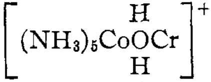
plexes $[CrXFe]^{+4}$, it is necessary to compare the rates at unit concentration of these species. The data on stabilities to make this comparison possible do not exist. It might be supposed, however, that the complexes would be enough more stable with F^- than Cl^- to reveal a higher specific rate of electron transfer in the chloride bridge complex.

The relative rates shown in Table VII are useful in making comparisons without inquiring into their meaning. The similarity of the relative rates in the two columns suggests that the activated complex involved when Fe^{++} and Fe(III) complexes exchange electrons is of the same type as that for the reaction of Cr^{++} with Fe(III) complexes. Comparison of the activation energies observed for electron exchange between Fe^{++} and Fe(III) complexes with that of substitution on Fe^{++} or Fe^{+++},[21] shows that the rate-determining act is not the substitution to form the bridged activated complex. The energy values are compatible with the assumption that a bridged chemical complex formed as an equilibrium process having ΔH° lower than the activation energy for substitution. If, as seems likely, ΔH° is positive the activation energy for electron transfer in the bridged complex must be small. The low rate for electron transfer in the bridged complex as compared to dissociation of the complex must then be a matter of a much lower temperature-independent factor, *i.e.*, a relatively specific relation of the positions of a large number of atoms is required to make the electron transfer possible.

A condition for a bridged activated complex to provide a more favorable pass for electron transfer than some other process is that at least one of the partners be able to undergo a substitution process readily. Thus although $(NH_3)_5CoH_2O^{+++}$ is inert to substitution, Cr^{++} is labile so that the bridge complex  $\left[\begin{array}{c}\text{H}\\ (NH_3)_5CoOCr\\ \text{H}\end{array}\right]^{+5}$ can still provide a path for electron exchange. A bridge other than that involving H_2O or OH^- is not readily accessible, however, because this would require substitution on Co(III). On the basis of present information, one cannot be certain that such a substitution may not take place under some labilizing influence of the other reactant, but neither are there any observations which suggest such an influence. Common cations which are fairly labile to substitution[22] and for which bridged activated complexes must be considered for oxidation–reduction or electron exchange reactions in water involving them are: Ti^{++}, Ti^{+++}, Ti(IV), V^{++}, V^{+++}, V(IV), V(V), Cr^{++}, Cr(IV) (?), Mn^{++}, Mn^{+++}, Fe^{++}, Fe^{+++}, Co^{++}, (Co_{aq}^{+++} possibly), Cu^+, Cu^{++}, Ag^+, Ag^{++}, Eu^{++}, Eu^{+++}, Ce^{+++}, Ce(IV), Tl^+, Tl^{+++}. It is admitted that not all electron transfer reactions involve such direct atom bridges. When both partners are substitution-inert and have the coördination spheres blocked, other types of activated complexes are almost certainly involved.

The authors are grateful to Mr. Franz A. Posey, whose skill and diligence in preparing many of the substances used greatly furthered the research. We are also grateful to Dr. E. L. King for valuable discussion of the work, and to the Office of Naval Research for financial support (Contract N6-Ori-02026).

[21] J. Bjerrum and K. R. Poulson, *Nature*, **169**, 463 (1952), have measured ~13 kcal. as the activation energy for substitution by CNS of solvent on Fe^{+++}. If the activation energy for substitution on Fe^{++} is similar to that on Ni^{++} and Co^{++}, it is even higher than 13 kcal.

