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[CONTRIBUTION OF CENTRAL EXPERIMENT STATION, BUREAU OF MINES, BRUCETON, PA.]

On the Formation, Structure and Properties of an Iron Carbonyl–Acetylene Complex Prepared by Reppe and Vetter[1,2]

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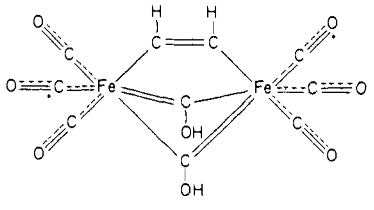
Evidence is presented that the complex $Fe_2C_{10}H_4O_8$ isolated by Reppe and Vetter possesses a binuclear bridged structure. The complex contains two acidic hydrogens which can be benzoylated and methylated. An improved method for the preparation of $Fe_2C_{10}H_4O_8$ using acetylene at atmospheric pressure is described.

The recent discovery[3] of an organometallic compound derived from acetylene and dicobalt octacarbonyl led us to speculate on the existence of a similar compound containing iron. Examination of the literature revealed that a crystalline substance having the empirical formula $Fe_2C_{10}H_4O_8$ had been obtained by Reppe and Vetter[1] from the reaction of acetylene at 20 atmospheres and 50° with an alkaline solution of iron hydrocarbonyl. These workers recognized that this complex behaved like an acid but offered no suggestion as to a possible structure.

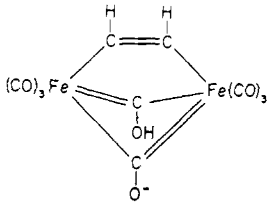
Structure of $Fe_2C_{10}H_4O_4$.—The method of preparation, elementary composition and molecular weight of $Fe_2C_{10}H_4O_8$ as reported by Reppe and Vetter[1] suggests that this iron complex is composed of the elements of $HFe(CO)_4$ and C_2H_2. Evidence obtained in the present work led to the assignment of the bridged structure I for this complex.[4] This assignment is based on the following observations:



I

The iron complex contains two acidic hydrogen atoms, as shown by two breaks in a potentiometric titration curve.

The infrared spectrum of a solution of $Fe_2C_{10}H_4O_8$ in carbon disulfide (Fig. 1) shows one strong and one somewhat weaker band in the –OH region at 3565 and 3463 cm.$^{-1}$ and three bands in the –C–O single bond region at 1271, 1174, and 1093 cm.$^{-1}$. The three sharp bands at 1998, 2033 and 2973 cm.$^{-1}$ are similar to those which appear in the spectrum of the cobalt acetylene complex[3] and in that of dicobalt octacarbonyl[5] where these bands have been attributed to C≡O stretching vibrations in the six terminal carbonyl groups. The hydroxyl groups in I are attached to carbon atoms which are part of a conjugated system and are comparable to enolic hydroxyl groups. This system is analogous to cyclobutadiene and is part of a resonating structure containing two $Fe(CO)_3$ groups. Since the ion II is highly stabilized by resonance, the pK_{1a} of the acid I might be expected to be comparable to that of a phenol whose



II

anion is highly resonance-stabilized. This is indeed the case. The pK_{1a} of $Fe_2C_{10}H_4O_8$, as determined from the pH at the half-neutralization point, is 6.30 (compare with p-nitrophenol, pK_a 7.16). The second hydrogen in $Fe_2C_{10}H_4O_8$ (pK_{2a} 9.14) is comparable to that in phenol (pK_a 9.89). Further evidence for the presence of enolic type hydroxyl groups is the shift to longer wave lengths and increase in intensity of the ultraviolet spectrum when excess alkali is added to an aqueous solution of I. This change is similar to that accompanying the phenol → phenolate ion transformation.

