection, a large difference between the stabilities of complexes with two and three ligands is indicated.

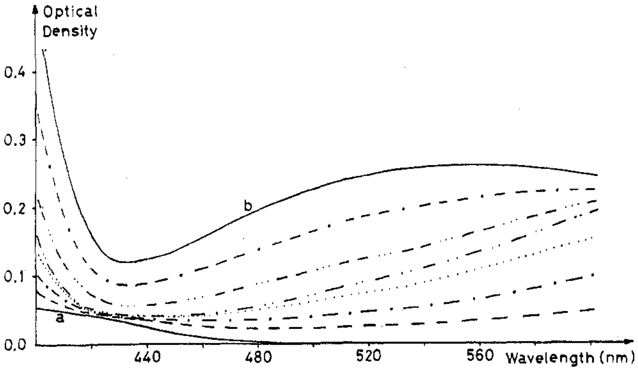

Figure 5. Visible spectra of Fe^{III}–PH_2 (1:3) solution. The conditions are the same as in Figure 4.

When the potentiometric titration was carried out in the normal manner using NaOH, the pH stabilized only very slowly (several hours) after the second inflection point. When, however, the initial acidic solution was treated with excess NaOH (pH ≃11) and then back-titrated with $HClO_4$, a plateau at pH 7–8 was observed and the color of the solution remained violet in this pH range indicating a change in the structure of the complex. The pH values in the buffer region were too low to account for a simple neutralization reaction of unreacted PH_2 present in solution. In addition, the number of equivalents of H^+ (2 equiv for $[P]_T/[Fe]_T = 3$, and 1.6 equiv for $[P]_T/[Fe]_T = 2.57$) corresponding to this buffer region is too large to be attributed only to the neutralization of the excess of PH_2 remaining after the formation FeP_2. Although the formation of FeP_3 might be taken into account for the potentiometric titration with $[P]_T/[Fe]_T = 3$, its formation is not compatible with the potentiometric equilibrium curves obtained for the ratios $[P]_T/[Fe]_T = 2.57$ and $[P]_T/[Fe]_T = 2.0$. Indeed, the number of equivalents of hydrogen ions neutralized in these two cases should be 1.2 and 0, respectively, whereas experimentally one finds 1.6 and 1. These considerations, as well as the fact that the stabilization of pH is very slow during the reaction with NaOH, suggest that hydrolysis of FeP_2 may take place in this pH range.

Interpretation of the Second Buffer Region. Since the number of equivalents of H^+ ions at the second buffer region is in accord with the formation of the complex FeP_2OH, the existence of complex species FeP_2, FeP_2OH, FeP_3, FeP_3H, and FeP_3H_2 was assumed in the case of $[P]_T/[Fe]_T = 3$. The corresponding formation constants are

$$K^{OH}{}_{2,Fe} = [FeP_2OH]/[FeP_2][OH]$$

$$K_{3,Fe} = [FeP_3/[FeP_2][P]$$

$$K^{H}{}_{3,Fe} = [FeP_3H]/[FeP_2][P][H^+]$$

$$K^{2H}{}_{3,Fe} = [FeP_3H_2]/[FeP_2][P][H^+]^2$$

The calculation of these equilibrium constants was carried out with the equation

$$F(H) = [H^+] - [OH] - C_A + C_B' = -[P](2\beta^{H}{}_2[H^+]^2 + \beta^{H}{}_1[H^+]) + [FeP_2]\{K^{OH}{}_{2,Fe}[OH] - 2K^{2H}{}_{3,Fe}[P][H^+]^2 - K^{H}{}_{3,Fe}[P][H^+]\}$$