[22] H. Taube, *Chem. Revs.*, **50**, 69 (1952).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF UTAH]

Citrate Complexes with Iron(II) and Iron(III)[1]

BY RANDALL E. HAMM, CHARLES M. SHULL, JR., AND DAVID M. GRANT

RECEIVED JULY 27, 1953

The results of *p*H titrations of iron(II) perchlorate and citric acid in 1:1 mixture, at ionic strength 1.0, showed that the iron(II) complexes with citrate may be formulated as FeHCit, $FeCit^-$ and $FeOHCit^=$. The formation constants of these complexes have been calculated. The results of *p*H titrations of iron(III) perchlorate and citric acid in 1:1 mixture, at ionic strength 1.0, showed that the iron(III) complexes with citrate may be formulated as $FeHCit^+$, FeCit, $FeOHCit^-$ and $Fe(OH)_2Cit^=$. The formation constants of these complexes have been calculated. Polarographic measurements on iron(II)–iron(III) mixtures in excess citrate, at ionic strength 1.0, demonstrated that two separate reduction processes are involved. The formation constants previously calculated were shown to be consistent with the data obtained polarographically, and the reversible polarographic processes were related to definite reactions.

Many different investigators have studied the citrate complexes of iron(III) with results which differ considerably. Bobtelsky and Jordan[2] have attempted to relate the breaks in the conductivity titration of iron(III) with citrate to the complex ion composition, but Bertin[3] has recognized that the change in the hydrogen ion concentration and the number of acid hydrogens in the complex were the important factors in causing the breaks in the conductance titration. A line of reasoning starting from *p*H titration curves led Bertin to conclude that the iron(III) citrate complexes were 1:1 complexes containing different numbers of acid hydrogens. A spectrophotometric study of iron(III) and citrate in acid solution, by the method of constant variations, permitted Lanford and Quinan[4] to identify $FeHCit^+$ as the form of the complex existing when the solution was 0.08 to 0.15 *M* in HNO_3. Lin-

[1] The work on this investigation was supported by National Science Foundation Research Grant NSF-G62.

[2] M. Bobtelsky and J. Jordan, THIS JOURNAL, **67**, 1824 (1945); **69**, 2286 (1947).

[3] C. Bertin, *Bull. soc. chim. France*, 489 (1949).

[4] O. E. Lanford and J. R. Quinan, THIS JOURNAL, **70**, 2900 (1948).

gane[5] and Meites[6] have studied the polarographic behavior of iron in citrate media but did not definitely relate any of the waves occurring to any particular reduction reactions. They did, however, indicate that one of the waves was reversible over a range of *p*H from 4.0 to 7.0.

Little has been reported of the nature of the iron (II) complexes with citrate. Knowledge of structure and stability of these complexes is important to a complete understanding of the iron(II)–iron(III) couple in citrate media. Dickman and Cloutier[7] have postulated that the iron(II) complexes with citrate and other organic acids are essential elements in the functioning of the aconitase enzyme system. In an attempt to study the citrate complexes of iron(II) by polarographic means, it became apparent that more knowledge was required about the iron(III) complexes with citrate. It was the purpose of this investigation to study the iron(II) and iron(III) complexes with citrate.

Experimental

Apparatus.—The polarographic measurements were made on two different Sargent polarographs; one a model XII, the other a model XXI. In each case the instrument was used without damping. The potentials were checked by means of an external potentiometer circuit and are estimated to be within about 0.002 volt. The *p*H titrations and *p*H determinations were made using a Beckman model G, *p*H meter, which was standardized against 0.05 *M* potassium acid phthalate.

