338. *The Stability of Iron Complexes. Part IV.* Ferric Complexes with Aliphatic Acids.*

By D. D. Perrin.

In acid solutions, ferric ion and aliphatic acids form complexes of the types $Fe(CH_3{\cdot}CO_2)^{2+}$ and $Fe_3(OH)_2(CH_3{\cdot}CO_2)_6^{+}$. The stability constants of the complexes for the series chloroacetic, formic, acetic, propionic, and *iso*butyric acids have been obtained at 20° and $I = 1$, in a medium consisting essentially of sodium perchlorate, from oxidation–reduction potentials. The stability of the complexes increases in the order given above for the acids. Several of the 3 : 2 : 6 complexes have high stability constants, of the order of 10^{20}. Stability constants have also been calculated for the corresponding 1 : 1 ferrous complexes with chloroacetic, acetic, and propionic acids.

Stability constants have been tabulated [1] for complexes of aliphatic acids with several cations, but not with iron. The amber colour of ferric acetate solutions suggests that complexes are present, and ferric acetates which are believed to be salts of the complexes, penta-acetatodihydroxytriferri-base and hexa-acetatodihydroxytriferri-base, have been isolated.[2] Evidence in support of the latter has also been obtained by electrometric titration of ferric chloride with sodium acetate [3] and by dialysis-coefficient measurements.[4] Similar complexes have been prepared with chloroacetic,[5] formic,[6] and propionic acids.[7] Electrometric titration confirms that these, and the corresponding butyric acid complex, are present in aqueous solution.[8] A ferric-hexaformate ion, $Fe(H{\cdot}CO_2)_6^{3-}$, has also been reported.[6] Ferric triacetate, which has with difficulty been crystallised from acetic acid,[9] is believed to be trimeric.[10] In all these cases, observations have been made only at high

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* Part III, *J.*, 1959, 290.

[1] Bjerrum, Schwarzenbach, and Sillén, " Stability Constants. Part I: Organic Ligands," The Chemical Society, London, Spec. Publ. No. 6, 1957.

[2] Weinland, Kessler, and Bayerl, *Z. anorg. Chem.*, 1924, **132**, 209.

[3] Treadwell and Fisch, *Helv. Chim. Acta*, 1930, **13**, 1209.

[4] Brintzinger and Jahn, *Z. anorg. Chem.*, 1936, **230**, 176.

[5] Weinland and Loebich, *ibid.*, 1926, **151**, 277.

[6] Weinland and Reihlen, *Ber.*, 1913, **46**, 3144.

[7] Weinland and Höhn, *Z. anorg. Chem.*, 1926, **152**, 1.

[8] Treadwell and Fisch, *Helv. Chim. Acta*, 1930, **13**, 1219.

[9] Krause, *Z. anorg. Chem.*, 1928, **169**, 273.

[10] Gmelin's " Handbuch der anorganischen Chemie," Verlag Chemie, Berlin, 1932, 8th edn., System number 59, B, p. 526.

concentrations. No intermediate complexes have been reported, although it has been suggested [8] that complex formation might proceed through the ion $FeOH^{2+}$. As would be expected,[11] ferric ion forms more stable complexes with aliphatic acid anions than does ferrous ion.[3,8]

In the present work, oxidation–reduction potentials have been used to obtain quantitative information on the kinds, and stabilities, of complexes formed by ferric ion in less concentrated aliphatic acid solutions. To ensure that conditions were chosen so that ferrous complex formation was negligible, preliminary estimates were obtained of log K_1 ($\sim 0{\cdot}6$) and log β_2 ($\sim 1{\cdot}2$) for ferrous–acetate complexes, using results for nickel–acetates [12] and assuming Irving and Williams's relation.[13] A value of log $K_1 = 0{\cdot}3$ was subsequently found by experiment. Ferrous complex formation should therefore have been negligible ($<5\%$) for acetate-ion concentrations less than 0·024M. The same concentration limit was assumed for the other acids.

EXPERIMENTAL

Ferric and ferrous perchlorates were prepared as already described.[11] All oxidation–reduction potential and pH measurements were made at 20° in sodium perchlorate–perchloric acid solutions of approximately unit ionic strength, as described previously.[11] The dissociation constants (pK) of chloroacetic, formic, acetic, propionic, and *iso*butyric acids in 1M-sodium perchlorate were found by potentiometric titration to be $2{\cdot}60 \pm 0{\cdot}01$, $3{\cdot}49 \pm 0{\cdot}02$, $4{\cdot}55 \pm 0{\cdot}01$, $4{\cdot}66 \pm 0{\cdot}01$, and $4{\cdot}63 \pm 0{\cdot}01$, respectively. These constants were calculated from the concentrations of the free acid and its anion, and the hydrogen-ion activity as measured by the glass electrode.