where C_B' is the excess of base present after the neutralization of excess acid initially present and of 2 equiv of pH_2. This equation was then solved by least-squares using values of [P] and $[FeP_2]$ obtained from charge and mass balance equations. Thus, the constants $K^{OH}{}_{2,Fe}$, $K_{3,Fe}$, and $K^{2H}{}_{3,Fe}$ can be evaluated. When this method is applied to titrations corresponding to $[P]_T/[Fe]_T = 3$, a value of log $K^{OH}{}_{2,Fe} = 6.4 \pm 0.5$ was obtained for the first parameter and showed the influence of the other parameters to be negligible in comparison. The same qualitative results were obtained when the calculation was performed on data corresponding to $[P]_T/[Fe]_T = 2.57$. Thus the formation of 1:3 complexes can be neglected even when the ratio $[P]_T/[Fe]_T = 3$. However, the formation of the complex FeP_2OH alone does not totally explain the second buffer region, as was shown by a graphical analysis of the experimental values carried out while considering only the species FeP_2 and FeP_2OH. This calculation showed that the value of $K^{OH}{}_{2,Fe}$ in the entire buffer region is not rigorously constant. This observation is in accordance with the least-squares result discussed above which indicated poor precision for the value of the constant. On the other hand, the pH in the buffer region was found to decrease with increase in $[Fe]_T$. This observation together with the fact that the equilibrium values of pH are attained slowly seems to show that a more complex hydrolysis than that of FeP_2OH takes place and that polynuclear complexes might be formed. However, the analysis of the data constituting the second buffer region by taking into account the species FeP_2, FeP_2OH, $(FeP_2)_2OH$, and $(FeP_2)_2(OH)_2$ did not yield satisfactory results.

Analysis of the First Buffer Region. We assumed the existence of the complexes FePH, FeP, FeP_2, FeP_2H, and FeP_2H_2, for which the equilibrium constants are

$$K_{1,Fe} = [FeP]/[Fe^{3+}][P]$$

$$K^{H}{}_{1,Fe} = [FePH]/[FeP][H^+]$$

$$K_{2,Fe} = [FeP_2]/[FeP][P]$$

$$K^{H}{}_{2,Fe} = [FeP_2H]/[FeP][P][H^+]$$

$$K^{2H}{}_{2,Fe} = [FeP_2H_2]/[FeP][P][H^+]^2$$

Since no inflection was observed in the potentiometric curve after the addition of 2 equiv of H^+, it was not possible to separately calculate the 1:1 and 2:1 complex formation constants. Hence, these constants were determined by using the entire buffer region for the calculation. On the other hand, the evaluation of $K_{1,Fe}$ and $K^{H}{}_{1,Fe}$ is complicated by the fact that no convenient pH range is available for studying the equilibrium

$$FeP \rightleftharpoons Fe^{3+} + P$$

Indeed the observed changes in color of the solutions (uv spectra, Figure 4), and previous observations made above, indicate that the following reaction takes place in the low-pH region

$$2Fe^{3+} + PH_2 \rightleftharpoons 2Fe^{2+} + Q + 2H^+$$

Since the systems PH_2/Q and Fe^{2+}/Fe^{3+} are reversible, the following equation can be obtained using the Nernst equation

$$K(E) = \frac{[Fe^{3+}]^2}{[Fe^{2+}]^2}\frac{[P]}{[Q]} = \exp\left[\frac{2E}{RT}(E_Q{}^{\circ} - E_{Fe}{}^{\circ})\right]$$

Substituting the values of $E_Q{}^{\circ} = 20.8$ mV[5] and $E_{Fe}{}^{\circ} = 749$ mV[6] into this equation, we obtained a value of $K(E) = 2.1 \times 10^{-25}$ for the equilibrium constant.

The hydrolysis of Fe^{3+} in this pH range was taken into account by assuming $FeOH^{2+}$ and $Fe(OH)_2{}^+$ to be present. The formation of binuclear hydroxo complexes is expected to be small even in the absence of other complexing agents because of the low concentration of Fe(III) used. The values of the metal hydrolysis constants used are[6]

$$\beta^{OH}{}_{1,Fe} = [FeOH]/[Fe^{3+}][OH] = 1.48 \times 10^{11}$$

$$\beta^{OH}{}_{2,Fe} = [Fe(OH)_2]/[Fe^{3+}][OH]^2 = 1.55 \times 10^{20}$$

The formation constants were calculated from the equation

$$F(H) = [OH] + 2[Q] + [P]\alpha_P + K_{1,Fe}[Fe^{3+}][P]\alpha^{P}{}_{Fe} + [Fe^{3+}]\alpha^{OH}{}_{Fe} = [H^+] - C_a + C_{in}$$

where

$$\alpha_P = 2 + \beta^{H}{}_1[H^+]$$

$$\alpha^{P}{}_{Fe} = (2 + K^{H}{}_{1,Fe}[H^+]) + [P](2K^{2H}{}_{2,Fe}[H^+]^2 + 3K^{H}{}_{2,Fe}[H^+] + 4K_{2,Fe})$$