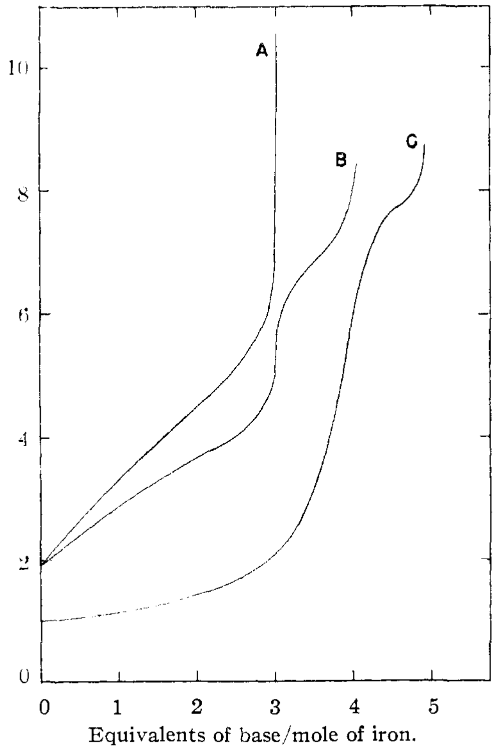

Fig. 1.—Titration with 0.5430 *N* NaOH: A, 0.05 *M* citric acid; B, equimolar iron(II) perchlorate–citric acid (0.05 *M* each); C, equimolar iron(III) perchlorate–citric acid (0.05 *M* each); sodium perchlorate added to make ionic strength = 1.0 in each case.

Reagents.—The ferrous perchlorate and ferric perchlorate were the product of the G. Frederick Smith Chemical Company. The sodium perchlorate was prepared in solution from 72% perchloric acid and carbonate-free sodium hydroxide solution by titration procedure. The citric acid and sodium citrate were reagent grade chemicals.

Procedures.—In the titration of mixtures of iron(II) perchlorate and citric acid it was necessary to take extreme precautions to avoid the presence of oxygen. The iron(II) perchlorate and the citric acid solutions each were subjected to a stream of pure hydrogen until all dissolved oxygen was removed. A sample of the iron(II) perchlorate was introduced into the citric acid solution under continuous bubbling of hydrogen. The titration was performed with a carbonate-free sodium hydroxide solution which had been subjected to a stream of hydrogen to remove dissolved oxygen. The stream of hydrogen was continued throughout the titration and served additionally as a means of stirring.

In the titration of mixtures of iron(III) and citric acid, the vessel was surrounded by a shield in order to prevent photochemical reduction of the iron.

Results and Discussion

The titration curves in Fig. 1 show the titration of: A, 0.05 *M* citric acid; B, 1:1 iron(II) perchlorate–citric acid (0.05 *M* in each) and C, 1:1 iron (III) perchlorate–citric acid (0.05 *M* in each). Curve B shows that the iron(II) complex acted as a tribasic acid stronger than citric acid and that a fourth equivalent of base was neutralized when the complex acted as a very weak acid. Curve C shows that the iron(III) complex acted as a moderately strong tetrabasic acid, the last step of which is somewhat weaker than the first three. A fifth equivalent of base was neutralized when the complex acted as a very weak acid.

From curve B it is proposed that the iron(II) complexes with citrate may be represented as FeHCit, $FeCit^-$ and $FeOHCit^=$, where H_3Cit represents the formula of citric acid. From curve C, we propose $FeHCit^+$ as the complex present in acid solution,[4] and propose FeCit, $FeOHCit^-$ and $Fe(OH)_2Cit^=$ as the forms of the complex in successively more basic solution.

To calculate the formation constants of the iron (II) complexes with citrate, the material balances used were

$$[Fe^{2+}] + [FeOH^+] + [FeHCit] + [FeCit^-] + [FeOHCit^=] = C_m \quad (1)$$

$$[H_3Cit] + [H_2Cit^-] + [HCit^=] + [Cit^{\equiv}] + [FeHCit] + [FeCit^-] + [FeOHCit^=] = C_L \quad (2)$$

where C_m is the total iron concentration and C_L is the total citrate concentration. The charge equation used was

$$2[Fe^{2+}] + [FeOH^+] + [Na^+] + [H^+] = [ClO_4^-] + [H_2Cit^-] + 2[HCit^=] + 3[Cit^{\equiv}] + [FeCit^-] + 2[FeOHCit^=] \quad (3)$$

These equations are completely general and were first solved at points where the $FeOHCit^=$ concentration could be assumed to be negligible, giving the formation constants for the following complexes by a method of successive approximations,

$$Fe^{2+} + HCit^= \rightleftarrows FeHCit \quad (4)$$

$$Fe^{2+} + Cit^{\equiv} \rightleftarrows FeCit^- \quad (5)$$

The ionization constants of citric acid used were given by Adell,[8] and the hydrolysis constant of

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[5] J. J. Lingane, *ibid.*, **68**, 2448 (1946).