Hydrolysis of Ferric Ion.—Because correction for hydrolysis of ferric ion was more important than in earlier Parts of this series, the acid dissociation constants, $^*K_1$, $^*\beta_2$, and $^*\beta_{22}$, of ferric ion, corresponding to the formation of $FeOH^{2+}$, $Fe(OH)_2^{+}$, and $Fe_2(OH)_2^{4+}$, were determined under the present experimental conditions. (Symbols used in this paper are the same as in Bjerrum, Schwarzenbach, and Sillén, "Stability Constants. Part II: Inorganic Ligands," The Chemical Society, London, Spec. Publ. No. 7, 1958). If a constant total ferric–ferrous concentration ratio is maintained and complex-forming species are absent, the pH-dependence of the ferric–ferrous potential, E, enables $^*K_1$, $^*\beta_2$, and $^*\beta_{22}$ to be obtained.[11,14] Thus, if the approximations are made that at constant ionic strength the liquid-junction potential and the activity coefficients of ferric and ferrous ion do not change appreciably as the pH of the solution is varied:

$$\begin{aligned}\text{antilog}\{(E_0' - E)/0{\cdot}0581\} &= [Fe^{3+}]_T/[Fe^{3+}] \\ &= 1 + {}^*K_1/[H^+] + {}^*\beta_2/[H^+]^2 + 2{}^*\beta_{22}[Fe^{3+}]/[H^+]^2 \quad . \quad . \quad . \quad . \quad \text{(i)}\end{aligned}$$

where E_0' is the potential of the experimental ferric–ferrous ratio under conditions where no hydrolysis occurs, and $[Fe^{3+}]_T$ is the total concentration of ferric iron. E_0' must be obtained by extrapolation because, at the high concentrations of hydrogen ion that are necessary before hydrolysis of ferric ion becomes negligible, the liquid-junction potential can no longer be assumed constant. If a ferric–perchlorate complex ion, $FeClO_4^{2+}$, was also present in the solution,[15] the form of eqn. (i) would remain unchanged but each stability constant would include the term, $1/(1 + K[ClO_4^-])$, where K is the stability constant of $FeClO_4^{2+}$. In 1M-sodium perchlorate solutions, and low ferric-ion concentrations, E reached a maximum near pH 1·7; E_0', obtained by successive approximation using eqn. (i), was 1·5 mv greater than this.

The results shown in Fig. 1 were obtained from titrations of acid solutions of ferric and ferrous perchlorates with sodium hydrogen carbonate and of less acid solutions with perchloric acid. From them, $^*K_1 = 1{\cdot}8 \times 10^{-3}$, $^*\beta_2 = 8{\cdot}9 \times 10^{-7}$, at 20°, in 1M-sodium perchlorate solution. Similarly, from the results in Table 1 for higher concentrations of ferric ion, $^*\beta_{22} = 1{\cdot}4 \times 10^{-3}$. From spectrophotometric measurements under these conditions, but without

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[11] Perrin, *J.*, 1958, 3120.

[12] Fronaeus, *Acta Chem. Scand.*, 1952, **6**, 1200.

[13] Irving and Williams, *J.*, 1953, 3192.

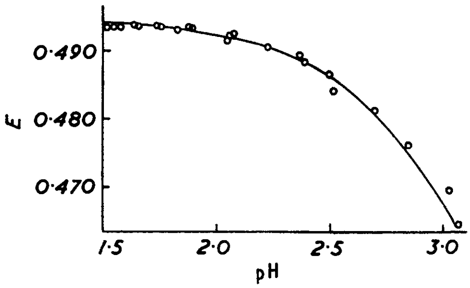
[14] Hedström, *Arkiv Kemi*, 1953, **6**, 1.

[15] Horne, *Nature*, 1958, **181**, 410.

correction for the presence of the 1 : 2 complex, Milburn[16] obtained $*K_1 = 1{\cdot}22 \times 10^{-3}$, $*\beta_{22} = 1{\cdot}5 \times 10^{-3}$. Estimates, by interpolation from earlier results, were[17] $*K_1 = 7 \times 10^{-4}$, $*\beta_2 = 4 \times 10^{-7}$, and $*\beta_{22} = 1 \times 10^{-3}$. In the present work, formation of $Fe_2(OH)_2^{4+}$ was significant only at the highest ferric-ion concentrations.