Although several metal carbonyls containing hydrogen such as cobalt and iron hydrocarbonyl have been synthesized and studied, the position of the hydrogen in these compounds has not been established.[5–7] The above data indicate that in the present complex the hydrogen is attached to oxygen. To obtain direct chemical evidence for the presence of hydroxyl groups, the complex $Fe_2C_{10}H_4O_8$ was treated with benzoyl chloride in pyridine. Dilution of the reaction mixture with water gave the dibenzoate of $Fe_2C_{10}H_4O_8$ in theoretical yield. The dimethyl ether of $Fe_2C_{10}H_4O_8$ was also obtained by treating an aqueous alkaline solution of the complex with dimethyl sulfate.

In a strong amine such as butylamine, the iron complex will probably be completely dissociated so that the spectrum will be that of the doubly

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[1] W. Reppe and H. Vetter, *Ann. Chem. Justus Liebig*, **582**, 133 (1953).

[2] For a preliminary communication, see I. Wender, R. A. Friedel, R. Markby and H. W. Sternberg, THIS JOURNAL, **77**, 4946 (1955).

[3] H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, R. Markby and I. Wender, *ibid.*, **76**, 1457 (1954).

[4] In structure I the terminal carbonyl groups are written as $M \cdots C \equiv O$ to indicate the fractional bond order as a result of resonance between the two forms $M{=}C{=}\ddot{O}$: and $M \leftarrow C{\equiv}O$:; see reference 5.

[5] R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, THIS JOURNAL, **77**, 3951 (1955).

[6] R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **35**, 681 (1939).

[7] W. F. Edgell and G. Gallup, THIS JOURNAL, **77**, 5762 (1955).

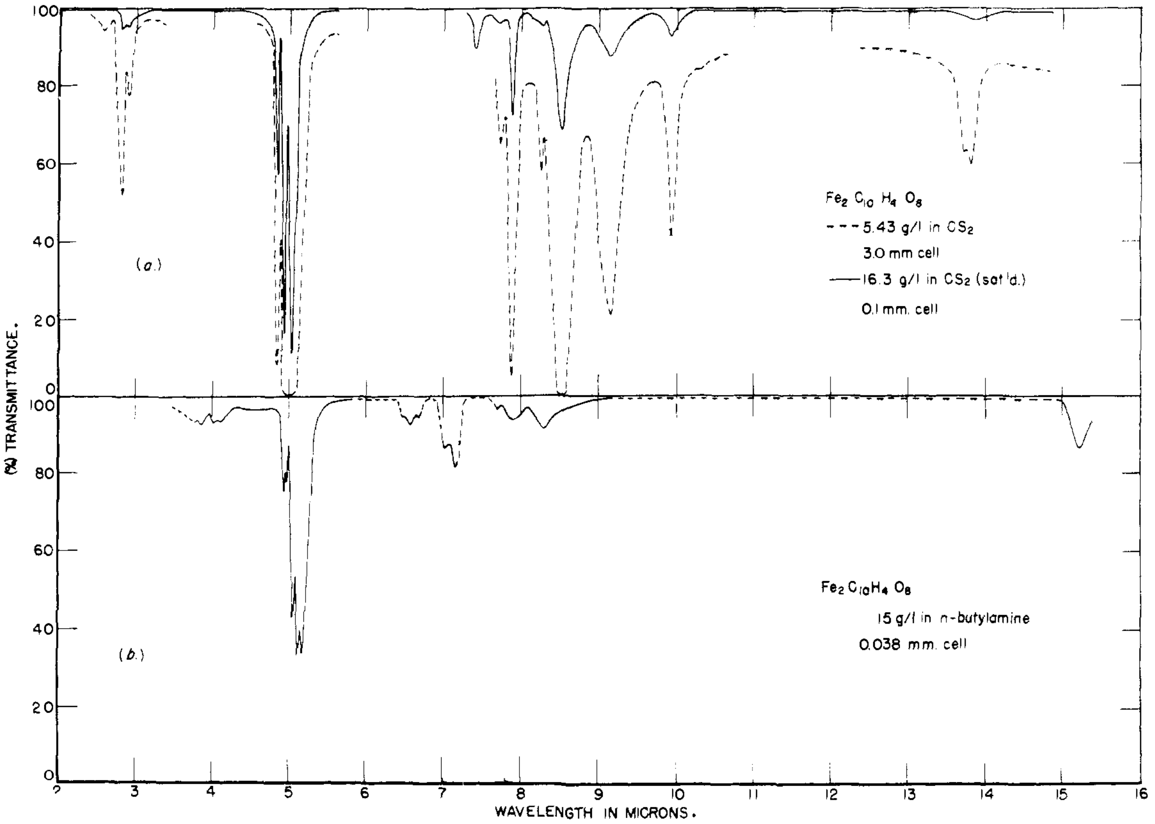
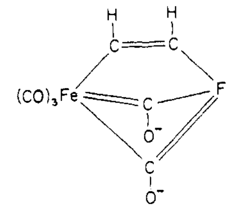