[6] L. Meites, *ibid.*, **73**, 3727 (1951).

[7] S. R. Dickman and A. A. Cloutier, *Arch. Biochem.*, **25**, 229 (1950).

[8] B. Adell, *Z. physik. Chem.*, **A187**, 66 (1940).

iron(II) was reported by Leussing and Kolthoff.[9] Using the constants previously calculated in the area between 3 and 4 equivalents of base per mole of iron(II), the formation constant was calculated for the complex.

$$Fe^{2+} + Cit^{=} + H_2O \rightleftarrows FeOHCit^{=} + H^+ \quad (6)$$

Similar material and charge balance equations were used to calculate the formation constants of the iron(III) complexes with citrate. These equations were first solved at points where the concentrations of $Fe(OH)_2^+$, $FeOHCit^-$ and $Fe(OH)_2Cit^=$ could be neglected, giving the formation constants for the following complexes by a method of successive approximations

$$Fe^{3+} + HCit^{=} \rightleftarrows FeHCit^+ \quad (7)$$

$$Fe^{3+} + Cit^{\equiv} \rightleftarrows FeCit \quad (8)$$

The hydrolysis constants of iron(III) recently were reported by Arden.[10] Moving further along the titration curve the formation constant was calculated for

$$Fe^{3+} + Cit^{\equiv} + H_2O \rightleftarrows FeOHCit^{=} + H^+ \quad (9)$$

and finally at points between 4 and 5 equivalents of base per mole of iron(II) the formation constant was calculated for

$$Fe^{3+} + Cit^{\equiv} + 2H_2O \rightleftarrows Fe(OH)_2Cit^- + 2H^+ \quad (10)$$

Polarographic measurements of iron(II)-iron(III) mixtures in citrate media at constant ionic strength showed that the reversible wave had a half-wave potential independent of citrate concentration. The data for these measurements are shown in Table I.

Table I

HALF-WAVE POTENTIAL OF THE REVERSIBLE WAVE RESULTING WHEN IRON(II)-IRON(III) MIXTURES IN EXCESS CITRATE ARE POLAROGRAPHICALLY MEASURED AT CONSTANT IONIC STRENGTH = 6.0

pH	Total citrate, mole/liter	$E_{1/2}$, volts *vs.* S.C.E.
7.00	1.0	0.332
	0.8	.333
	.2	.342
	.18	.334
	.12	.339
	.06	.334
6.00	.50	.197
	.40	.200
	.20	.202
	.10	.202

The consequence of these measurements is that the citrate complex of both iron(II) and iron(III) have the same ratio of iron:citrate.

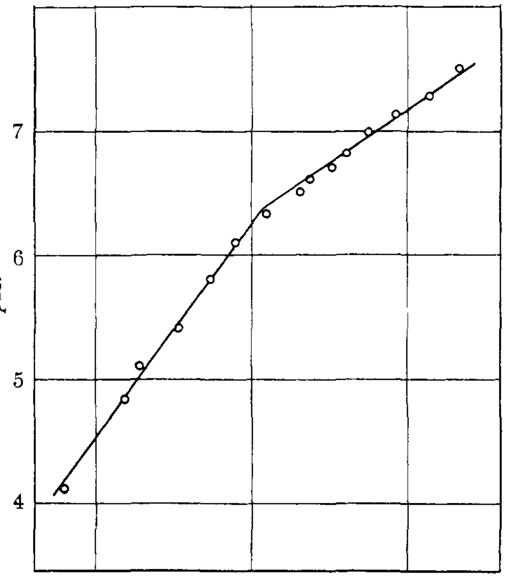

Fig. 2.—Variation of half-wave potential with pH in solution 2.5 millimolar iron(II) perchlorate-2.5 millimolar iron(III) perchlorate in $^1/_6$ M sodium citrate.