Ferric–Acetate Complexes.—Although stable and reproducible oxidation–reduction potentials were obtained in perchlorate solutions containing ferric ion, ferrous ion, and acetic acid, preliminary experiments showed that these potentials depended on several independent variables: (i) At constant pH and constant free ferric-ion concentration, potentials varied with acetate-ion concentration. (ii) At constant free ferric-ion and acetate-ion concentrations, potentials were pH-dependent. (iii) At constant pH, acetate-ion concentration and ferric–ferrous ratio, potentials varied with ferric-ion concentration. On the other hand, the presence or absence of acetic acid did not appear to affect the ferric–ferrous potential observed in high concentrations of perchloric acid.

FIG. 1. *Hydrolysis of* Fe^{3+}.



$[Fe^{3+}]_T = 0{\cdot}00050$M.

Curve is for $E = 0{\cdot}4956 - 0{\cdot}0581 \log\left(1 + \frac{1{\cdot}08 \times 10^{-3}}{[H^+]} + \frac{8{\cdot}9 \times 10^{-7}}{[H^+]^2}\right)$

TABLE 1. *Evaluation of* $*\beta_{22}$ *from oxidation–reduction potentials.*

$[Fe^{3+}]_T = 0{\cdot}050$M. 1M in $NaClO_4 + HClO_4$. $*K_1$ and $*\beta_2$ obtained from Fig. 1.

pH	$E_0 - E$	$[Fe^{3+}]_T/[Fe^{3+}]$	$*K_1/[H^+] + *\beta_2/[H^+]^2$	$-\log *\beta_{22}$
1·89	0·0108	1·535	0·089	2·92
2·04	0·0163	1·907	0·130	2·88
2·22	0·0242	2·611	0·204	2·84
2·32	0·0287	3·118	0·265	2·84
2·41	0·0332	3·730	0·332	2·84

These results were interpreted to mean that complex formation occurred between ferric and acetate ions, that some or all of the complexes formed were ferric hydroxy-acetates, and that polynuclear complexes were present.

To obtain an estimate of the average number of ferric ions in the complexes, potential measurements were made at constant pH and constant acetate- and ferrous-ion concentrations but with varying amounts of ferric ion. Now if β_{xyz} ($x \geqslant 1$; y, $z \geqslant 0$) is the overall stability constant of any complex, $Fe_x(OH)_yL_z$, it can be deduced (see Appendix) from the electrode equation and the mass-action equation, that

$$\frac{0{\cdot}0581}{\partial E/\partial \log [Fe^{3+}]_T} = \frac{\sum x^2\beta_{xyz}[Fe^{3+}]^x[H^+]^{-y}[L^-]^z}{\sum x\beta_{xyz}[Fe^{3+}]^x[H^+]^{-y}[L^-]^z} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

where $[Fe^{3+}]_T$ is the total concentration of tervalent iron and $[Fe^{3+}]$ is the concentration of free ferric ion, provided only that the activity coefficients of the various ionic species remain constant. Eqn. (ii) is independent of the extent of any ferrous complex formation. Hence the slope of the plot of $0{\cdot}0581 \log [Fe^{3+}]_T$ against E depends on the degree of aggregation of the complexes; for any ferric-ion concentration the slope gives directly the average number of ferric ions that occur together in the solution.

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[16] Milburn, *J. Amer. Chem. Soc.*, 1957, **79**, 537.
[17] Perrin, *J.*, 1958, 3125.

Results plotted in Fig. 2, for a solution 0·058M in acetate ion and of pH 2·77, give a slope close to 3·0 as ferric iron varies from 5×10^{-5} to 1×10^{-2}M. In a similar experiment, at pH 2·37 and an acetate concentration of 0·0037M, the slope was about 2 for ferric-ion concentrations between 5×10^{-5} and 5×10^{-4}M, increasing to near 3 at higher concentrations.

