CXLVIII.—*Organic Ferric Salts.*

By SPENCER UMFREVILLE PICKERING.

THE view that the copper in the cupri-compounds is in the electro-negative portion of the molecule, and that it is quadrivalent, has not found ready acceptance amongst chemists. That it is electro-negative can, however, no longer be doubted; it is only necessary to electrolyse these substances in order ocularly to demonstrate that such is the case; the quadrivalent condition of the element seems to be an almost inevitable consequence of this. Taking the simplest case, such as that of the cupriglycerate, which differs from the corresponding normal salt only by the elements of one molecule of water, since the copper is in the electronegative ion, the electropositive ion *must* be hydrogen; this hydrogen can only be derived from the elements of water which have been added on to the normal salt. The formula $\cdot\text{C}(\text{OH})_2\cdot\text{O}\cdot\text{Cu}\cdot\text{O}\cdot\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\cdot$, similar to that of monohydrated copper sulphate, is unacceptable, as such a compound would, on electrolysis, give copper as the electropositive ion; the only possibilities are:

which is extremely improbable, and

with the copper quadrivalent. The latter has been found to harmonise with some fifty or sixty cupri-compounds which have been isolated, and it now receives further support from the striking similarity found between these cupri-compounds and those of quadrivalent iron.

The so-called ferric salts of organic acids, except the oxalate, form very deep-coloured solutions, from which alcohol precipitates an emulsion, and on evaporation their solutions yield the solid in a scaly form, whilst the iron in them is found to be entirely in the electronegative portion of the molecule. In all these respects they closely resemble such a compound as the cupriglycerate, and are sharply differentiated from ordinary ferric salts. Many of the ferric organic compounds are on the market, and it has long been known that they do not give the ordinary reactions of iron, but the significance of this fact does not seem to have been realised; it is quite impossible that, for instance, ferric ferrocyanide should not be formed on the addition of a ferrocyanide, if the iron is the

[To face p. 1359.

electropositive ion of the salt, and its not being formed* is conclusive that these salts cannot be ordinary ferric compounds. In demonstration of this, it is found that the iron on electrolysis is present as a dark brown, electronegative ion. The accompanying figure reproduces photographs of the connecting tube of gelatin used in the electrolysis apparatus in the case of copper and iron compounds. The uppermost figure shows the results with copper sulphate; here a light blue electropositive ion is observed travelling through the gelatin, but, as it is not visible in a photograph, the gelatin was impregnated with potassium ferrocyanide, and the coloured zone looks dark. The second figure gives the results with cuprimalate, and here the presence of a dark blue electronegative ion is evident; this does not react with the ferrocyanide, which was present in the gelatin tube in this case also. There is at the same time some light blue, electropositive copper (which looks dark in the photograph owing to its reaction with the ferrocyanide) moving in the opposite direction. Solutions of most cupri-compounds are partly decomposed, giving some of the normal cupric salts, but, independently of this, the presence of electropositive copper would result from acid formed by the electrolysis of the sodium chloride, which is added to the gelatin to render it conducting, this acid decomposing the cupri-compound with the formation of cupric chloride.

The results with ferric compounds are strictly similar; the third and fourth figures are those obtained with ferric chloride, with and without ferrocyanide in the gelatin, respectively, and the fifth and sixth are those obtained with the malate. Judging by the entire absence of reaction on testing the malate for iron with ordinary reagents, the electropositive iron appearing on electrolysis is solely due to the presence of the sodium chloride in the gelatin.

Similar results were obtained with the citrate, ammoniocitrate, potassic citrate, tartrate, and more questionably so with the acetate, but the oxalate gave only electropositive iron. The last two, it may also be mentioned are not precipitated by alcohol from their aqueous solutions.

As regards their colour in solution, this appears to be of the same tint as that of ferric iron in inorganic salts, but very much more intense—the oxalate, again, being exceptional, and showing an intensity scarcely greater than that of ferric chloride. The question of colour intensity will be dealt with subsequently.

* The existing statements on this point are not very concordant. It has been found, however, that if the compound is quite neutral—which may be ensured by exposing it to ammonia gas, and heating at 100°—no trace of colour is produced by ferrocyanides, the only exceptional case being that of the oxalate, which in other respects, also, behaves like an ordinary ferric salt.

As minor peculiarities in which they resemble the cupri-compounds may be mentioned that, although they dissolve to a very great, and apparently unlimited, extent in water, most of them dissolve but slowly (like the cuprimalate, etc.), and after heating at 100° and exposure to moist air, most of them "scatter," like the scaly cupritartrate does (T., 1911, **99**, 170), so much so in the case of the ammoniocitrate that this salt cannot be weighed without special precautions.

As these compounds are not ferric salts, they must be ferri-compounds; their formula, however, cannot be identical with that of the cupri-compounds, for they contain the acid radicle and iron in the proportion of $R''_3:Fe_2$, instead of $R''_2:Fe$.

Formulae based on the same principle as those suggested for the cupri-compounds would be:

in one case the iron atoms being quadrivalent and not linked together; in the other, sexavalent, and united. These formulae differ from that of an anhydrous normal salt by the elements of $2H_2O$, but the difference would extend to $6H_2O$ if all the CO_2 groups became $C(OH)_2$ groups. There is no possibility of determining the proportion of constitutional water present, as the compounds dissolve very slowly after drying, and their solutions have the property of dissolving any ferric oxide which might have been liberated.*

The corresponding normal salts have not yet been obtained, as with the cupriglycerate and cuprimalate, (although, as mentioned, the oxalate is a normal salt, as also is the insoluble salicylate); but compounds with excess of ferric oxide have been prepared, both as ferri-compounds and as ferric salts, as in the case of the copper compounds with citric acid. These are represented by $R''_3Fe_2, Fe_2O_3, 6H_2O$ in the case of the tartrate, and probably by the same formula in the case of the malate (certainly so as regards the ferrimalate form of it); the citrate compounds are probably also similar, but evidence as to their composition is less satisfactory.