Figure 2 shows a plot of pH against half-wave potential for the reversible wave that results when an equimolar solution of iron(II) and iron(III) perchlorates (4 millimolar in total iron) in 1/6 M sodium citrate is treated at the dropping mercury electrode. The slopes of the solid lines in Fig. 2 are the theoretical slopes for a one hydrogen ion change and a two hydrogen ion change. The reaction in the more acid section of the range in Fig. 2 may be written as

$$FeOHCit^- + H^+ + e^- \longrightarrow FeCit^- + H_2O \quad (11)$$

and in the more basic section may be written as

$$Fe(OH)_2Cit^{=} + 2H^+ + e^- \longrightarrow FeCit^- + 2H_2O \quad (12)$$

Using the equation presented by Lingane,[11] the equation derived for the reduction represented by equation 11 was

$$(E_{1/2})_c - (E_{1/2})_s = \frac{0.0591}{1}\log\frac{K_5}{K_9} - 0.0591pH \quad (13)$$

and the equation derived for the reduction represented by equation 12 was

$$(E_{1/2})_c - (E_{1/2})_s = \frac{0.0591}{1}\log\frac{K_5}{K_{10}} - 2 \times 0.0591pH \quad (14)$$

where the subscripts c and s represent the complex and the simple metal, and the subscripts on K refer to equation number in this paper. Using equations 13 and 14, a value of 0.525 for $(E_{1/2})_s$, and the value for K_5 which had been evaluated from pH titration, K_9 and K_{10} were calculated.

Table II contains the formation constants which have been calculated from the data taken. The

Table II

FORMATION CONSTANTS OF THE IRON(II) AND IRON(III) COMPLEXES WITH CITRATE AT IONIC STRENGTH 1.0 AND 25°

	pH titration	Polarographic	Literature[4]
K_4	1.4×10^2		
K_5	1.2×10^3		
K_6	0.35		
K_7	2.0×10^6		2.04×10^6
K_8	7.0×10^{11}		
K_9	2.5×10^9	1.3×10^9	
K_{10}	8.0×10^1	4.2×10^2	

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(9) D. L. Leussing and I. M. Kolthoff, THIS JOURNAL, **75**, 1274 (1953).

(10) T. V. Arden, *J. Chem. Soc.*, 350 (1951).

(11) J. J. Lingane, *Chem. Revs.*, **29**, 1 (1941).

results calculated for K_9 and K_{10} by the two methods, while in poor agreement, are of the same order of magnitude. The value of K_{10} calculated from *p*H titration may be in error because of formation of colloidal ferric hydroxide, since at points slightly beyond those used for calculation it was apparent that precipitation was taking place. The polarographic results depend upon the value of K_5, which may be in error.

Bobtelsky and Jordan[2] titrated an iron(III) solution with sodium citrate and found an increase in conductivity as the citrate was first added. In this titration the reactions represented by equations 8 and 9 would be expected to occur. The hydrogen ion produced by the second of these reactions would cause the *p*H to decrease. A check at the beginning of this titration showed that the *p*H did decrease, thus causing a conductivity increase as reported by Bobtelsky and Jordan. As the *p*H decreases one would expect relatively more of the material reacting to follow equation 8 and also the competitive reaction

$$Cit^{\equiv} + H^+ \longrightarrow HCit^{=} \qquad (15)$$

The hydrogen ion concentration would then decrease, resulting in a conductivity decrease, which would continue even after all of the iron was complexed because of 15. Finally the conductivity would start to increase because of the addition of sodium citrate. The breaks in the conductivity curve would, according to this explanation, bear no direct relationship to the complex ion composition.