The compositions and stability constants of the main complexes present were then sought. From the observed oxidation–reduction potentials, the ratio $[Fe^{3+}]_T/[Fe^{3+}]$, and hence $[Fe^{3+}]$, was calculated by using eqn. (i). But, in the presence of complex-forming species: [11]

$$[Fe^{3+}]_T/[Fe^{3+}] - (1 + \delta) = \sum x\beta_{xyz}[Fe^{3+}]^{x-1}[H^+]^{-y}[L^-]^z \quad (= R) \quad . \quad . \quad . \quad (iii)$$

where δ, the correction term for hydrolysis of ferric ion, is $*k_1/[H^+] + *\beta_2/[H^+]^2 + 2*\beta_{22}[Fe^{3+}]/[H^+]^2$, and x,y,z have the same significance as in eqn. (ii). When mainly one complex is present, eqn. (iii) can be written:

$$\log R - (x - 1) \log [Fe^{3+}] \simeq z \log [L^-] + y \text{ pH} + \log \beta_{xyz} + \log x \quad . \quad . \quad (iv)$$

The data in Fig. 3 were obtained where ferric iron was present mainly in trimeric complexes: this conclusion was based on the results discussed above. It was assumed, and subsequently confirmed from the stability constants obtained in the present work, that only one complex was important over the two ranges studied in Fig. 3. In the first experiment, made at constant pH (2·40), the plot of $\log R - 2 \log [Fe^{3+}]$ against $\log [L^-]$ gave $z = 6$. In the second experiment, at constant acetic acid concentration, but at varying pH, plotting the same quantities should give a line of slope, $y + z$. (This follows from the identity, pH = pK + log $[L^-]$ − log [HL]). In this way, a value of $y + z = 8$ was obtained. That is, the complex is $Fe_3(OH)_2(OAc)_6^+$. From the two sets of data in Fig. 3, the overall log stability constant, $\log \beta_{326}$, for $[Fe_3(OH)_2(OAc)_6^+][H^+]^2/[Fe^{3+}]^3[OAc^-]^6$, is 19·6 and 20·0, respectively. The value of this constant is extremely dependent on the accuracy of the pH measurement (which determines both $[OAc^-]$ and $[H^+]$).

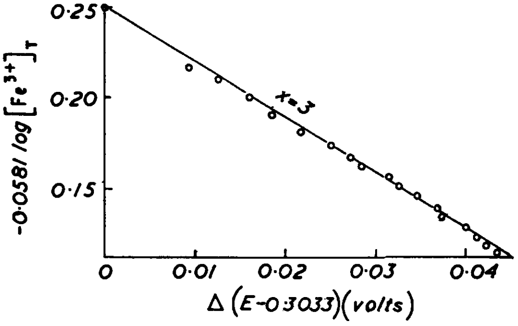


FIG. 2. *Determination of degree of aggregation of ferric iron in acetate solutions.*
pH = 2·77. $[OAc^-]$ = 0·058M.

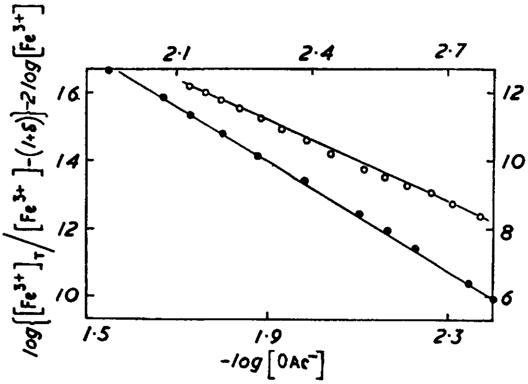


FIG. 3. *Determination of number of acetate and hydroxyl radicals in ferric complex.*
○ $[Fe^{3+}]_T$ = 0·00463M; pH = 2·40.
● $[Fe^{3+}]_T$ = 0·00425M; pH range 1·90—2·79.
Scales top and right are for open circles.

The results summarised in Tables 2 and 3 were obtained from measurements on solutions the compositions of which were varied by small, successive additions of 1M-$NaHCO_3$, 1M-$HClO_4$, or acetic acid–sodium acetate mixtures. As shown in Table 2, the assumption that only the

3 : 2 : 6 complex is present gives consistent stability constant values over wide range of conditions, with a mean value of log β = 19·8.