Fig. 1.—Infrared spectra of $Fe_2C_{10}H_4O_8$; Perkin-Elmer model 21 (double-beam) spectrophotometer.

charged anion III. It may be further assumed that the >C—O⁻ single bond will acquire a consid-



III

erable amount of double bond character due to the large number of possible resonance forms. These assumptions are supported by a comparison of the spectrum of a solution of $Fe_2C_{10}H_4O_8$ in carbon disulfide with that of a solution of $Fe_2C_{10}H_4O_8$ in *n*-butylamine (Fig. 1). In the latter spectrum the bands attributable to -OH and C-O are absent, while the complexity, *i.e.*, the number of infrared active carbonyl stretching vibrations in the 1900 to 2100 cm.$^{-1}$ region, has increased.

The configuration of I may be assumed to be analogous to that in iron enneacarbonyl where the iron atoms are located at the centers of two octahedra joined face to face.[8] In I the C–C axis is parallel to the Fe–Fe axis and the bonds linking the iron atoms with the acetylene group are shown as localized bonds. Two other structures (not shown) are possible where the C–C axis is perpendicular to and either in the same plane as the Fe–Fe axis or in a different plane. Neither of these two structures can be expressed in terms of localized bonds.

The assignment of structure I merely implies that the acetylene group occupies a place between the two iron atoms. Since the infrared spectrum of $Fe_2C_{10}H_4O_8$ does not show any bands which may be unambiguously attributed to either a C–C or a C–H linkage, it does not seem profitable at present to speculate on the type of C–C bonding that exists in the acetylene group in $Fe_2C_{10}H_4O_8$.

It is of interest to note that I contains an M=C-OH grouping, a type of linkage postulated[9] in surface intermediates in the Fischer–Tropsch reaction.

Preparation and Properties of $Fe_2C_{10}H_4O_8$.—The iron complex is obtained by treating an alkaline aqueous solution of $NaHFe(CO)_4$ with acetylene and acidifying the reaction mixture after the uptake of acetylene is completed. The reactions involved are expressed by equations 1 and 2.

$$2NaHFe(CO)_4 + C_2H_2 = Na_2Fe_2C_{10}H_2O_8 + H_2 \quad (1)$$

$$Na_2Fe_2C_{10}H_2O_8 + 2HCl = 2NaCl + Fe_2C_{10}H_4O_8 \quad (2)$$

Equation 1 indicates that the presence of the ion $[HFe(CO)_4]^-$ is essential for the reaction. This assumption is supported by the fact that the uptake of acetylene is extremely slow in the presence of excess alkali where, according to equation 3,

$$NaOH + NaHFe(CO)_4 = Na_2Fe(CO)_4 + H_2O \quad (3)$$

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(8) H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 286 (1939).