Definite points of difference exist with Lingane[5] and Meites[6] with regard to the polarographic measurements. Lingane has claimed that the half-wave potential may be represented by an equation linear in *p*H from 4 to 12. The slope given by this equation is intermediate between the slopes of the two portions of our plot, and may have resulted from Lingane's larger but less detailed range of study. The differences with Meites are harder to explain since we have found only a single wave at all *p*H values. Meites suggested that his differences from Lingane might be the result of the fact that Lingane had used 0.005% gelatin. We did not use gelatin, but have results corresponding more closely with those of Lingane.

Acknowledgment.—We would like to express our thanks to Dr. S. R. Dickman who originally suggested the study of the citrate complexes of iron(II) and assisted by giving summer support to one of us (C.M.S.) from U.S. Public Health funds under his direction, as the investigation first started.

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[CONTRIBUTION FROM DEPARTMENT OF RADIATION BIOLOGY, UNIVERSITY OF ROCHESTER, SCHOOL OF MEDICINE AND DENTISTRY]

Spectrophotometric Studies of the Uranyl–Lactate, –Malate and –Tartrate Systems in Acid Solution[1]

BY ISAAC FELDMAN AND JEAN R. HAVILL

RECEIVED NOVEMBER 19, 1953

Absorption spectra and Job's method of continuous variations have been employed to determine the stoichiometry of the possible complexes in the uranyl–lactate, –malate and –tartrate systems in acid solution. Only a combining ratio of unity is evident in the uranyl–lactate system at *p*H 3.5. In the uranyl–malate system at *p*H 3.5 complexes having uranyl/malate combining ratios of one and two exist. The former ratio predominates in equimolar uranyl–malate mixtures and in excess malate up to at least *p*H 4.8. In the uranyl–tartrate systems, it is probable that there exist complexes having combining ratios of one, two and three. Although only 1:1 stoichiometry prevails in excess tartrate up to at least *p*H 4.6, it is probable that in the *p*H range 3.6–5 an equimolar uranyl–tartrate mixture contains a small fraction of a species having a combining ratio greater than one.

As part of a program of investigation of the reactions of uranyl ions with carboxylic acids, spectrophotometric studies were carried out to determine the stoichiometry of the possible complexes in the uranyl–lactate, –malate and –tartrate systems. The uranyl–citrate system has been studied previously.[2]

Experimental

The experimental procedure followed was as described in the earlier paper[2] with one modification: the solutions were prepared in semi-darkness and stored in the dark. The spectral absorbences, $A = \log_{10} I_0/I$, of the uranyl–lactate solutions were measured two hours after the solutions were prepared, since apparently decomposition occurs on standing overnight. Absorbences of the uranyl–lactate mixtures remained constant from two to six hours. Below about *p*H 5 uranyl–malate and uranyl–tartrate solutions, if stored in the dark, gave constant absorbences from less than one hour to at least 24 hours. Therefore, all spectral measurements on uranyl–malate and uranyl–tartrate solutions were made after 18–24 hours.

Results and Discussion

Absorption Spectra at *p*H 3.5.—The absorption spectra of various uranyl nitrate–lactic acid mixtures, uranyl nitrate–malic acid mixtures and uranyl nitrate–tartaric acid mixtures raised to *p*H 3.5 are presented in Figs. 1A, 1B and 1C, respectively. The portions below 400 mμ are omitted to save space. In each curve there is a relatively broad minimum near 380 mμ followed by rapidly increasing general absorption with decreasing wave length.

In each of these graphs the 1:1 and 1:9 curves seem sufficiently similar to indicate that in none of these systems does there exist appreciable concentration of a complex with a combining ratio of less than unity at *p*H 3.5.

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[1] This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, N. Y.

[2] I. Feldman and W. F. Neuman, THIS JOURNAL, **73**, 2312 (1951).