TABLE 2. *The stability constant of* $\mathrm{Fe_3(OH)_2(OAc)_6^+}$ *at 20° and unit ionic strength.*

$[\mathrm{Fe^{3+}}]_T$(M)	pH	log R*	−log $[\mathrm{Fe^{3+}}]$	− log $[\mathrm{L^-}]$	log β ± S.E. (no. of obs.)
0·000050	2·28—2·79	0·83—2·12	5·23—6·50	1·75—2·38	19·9 ± 0·2 (9)
0·000050	3·18—3·19	1·30—2·88	5·70—7·23	1·53—2·39	19·8 ± 0·2 (16)
0·00050	2·50	0·33—2·00	3·86—5·36	2·06—2·89	19·6 ± 0·1 (17)
0·0050	1·93—2·18	0·94—1·64	3·33—4·02	2·44—2·93	20·1 ± 0·1 (8)
0·0050	2·19—3·01	0·26—3·90	2·83—6·30	1·66—3·18	19·9 ± 0·2 (15)
0·050	2·33—2·41	1·73—1·94	3·11—3·33	2·78—2·98	20·3 ± 0·1 (9)
0·050	2·33—2·99	1·94—4·45	3·33—5·87	1·68—2·78	19·9 ± 0·1 (21)
				Overall mean	19·8 ± 0·2 (95)

* $R = [\mathrm{Fe^{3+}}]_T/[\mathrm{Fe^{3+}}] - (1 + \delta)$.

TABLE 3. *The stability constant of* $\mathrm{FeOAc^{2+}}$ *at 20° and unit ionic strength.*

$[\mathrm{Fe^{3+}}]_T$(M)	pH	$R_{\mathrm{corr.}}$ *	− log $[\mathrm{Fe^{3+}}]$	− log $[\mathrm{L^-}]$	log K_1 ± S.E. (no. of obs.)
0·000050	2·50	0·24—3·27	4·57—5·13	2·48—3·58	3·0 ± 0·05 (8)
0·000050	1·73—2·28	1·10—9·75	4·71—5·42	2·27—2·82	3·1 ± 0·2 (3)
0·000050	3·19—3·24	1·71—11·7	5·13—5·61	2·49—3·34	3·5 ± 0·03 (5)
0·00050	2·50	0·33—0·84	3·55—3·72	3·06—3·58	3·1 ± 0·02 (4)
0·0050	1·86—2·12	0·12—2·99	2·43—3·07	3·05—4·16	3·3 ± 0·1 (8)
0·0050	2·50	0·58—1·80	2·71—3·15	3·09—3·77	3·5 ± 0·03 (5)
				Overall mean	3·2 ± 0·2 (33)

* $R_{\mathrm{corr.}} = [\mathrm{Fe^{3+}}]_T/[\mathrm{Fe^{3+}}] - (1 + \delta)$, corrected for the 3 : 2 : 6 complex, using log β = 19·8.

TABLE 4. *Stability constants of ferric complexes of other aliphatic acids at 20° and unit ionic strength.*

$[\mathrm{Fe^{3+}}]_{T,M}$	pH	log R *	− log $[\mathrm{Fe^{3+}}]$	− log $[\mathrm{L^-}]$	log K_1 ± S.E. (no. of obs.)	log β_{326} † ± S.E. (no. of obs.)
Chloroacetic acid						
0·0050	2·47	−0·57—+0·22	2·64—2·87	1·99—2·68	2·16 ± 0·03 (6)	
0·0050	1·05—1·25	0·77—1·11	3·07—3·41	1·07—1·26	2·10 ± 0·06 (3)	
0·0050	2·47—3·04	0·44—1·48	2·96—3·86	1·47—1·85		11·2 ± 0·2 (8)
Formic acid						
0·010	2·33—2·47	−0·11—+0·97	2·49—3·10	2·18—3·31	3·12 ± 0·04 (11)	
0·010	2·33—2·85	1·05—2·19	3·18—4·28	1·67—2·11		14·3 ± 0·2 (4)
Propionic acid						
0·00050	2·49—2·56	−0·85—+0·07	3·56—3·80	3·39—4·22	3·38 ± 0·07 (5)	
0·00050	2·48	−1·42—−0·02	3·47—3·73	3·26—4·52	3·14 ± 0·06 (8)	
0·00050	3·07—3·08	−0·63—+0·75	3·89—4·29	3·20—4·34	3·80 ± 0·11 (6)	
0·0050	2·11—2·32	−0·09—+0·39	2·61—2·88	3·27—3·76	3·63 ± 0·03 (4)	
0·00050	2·61—2·71	0·63—1·40	4·15—4·85	2·69—3·06		21·2 ± 0·03 (6)
0·00050	2·50—3·52	0·63—3·15	4·17—6·59	1·92—2·90		20·4 ± 0·2 (7)
0·00050	2·30—2·80	1·61—2·91	4·94—6·23	1·89—2·38		20·6 ± 0·1 (5)
0·00050	3·08—3·20	0·94—2·54	4·42—5·97	2·21—3·05		21·0 ± 0·1 (13)
0·0050	2·00—3·17	0·71—4·48	3·03—6·85	1·50—3·07		20·6 ± 0·1 (18)
iso*Butyric acid*						
0·00050	3·01	−0·60—+0·14	3·85—3·97	3·67—4·36	3·78 ± 0·02 (3)	
0·00050	2·50—2·52	−1·14—−0·51	3·52—3·59	3·85—4·56	3·35 ± 0·18 (3)	
0·00050	2·97—3·06	0·33—2·28	4·04—5·68	2·57—3·50		22·3 ± 0·2 (10)
0·00050	2·56—2·63	0·47—1·43	4·01—4·85	2·80—3·23		21·9 ± 0·1 (6)