(9) H. H. Storch, N. Golumbic and R. B. Anderson, "The Fischer–Tropsch and Related Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 592.

most of the ion $[HFe(CO)_4]^-$ is converted[10] to the ion $[Fe(CO)_4]^=$. It follows from the above that excess alkali should be avoided and that the solution of $NaHFe(CO)_4$ should be prepared according to the stoichiometry expressed in equation 4.

$$Fe(CO)_5 + 3NaOH = NaHFe(CO)_4 + Na_2CO_3 + H_2O \qquad (4)$$

Reppe and Vetter reported[1] that a 1 *M* solution of $NaHFe(CO)_4$, when treated in a rocking autoclave with acetylene at 15 atm. and 45° to 50°, took up about 0.5 mole of acetylene per mole of $NaHFe(CO)_4$ in 16 hr. and gave crude $Fe_2C_{10}H_4O_8$ in a yield of 45% based on the amount of $NaHFe(CO)_4$ used. In a typical experiment carried out at atmospheric pressure and room temperature, we found that a 1 *M* solution of $NaHFe(CO)_4$ took up 0.6 mole of acetylene per mole of $NaHFe(CO)_4$ in 9 hr. and gave crude $Fe_2C_{10}H_4O_8$ in a yield of 70%. These results indicate that for the formation of the complex elevated temperatures are not required and may even be detrimental.

Equation 1 shows that hydrogen is liberated by the reaction of acetylene with $NaHFe(CO)_4$. An analysis of the gas mixture showed that hydrogen was indeed present. In addition to acetylene and hydrogen, the gas mixture also contained ethylene, an indication that some of the hydrogen had reacted with acetylene to give ethylene. The total amount of hydrogen evolved (hydrogen + hydrogen used in the formation of ethylene from acetylene) is considerably less than that required by equation 1. This is indicated in Table I where the yields of reaction product, hydrogen and ethylene are shown as well as the amount of acetylene taken up. These data show that 0.57 mole more of acetylene was absorbed and 0.53 mole less of total hydrogen (hydrogen + hydrogen in ethylene) evolved than was expected on the basis of the formation of 0.71 mole of reaction product. A possible explanation for this result may be that a side reaction takes place where hydrogen and acetylene react in the presence of a metal carbonyl to give condensation products.[11]

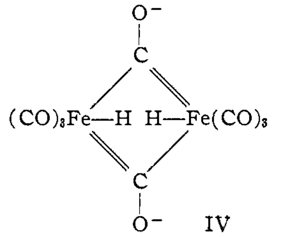
TABLE I

PRODUCTS AND YIELDS OBTAINED IN THE REACTION BETWEEN $NaHFe(CO)_4$ AND C_2H_2

	Moles of reagents			Moles of products		
	$NaHFe(CO)_4$	C_2H_2		$Na_2Fe_2C_{10}H_2O_8$	H_2	C_2H_4
Used	2.00	1.28	Formed	0.71	0.1	0.08
Calcd., eq. 1	2.00	1.00	Calcd., eq. 1	1.00	1.0	.00

To determine whether the same type of complex could be obtained from a substituted acetylene, the reaction between methylacetylene and an aqueous solution of $NaHFe(CO)_4$ was studied. Although methylacetylene was absorbed, a complex could not be isolated under these conditions. However, when methylacetylene was allowed to react with an aqueous solution of $Na_2Fe(CO)_4$ containing 30% of methanol over a period of three weeks, the corresponding methyl derivative, $Fe_2C_{11}H_6O_8$, was obtained in 18% yield based on the amount of $Na_2Fe(CO)_4$ used. The complex forms yellow crystals which melt at 100–105° dec.

The fact that ethylene is evolved may provide a clue to the mechanism of the formation of $Fe_2C_{10}H_4O_8$. If it is assumed that a bridged complex[12] such as IV is formed from two $[HFe(CO)_4]^-$ ions in



IV

the first step of the reaction, then it is seen readily that interaction of acetylene with the two iron and hydrogen atoms could lead either to the formation of ethylene or to substitution of the hydrogen atoms by acetylene followed by evolution of hydrogen.