$$\alpha^{OH}{}_{Fe} = \beta^{OH}{}_{1,Fe}[OH] + 2\beta^{OH}{}_{2,Fe}[OH]^2$$

C_a is the amount of acid added during the titration and C_{in} is the initial concentration of base added in excess at the initial point. As before, [P] was calculated with mass and charge balance equations, and values of $K_{1,Fe}$, $K^{H}{}_{1,Fe}$, $K_{2,Fe}$, $K^{H}{}_{2,Fe}$, and $K^{2H}{}_{2,Fe}$ were determined by a least-squares computer calculation using the MALIK program.

The results of these calculations show that the formation of FeP_2H_2 and FePH can be neglected. Examination of the spectra of Figures 4 and 5 indicates that the formation of FeP_2H is probably not important. Indeed isosbestic points are obtained in the pH region 4–6 and only the bands characteristic of PH_2 and P appear in this region. On the other hand, the computer calculation indicates that the formation of FeP_2H cannot be totally neglected. However its overall contribution does not seem to be very important, and the precision of the value given for its formation constant is rather poor, as would be expected for a minor species. The final values of the parameters obtained in this way are $\log K_{1,Fe} = 19.84 \pm 0.08$, $\log K_{2,Fe} = 15.11 \pm 0.08$, and $\log K^{H}{}_{2,Fe} = 19.3 \pm 0.4$. Their order of magnitude seems to be in accordance with the stability constants of Fe(III) complexes with compounds similar to PH_2 such as Tiron, 2,3-dihydroxynaphthalene-6-sulfonic acid, and 3,4-dihydroxybenzenesulfonic acid.[6]

Discussion

Although the results given above for the pH range 7–9 do not completely exclude the possibility of a reaction such as

$$Fe^{III}P_2 + PH_2 \rightleftharpoons Fe^{II}P_2 + SQ + 2H^+ \qquad (2)$$

the equilibrium constant of such a reaction must be very small indeed. This reaction taken by itself would not explain the number of equivalents of H^+ observed in the second buffer region of the various titration curves, in particular for the ratio $[P]_T/[Fe]_T = 2$. Solutions of $Fe^{II}P_2$ are colorless between pH 7 and 10, whereas intense violet coloration is observed at this pH range for Fe^{III}–PH_2 solutions. The UV spectra of Fe^{II}–PH_2 and Fe^{III}–PH_2 solutions are very similar when the pH lies between 9 and 11 and the narrow band of semiquinone is not observed in both cases. Therefore it is unlikely that semiquinone is present in appreciable concentration under these conditions. However, it cannot be unambiguously concluded that SQ is totally absent because of the overlapping of SQ and PH_2 bands in the UV spectrum.

It should be pointed out that some authors[7-9] have postulated the formation of 1:3 complexes of Fe(III) with *o*-dihydroxyaromatic compounds such as Tiron, 3,4-dihydroxybenzenesulfonic acid, and 2,3-dihydroxynaphthalene-6-sulfonic acid. Murakami et al.[8] also reported a slow stabilization of pH in the region corresponding to 4–6 equiv of H^+ and attributed it to the slow formation of the 1:3 complex. However, in the case where the ratio of ligand to total iron is less than or equal to 3:1, it is also possible to explain their observations as being a result of the formation of hydrolyzed species of Fe(III) complexes. In the concentration range 10^{-4}–10^{-3} M and in the absence of excess ligand, it is therefore not possible to say with certainty the type of complex formed in the region corresponding to 4–6 equiv of H^+. Because of the overlapping of absorption bands of several other species (PH_2, PH, FeP_2, hydrolyzed species) in the range of interest (335–365 nm), it is unfortunately not possible to decide with certainty from the observation of the UV spectra whether 1:3 complexes form at all.