* $R = [\mathrm{Fe^{3+}}]_T/[\mathrm{Fe^{3+}}] - (1 + \delta)$.

† Corrected for 1 : 1 complex, using appropriate mean log K_1.

Summary of Table 4.

Acid	pK	log K_1	log β_{326}	Acid	pK	log K_1	log β_{326}
Chloroacetic	2·60	2·1 ± 0·05	11·2 ± 0·2	Propionic ...	4·66	3·45 ± 0·3	20·7 ± 0·3
Formic	3·49	3·1 ± 0·04	14·3 ± 0·2	*iso*Butyric ...	4·63	3·6 ± 0·2	22·1 ± 0·2
Acetic	4·55	3·2 ± 0·2	19·8 ± 0·2				

However, this constant underestimates the extent of complex formation at low concentrations and, to fit the results given in Table 3, it is necessary to assume that a 1 : 1 ferric-acetate complex, $\mathrm{FeOAc^{2+}}$, is also present, with a log stability constant of 3·2. This estimate is subject to rather large experimental uncertainty, because it is obtained under conditions where correction for hydrolysis of ferric ion becomes important and where differences in oxidation–reduction potentials are small.

Ferric Complexes with Other Aliphatic Acids.—Measurements of ferric–ferrous potentials were also made with solutions containing chloroacetic, formic, propionic, and *iso*butyric acids. At low iron concentrations in formic acid solutions, potentials were not stable but decreased steadily with time, probably indicating reduction of ferric ion; this drift was much slower at high ferric concentrations. For all the acids examined, the results (Table 4) can be interpreted quantitatively on the assumption that only 1 : 1 and 3 : 2 : 6 ferric complexes are present in significant amounts.

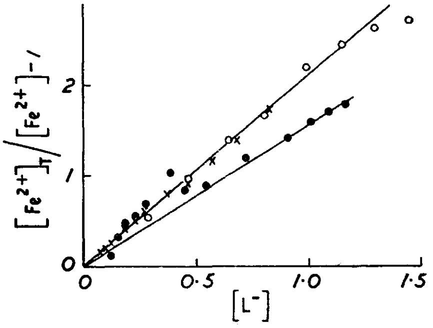


FIG. 4. *Determination of* K_1 *for 1 : 1 ferrous-aliphatic acid complexes.*

○ Acetic acid.
● Chloroacetic acid.
× Propionic acid.

TABLE 5. *Ferrous complex formation.*

$[\mathrm{Fe}^{2+}]_T = [\mathrm{Fe}^{3+}]_T = 0\cdot0050$M.

pH	$(E_0 - E)/$ 0·0581	$-\log[\mathrm{L}^-]$	$[\mathrm{Fe}^{2+}]_T/$ $[\mathrm{Fe}^{2+}]$	pH	$(E_0 - E)/$ 0·0581	$-\log[\mathrm{L}^-]$	$[\mathrm{Fe}^{2+}]_T/$ $[\mathrm{Fe}^{2+}]$
Chloroacetic acid							
1·40	1·373	0·932	1·12	2·21	3·009	0·263	1·88
1·52	1·600	0·821	1·33	2·41	3·322	0·140	2·19
1·62	1·798	0·731	1·49	2·60	3·597	0·042	2·41
1·72	2·016	0·644	1·56	2·71	3·733	−0·005	2·58
1·82	2·215	0·559	1·69	2·80	3·838	−0·038	2·69
2·00	2·546	0·413	2·03	2·89	3·941	−0·067	2·77
2·09	2·780	0·347	1·83				
Acetic acid							
3·73	6·397	0·540	1·54	4·52	7·66	0·003	3·19
3·99	6·875	0·332	1·96	4·67	7·85	−0·061	3·44
4·19	7·20	0·190	2·39	4·82	8·03	−0·113	3·61
4·35	7·45	0·093	2·66	5·00	8·23	−0·161	3·70
Propionic acid							
2·85	4·540	1·519	1·06	3·87	6·935	0·568	1·61
3·10	5·166	1·275	1·13	4·04	7·272	0·430	1·80
3·25	5·547	1·130	1·16	4·17	7·526	0·332	1·91
3·37	5·837	1·017	1·20	4·30	7·741	0·241	2·15
3·49	6·121	0·905	1·25	4·42	7·924	0·166	2·39
3·67	6·516	0·741	1·41	4·57	8·135	0·081	2·71
3·78	6·756	0·644	1·50				