Experimental[13]

Preparation and Properties of $Fe_2C_{10}H_4O_8$.—The preparation of the $NaHFe(CO)_4$ solution and treatment thereof with acetylene was carried out in the absence of air. A 250-ml. erlenmeyer flask provided with the necessary side arms, ground joints and stopcocks was used for this purpose.

Fifty ml. of oxygen-free water containing 4.44 g. (111 millimoles) of NaOH was placed in the flask, the flask purged with helium and, after addition of 5 ml. (37 millimoles) of $Fe(CO)_5$, stoppered. The flask was attached to a mechanical shaker, shaken for 24 hr. and opened while a current of helium was passed through one of the side arms; a glass-enclosed stirring bar was then placed in the flask and the flask attached to a gas buret. After flask and buret had been purged with acetylene, the gas volume was recorded and the contents of the flask stirred by means of a magnetic stirrer. The uptake of gas which is rapid at the start—about 150 ml. per hour—slows down gradually and finally comes to a halt. In the course of 9 hr. 488 ml. (S.T.P.) or 21.8 millimoles of gas were absorbed. A mass spectroscopic analysis of the residual gas showed that 1.5 millimoles of ethylene had been formed and 2.0 millimoles of hydrogen evolved. Since the evolution of hydrogen is accompanied by volume increase, while the formation of ethylene from acetylene and hydrogen is not, it follows that a total of 23.8 millimoles of acetylene had been absorbed.

After gas absorption had stopped, the flask was detached from the gas buret and the reaction mixture poured into a mixture of 80 g. of ice and 20 ml. of concentrated HCl. After a few hours, the precipitate was filtered, washed with water and dissolved in dilute aqueous NaOH. The alkaline solution was extracted several times with benzene, filtered and the filtrate collected in a flask containing dilute HCl. It must be emphasized that all operations up to this point should be carried out in a well ventilated hood since the acidification of the reaction mixture may produce consider-

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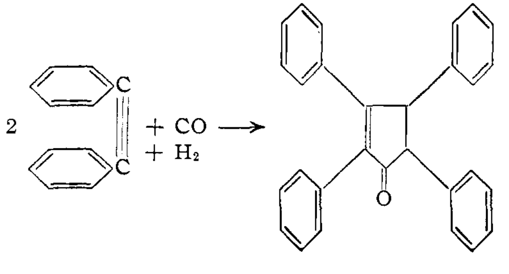
[10] P. Krumholz and H. M. A. Stettiner, THIS JOURNAL, **71**, 3035 (1949).

[11] G. P. Mueller and F. L. McArtor, *ibid.*, **76**, 4621 (1954), found that treatment of diphenylacetylene with nickel carbonyl and hydrochloric acid in dioxane–ethanol gave 2,3,4,5-tetraphenylcyclopenta-2-en-1-one:



[12] Evidence for the existence of complex IV has recently been obtained: H. W. Sternberg, R. Markby and I. Wender, unpublished work.

[13] Microanalyses by Galbraith Laboratories, P. O. Box 32, Knoxville, Tenn.; Macroanalyses by W. Rosinski and W. Dieter, Analytical Chemists, Central Experiment Station, Bureau of Mines, Bruceton, Pa.