The fact that 1,2-dihydroxynaphthalene-4-sulfonic acid does not form 1:3 complexes below pH 7 seems to be a favorable factor for subsequent studies on catalytic properties of the complex $Fe^{III}P_2$ in the oxidation of certain organic compounds by oxygen. Two of the coordination sites on Fe(III) are available for reaction with oxygen as shown in the scheme proposed by Tyson and Martell[3] for certain diphenolic complexes of Mn(II) and for the Fe(III)- and Cu(II)-catalyzed oxidation of ascorbic acid. Such a complex might then act as an intermediate for electron transfer to oxygen. This conclusion seems to be confirmed by some results already obtained in the preliminary studies in this field.[5]

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Registry No. PH_2, 16223-99-7; Fe(II), 15438-31-0; Fe(III), 20074-52-6.

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Addition Compounds of Alkali Metal Hydrides. 13. Reactions of Alkali Metal Hydrides with Trialkylboranes. Synthesis and Dissociation of Alkali Metal Trialkylborohydrides. Ethyl Ether–Organoborane as a Reversible "Solvent" for Lithium Hydride[1]

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Lithium hydride reacts with trimethyl- and triethylborane in ethereal solvents to give the corresponding lithium trialkylborohydrides as monoetherates. Removal of the solvent from the monoetherate adduct is possible leaving behind the solvent-free alkali metal trialkylborohydrides. These can be reversibly decomposed by heating to yield "activated" lithium hydride and trialkylborane. Sodium hydride reacts with trialkylboranes in the absence of solvents yielding sodium trialkylborohydrides. The corresponding reactions with commericial lithium hydride do not proceed. However, the "activated" lithium hydride does react with trialkylboranes in the absence of solvents to form unsolvated lithium trialkylborohydrides. Thus, a mixture of trialkylborane and ethyl ether can be considered to be a reversible "solvent" for lithium hydride, permitting its solution and recovery in active form.

Introduction

Addition compounds of alkali metal hydrides with trialkylboranes were first discovered during the course of war research (1942–1943).[3] Except for their brief observation, very little attention was devoted to exploring the chemistry of these derivatives in preference to matters which were more important at the time. This study revealed that lithium hydride in ether reacts with trimethylborane to form a solid etherate of lithium trimethylborohydride which reversibly decomposes at elevated temperature to give back the ether, lithium hydride, and trimethylborane. It was also noted that lithium hydride in the absence of ether would not react with trimethylborane. However, triethylborane reacted vigorously with sodium hydride in the absence of solvents to form an acid–base adduct, unsolvated sodium triethylborohydride ($NaEt_3BH$). The synthesis and properties of alkali metal triphenylborohydrides were briefly explored in ethereal solvents.[4] More recently, reaction of alkali metal hydrides with trialkylboranes has been examined in considerable detail.[5] Unfortunately, the majority of these reactions have been carried out under drastic reaction conditions, resulting in rather poor yields of the trialkylborohydrides. Thus a lack of systematic and organized research on these derivatives was evident. Consequently, we undertook a systematic study of the reaction under mild standardized conditions of alkali metal hydrides with trialkylboranes. The results of this investigation are reported in the present paper.

Results and Discussion

Trimethyl- and triethylborane were selected as representative trialkylboranes. Their reactivity toward lithium hydride and sodium hydride in the absence and presence of various ethereal solvents was investigated. The majority of these reactions were carried out in vacuum lines, and the course of the reaction was monitored by vapor pressure–composition measurements.

Table I. Pressure–Composition Data for the Lithium Hydride–Trimethylborane–Ethyl Ether System at 0 °C[a]

Me_3B added,[b] mmol	Mole ratio Me_3B/LiH	Total pressure, mm
0	0	186
0.454	0.288	185
0.728	0.461	182
1.36	0.857	177
1.56	0.982	173
2.38	1.51	228
2.99	1.89	261
3.48	2.20	301

[a] Initial amounts of lithium hydride and ethyl ether were 1.58 and 10.3 mmol, respectively. [b] The numbers indicate the cumulative amount added.

Vapor Pressure–Composition Studies. Lithium Hydride–Trimethylborane–Ethyl Ether System. Lithium hydride reacts with trimethylborane in the presence of ethyl ether at 0 °C to form the 1:1 complex lithium trimethylborohydride (eq 1).

$$\mathrm{LiH} + \mathrm{Me_3B} \xrightarrow[0\,^{\circ}\mathrm{C}]{\mathrm{Et_2O}} \mathrm{LiMe_3BH} \tag{1}$$

The addition of incremental amounts of trimethylborane to a mixture of lithium hydride and ethyl ether results in a gradual but slow decrease in the total pressure of the system