Ferrous Complexes with Aliphatic Acids.—If higher ferric complexes are not formed when the concentrations of aliphatic acid anions are increased further, evidence of ferrous complex formation can be sought from oxidation–reduction potentials, by use of the equations:

$$\log [\mathrm{Fe}^{2+}] = (E_0 - E)/0\cdot0581 + 1/3 \log [\mathrm{Fe}^{3+}]_T - 2 \log [\mathrm{L}^-] - 2/3\ \mathrm{pH} - 1/3 \log 3\beta_{326}$$

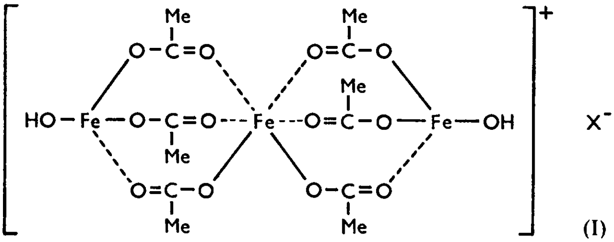
(which can be deduced from the mass action and electrode equations), and [11]

$$[\mathrm{Fe}^{2+}]_T/[\mathrm{Fe}^{2+}] - 1 = K_1[\mathrm{L}^-] + \beta_2[\mathrm{L}^-]^2 + \ldots .$$

Experimental data for chloroacetic, acetic, and propionic acids, summarised in Table 5, give K_1 = 1·6, 2·1, and 2·1, respectively (Fig. 4), but are not sufficiently extensive for K_2 to be estimated.

DISCUSSION

The present results suggest that, in acid solutions, anions of aliphatic acids form two series of stable ferric complexes. At low reactant concentrations the 1 : 1 complex, FeL^{2+}, is present. At higher concentrations the complex, $Fe_3(OH)_2L_6^+$, is the major species. The assumption that ferric-complex formation does not continue significantly beyond the 3 : 2 : 6 complex, at least in moderate concentrations of aliphatic acid anion, enables the stability constants of the 1 : 1 ferrous complexes to be obtained. This appears to be a reasonable assumption because the values so calculated are consistent with results for other cations.[1] Formic acid is anomalous; in high concentrations of formate ion a colourless complex is produced. For the acids examined, values of log β_{326} largely confirm earlier conclusions [3,8] concerning the sequence of stabilities of the ferric complexes. The increase from chloroacetate to propionate would be expected from the p*K*s of the acids, but the further increase to *iso*butyrate indicates that other factors are also involved.



(I)

The absence of appreciable concentrations of intermediate complexes implies that the 3 : 2 : 6 ferric complexes have a particularly stable configuration in solution. These complexes are probably analogous to the hexa-acetatodihydroxytrichromic complexes, first isolated by Weinland [18] and Werner.[19] In both cases it has been suggested [20] that the middle metal atom is at the centre of an octahedron, with 6 acetate radicals occupying the corners. Each of two opposite faces of the octahedron is the base of a tetrahedron, with a metal atom at its centre and a hydroxyl group at its apex. Thus the 3 : 2 : 6 ferric-hydroxyacetate complex would be as shown in (I). The alternative hypothesis, that a ring complex is formed,[21] is less convincing.[3]