able amounts of $H_2Fe(CO)_4$ and $Fe(CO)_5$. The yellow crystalline precipitate $Fe_2C_{10}H_4O_8{\cdot}H_2O$ was filtered and, after drying over P_2O_5, weighed 4.8 g. corresponding to a yield of 71%, based on the amount of $Fe(CO)_5$ used. If necessary, the iron complex may be further purified by repeating the precipitation from its alkaline solution as described above. Since in alkaline solution the iron complex is rather sensitive toward oxygen, it is advisable to filter the alkaline solution of $Fe_2C_{10}H_4O_8$ under nitrogen and to restrict the time during which the iron complex is dissolved in alkali to a minimum. The anhydrous iron complex, $Fe_2C_{10}H_4O_8$, is prepared by drying the filtered and washed precipitate, $Fe_2C_{10}H_4O_8{\cdot}H_2O$, in the vacuum desiccator over P_2O_5 for 4–8 hr. The anhydrous complex, $Fe_2C_{10}H_4O_8$, forms light yellow needles which melt at 80–85° with decomposition. The anhydrous complex, $Fe_2C_{10}H_4O_8$, is hygroscopic and much less stable than the monohydrate, $Fe_2C_{10}H_4O_8{\cdot}H_2O$. To obtain the monohydrate the anhydrous complex is placed in a desiccator containing some water and the air in the desiccator replaced by helium. After about 8 hr. the required amount of water to form the monohydrate, $Fe_2C_{10}H_4O_8{\cdot}H_2O$, is taken up and the weight of the sample has become constant. The monohydrate, $Fe_2C_{10}H_4O_8{\cdot}H_2O$, forms light yellow to orange needles which melt in the vacuum capillary at 104–110° dec.[14]

Anal. Calcd. for $Fe_2C_{10}H_4O_8{\cdot}H_2O$: C, 31.45; H, 1.58; Fe, 29.25. Found: C, 31.40; H, 1.64; Fe, 29.06.

Both the anhydrous complex and the monohydrate are sparingly soluble in water and readily soluble in ether, alcohol and acetone. They differ considerably in their solubilities in other organic solvents, the anhydrous complex being considerably more soluble than the monohydrate. For example, the solubility of the anhydrous complex in *n*-hexane, carbon disulfide and benzene is 0.41, 1.63 and 5.82, while that of the monohydrate is 0.014, 0.025 and 0.188 g. per 100 ml. of solvent. It is reasonable to assume that the monohydrate is soluble in these solvents only to the extent to which it is dissociated into anhydrous complex. This assumption is supported by the fact that the infrared spectra of solutions of monohydrate and anhydrous complex in carbon disulfide are identical.

The stabilizing effect of the water of crystallization as evidenced by the higher melting point and greater storage stability of the monohydrate is worthy of note. In its crystalline form and in the absence of oxygen the monohydrate is stable to light. A sample of the monohydrate which had been crystallized several times was stored under helium at room temperature for 6 months without showing any signs of decomposition. In aqueous solution in the presence of oxygen, the complex decomposes within a few days. As observed by Reppe and Vetter,[1] the monohydrate readily loses one mole of water when placed in a vacuum desiccator over phosphorus pentoxide. The anhydrous complex is considerably less stable than the monohydrate and shows signs of decomposition after 12 hr., even when stored in the dark and in the absence of air.

Preparation of the Methylacetylene Analog of $Fe_2C_{10}H_4O_8$.—A solution of $Na_2Fe(CO)_4$ was prepared by shaking 5 ml. (37 millimoles) of $Fe(CO)_5$ and 5.92 g. (148 millimoles) of NaOH in 50 ml. of water for 24 hr. After addition of 25 ml. of methanol, the solution was treated with acetylene as described above. In the course of 3 weeks 31 millimoles of acetylene was absorbed. The reaction mixture, treated as described above, gave 1.27 g. (18%) of crude material. Sublimation of the crude product at 70° and 10^{-5} mm. yielded yellow crystals which melted at 100–105° dec.

Anal. Calcd. for $Fe_2C_{11}H_6O_8$: Cl, 34.96; H, 1.60; Fe, 29.56. Found: C, 34.67; H, 1.58; Fe, 29.30.