The absorption spectra of the 3 : 2 : 6 ferric complexes of the aliphatic acids are very similar, with maxima at 337·5 and 465 mμ, inflexions near 395 and 515 mμ, and a minimum near 443 mμ. In addition there is a weak maximum near 448 mμ, with $\varepsilon_{448} < \varepsilon_{465}$ for the acetate complex, $\varepsilon_{448} \sim \varepsilon_{465}$ for propionate and chloroacetate, and $\varepsilon_{448} > \varepsilon_{465}$ for *iso*butyrate. Molecular extinction coefficients of 5010 and 199 were found at 337·5 and 465 mμ respectively for the ferric–acetate complex in 2M-sodium acetate–2M-acetic acid solution. In neutral and alkaline solution, changes in absorption spectra indicate that further complex formation occurs, but this has not been investigated. Except for a uniform reduction in intensity because of less complete formation of the complex, the ferric–acetate spectrum in 50% acetic acid [22] is the same as in less acid solutions. The absorption maximum at 337·5 mμ is probably similar in origin to the maximum at 335 mμ (log $\varepsilon = 4{\cdot}9$),[23] given by the dinuclear complex, $Fe_2(OH)_2^{4+}$, but not by mononuclear species such as Fe^{3+}, $FeOH^{2+}$, and $Fe(OH)_2^+$.[23]

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[18] Weinland, *Ber.*, 1908, **41**, 3236.
[19] Werner, *ibid.*, p. 3447.
[20] Reihlen, *Z. anorg. Chem.*, 1920, **114**, 65.
[21] Henrichsen, in Weinland's "Einführung in die Chemie der Komplexverbindungen," F. Enke, Stuttgart, 1924, 2nd edn., p. 398.
[22] Reiss, Hazel, and McNabb, *Analyt. Chem.*, 1952, **24**, 1646.
[23] Mulay and Selwood, *J. Amer. Chem. Soc.*, 1955, **77**, 2693.

APPENDIX

Derivation of Equation (ii).—If

$$\beta_{xyz} = [\mathrm{Fe}_x(\mathrm{OH})_y\mathrm{L}_z][\mathrm{H}^+]^y/[\mathrm{Fe}^{3+}]^x[\mathrm{L}^-]^z$$

for any complex, $\mathrm{Fe}_x(\mathrm{OH})_y\mathrm{L}_z$(where $x \geqslant 1$; $y, z \geqslant 0$), including hydrated ferric ion and its hydroxy-complexes, the total ferric-iron concentration,

$$\begin{aligned}[\mathrm{Fe}^{3+}]_\mathrm{T} &= \textstyle\sum x[\mathrm{Fe}_x(\mathrm{OH})_y\mathrm{L}_z] \\ &= \textstyle\sum x\beta_{xyz}[\mathrm{Fe}^{3+}]^x[\mathrm{H}^+]^{-y}[\mathrm{L}^-]^z\end{aligned}$$

Therefore,
$$\begin{aligned}\frac{\partial \log [\mathrm{Fe}^{3+}]_\mathrm{T}}{\partial \log [\mathrm{Fe}^{3+}]} &= \frac{[\mathrm{Fe}^{3+}]}{[\mathrm{Fe}^{3+}]_\mathrm{T}} \cdot \frac{\partial[\mathrm{Fe}^{3+}]_\mathrm{T}}{\partial[\mathrm{Fe}^{3+}]} \\ &= \frac{\sum x^2\beta_{xyz}[\mathrm{Fe}^{3+}]^x[\mathrm{H}^+]^{-y}[\mathrm{L}^-]^z}{\sum x\beta_{xyz}[\mathrm{Fe}^{3+}]^x[\mathrm{H}^+]^{-y}[\mathrm{L}^-]^z} \quad . \; . \; . \; . \; . \; . \; . \quad (1)\end{aligned}$$

($= x$ when all complexes present contain x atoms of ferric iron). But, at 20° and constant ionic strength,

$$E = E_0 + 0{\cdot}0581 \log [\mathrm{Fe}^{3+}]/[\mathrm{Fe}^{2+}]$$

Hence, at constant pH, $[\mathrm{Fe}^{2+}]$, and ligand concentration,

$$\partial\mathrm{E}/\partial \log [\mathrm{Fe}^{3+}]_\mathrm{T} = 0{\cdot}0581 \times \partial \log [\mathrm{Fe}^{3+}]/\partial \log [\mathrm{Fe}^{3+}]_\mathrm{T}$$

i.e.,
$$\frac{0{\cdot}0581}{\partial\mathrm{E}/\partial \log [\mathrm{Fe}^{3+}]_\mathrm{T}} = \frac{\partial[\log \mathrm{Fe}^{3+}]_\mathrm{T}}{\partial[\log \mathrm{Fe}^{3+}]} = (1) \text{ (above)}$$

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