Benzoylation of $Fe_2C_{10}H_4O_8$.—To a solution of 1.53 g. of the anhydrous complex $Fe_2C_{10}H_4O_8$ in 100 ml. of dry pyridine was added 4 ml. of freshly distilled benzoyl chloride, the reaction mixture allowed to stand overnight at room temperature under nitrogen and then poured into about 700 ml. of water. The mixture was allowed to stand in the refrigerator for a few hours, filtered and dried in the vacuum desiccator over P_2O_5. The dried residue (2.77 g.) was dissolved in 400 ml. of absolute ethanol at room temperature, 30 ml. of water added and the benzoate allowed to crystallize at −20°. The precipitate was filtered and dried in the vacuum desiccator over $CaCl_2$ and finally over P_2O_5. The yellow microscopic crystals melted at 155–160° dec.

Anal. Calcd. for $Fe_2C_{24}H_{12}O_{10}$: C, 50.39; H, 2.11; Fe, 19.53. Found: C, 50.34; H, 2.13; Fe, 19.33.

Methylation of $Fe_2C_{10}H_4O_8$.—To 50 ml. of an aqueous solution containing 2.16 g. (54 millimoles) of NaOH and 10.3 g. (27 millimoles) of $Fe_2C_{10}H_4O_8{\cdot}H_2O$ was added 7 ml. (74 millimoles) of dimethyl sulfate in 1-ml. portions and the solution vigorously shaken between additions. During the addition which was carried out under nitrogen a bright yellow precipitate (the dimethyl ether) formed. The reaction mixture was made alkaline, the alkaline solution along with the yellow precipitate transferred to a separatory funnel and extracted with about one liter of ether. The ether extract was extracted several times with dilute NaOH, dilute H_2SO_4 and finally with water. After drying with Drierite (anhydrous $CaSO_4$) the ether solution was filtered, concentrated to a volume of about 400 ml. in a current of nitrogen and allowed to stand at −20° overnight. The dimethyl ether crystallized in bright orange crystals, which, after washing with a few ml. of cold ether and drying in a vacuum desiccator over Drierite, melted at 155.2–156.4°. A recrystallization from ether did not change the melting point. The yield was 4.66 g. or 44% of theory. The mother liquor yielded 2.33 g. (22%) of crystals melting at 154–156°.

Anal. Calcd. for $Fe_2C_{12}H_6O_8$: C, 36.77; H, 2.04; Fe, 28.52. Found: C, 36.90; H, 2.20; Fe, 28.47.

Potentiometric Titrations.—A Beckman *p*H meter (model H2) was used in conjunction with a Beckman Type "42" glass electrode which permitted measurements in the range of −1 to 14 *p*H. The samples were titrated in an atmosphere of helium.[15]

To 0.4951 g. of anhydrous $Fe_2C_{10}H_4O_8$ was added 75 ml. of oxygen-free water, the mixture stirred and titrated with 0.050 *N* KOH solution. From these data a value of 9.14 for pK_{2a} (*p*H at the second half-neutralization point) was obtained.

The value for pK_{1a} could not be obtained from the above titration since at the first half-neutralization point, *i.e.*, after the addition of 1.40 ml. of the titrant, the sample was not completely dissolved. To determine the value of pK_{1a}, 100 ml. of an aqueous solution of $Fe_2C_{10}H_4O_8$ was titrated. From these data, a value of 6.30 was obtained for pK_{1a}.

BRUCETON, PENNA.

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[14] Reppe and Vetter[1] reported a melting point of 110–111° (with decomposition) but did not specify whether this melting point referred to the monohydrate or to the anhydrous complex. Their statements concerning the stability and solubility of the complex indicate that they were dealing with the monohydrate.

[15] Reppe and Vetter[1] reported that the complex contained one acidic hydrogen. However, their potentiometric titration gave an equivalent weight of 284 instead of that calculated for $Fe_2C_{10}H_4O_8$, which is 363 for a monobasic acid or 182 for a dibasic acid. The failure of these workers to observe two sharp breaks in their titration curve may have been due to the presence of oxygen.