* For the citrate, Rieckher (*Jahrb. Chem.*, 1873, **40**, 65) gives $R'''_2Fe_2, 3H_2O$ at 100°, anhydrous at 120°; Kämmerer (*Annalen*, 1873, **170**, 186) gives $3H_2O$ as retained on the air-dried salt, and Fehling (*Neues Handw.*, II, 744) mentions (without giving references) a salt with $6H_2O$, losing $3H_2O$ at 120°, and all the water at 150°. These data are of questionable value (see below).

The Compounds $[R''_3R'''_2]Fe_2, Fe_2O_3$.

Ferri-compounds of this formula are precipitated as emulsions by the addition of alcohol to solutions of the so-called ferric tartrate, malate, or citrate, whether these are neutral, saturated with ferric hydroxide (which they dissolve in excess of that required by the formula R''_3Fe_2), or whether considerable excess of acid is present. On exposure to air, the drops of the very strong solutions which constitute these emulsions coalesce readily, the whole becoming liquid. The substances in these solutions must, of course, be highly soluble, but when dried in a vacuum—which can be done without any apparent liquefaction, if small quantities are dealt with—the resulting buff or brown powders contain, in the case of the tartrate, only a small proportion of soluble salt, and the greater part of that, even, will change into the insoluble form, if a solution of it is left for several days. The insoluble salt, which there is no reason to regard otherwise than an ordinary basic salt, is also generally obtained as a light brown, minutely crystalline deposit when a solution of the normal tartrate is left to evaporate slowly over acid, the whole mass gradually solidifying. It is obtained in larger and much darker crystals when a weaker solution is kept without evaporation for several months: the crystallisation does not start for several weeks, and if it has been kept in the light, some ferrous tartrate is eventually formed. Its solubility is 0.008 gram of iron per 100 c.c., but it is probable that this solubility is only apparent, being due to a partial transformation of it into the ferri-compound, since the iron in solution is electronegative.

The precipitated ferrimalate and ferricitrate emulsions on drying appear also to be transformed partly into the corresponding basic salts, but are reconverted into the ferri-compounds on treatment with water to a much greater extent than with the tartrate, so that quite strong, dark solutions of them are obtainable, especially with the malate, although dissolution is very slow, requiring one hour or more, the time varying considerably according to the previous treatment of the salt. Solutions of these ferri-compounds gradually deposit basic precipitates, but it has not been established that these are metameric with the corresponding ferri-compounds, as in the case of the tartrate, and they have not been obtained crystallised. On boiling, the solutions give a somewhat highly basic precipitate, which redissolves in the cool liquid after a day or two.

The experimental data are:

Eight preparations of *ferrimalate* precipitated by alcohol gave as means:

	Dried at 100°.	Dried at 130°.	
Normal salt taken	28.52	30.56	per cent. Fe
Salt with excess of hydroxide	28.59	30.39	" "
" " " " acid	28.52	30.68	" "
Calc. for $R''_3Fe_2, Fe_2O_3, 6H_2O$	28.80	—	" "
" " $R'_3Fe_2, Fe_2O_3, 3H_2O$	—	30.96	" "

In four other cases—not all cases in which excess of acid was present—lower values down to 26.1 per cent. at 100° were found. None of these approached that of the normal salt, which, even in the anhydrous condition, contains 21.94 per cent. of iron.

The *ferritartrate* showed greater variation, although not apparently connected with the presence of excess of hydroxide or acid in the solutions taken :

	Dried at 120°.	
Three preparations gave values up to.....	29.7	per cent. Fe
Two " " " down to ...	23.4	" "
Seven " " " of mean ...	27.09	" "
Mean of the twelve preparations ...	27.07	" "
Calc. for $R'_3Fe_2, Fe_2O_3, 6H_2O$	27.12	" "

The crystalline basic salt gave, as a mean for two preparations, 27.29 per cent. of iron at 120°. This temperature was selected for desiccation, as the preparations lost water very slowly indeed, and did not become satisfactorily constant, at 100°. The iron percentage on the weights at 100° were about 0.8 lower.

With the *ferricitrate* the results were unsatisfactory. The emulsion was so finely divided that filtration and washing was very difficult, a porous candle having to be used. Four preparations gave 25.74 per cent. of iron at 100° (24.8 to 26.6; this falls short of the requirements of a compound $R'''_2Fe_2, Fe_2O_3, 6H_2O$ (29.49 per cent. Fe), but is in excess of those of the normal salt, which, even if anhydrous, would contain 22.8 per cent.

Solutions of the oxalate and acetate are not precipitated by alcohol. The ferric benzoate, succinate and valerate on the market are insoluble basic salts, represented approximately by the formula $[R''_3R'_6]Fe_2, Fe_2O_3, 3H_2O$ after drying at 100°, and there is a basic acetate $(R_6Fe_2)_3Fe_2O_3$.

The Compounds $(R'_6R''_3)Fe_2$.

The existence of the scale preparations of organic ferric salts as definite compounds has been called in question by F. B. Power (*Pharm. Rundschau*, 1891, **9**, 205), and his doubts seem to be justified by the antiquated and unsatisfactory state of the literature on the subject,* although evidence has now been obtained

* In several cases the statements in books of reference seem to be at variance with the evidence on which they are founded.

as to the individuality of these compounds. Attention had previously been directed chiefly to the citrate, and amongst the statements respecting it the most important is that of Rieckher (footnote, p. 1371) that some crystals were obtained agreeing fairly well with the composition $R'''_2Fe_2, 3H_2O$ at 100° . No such crystals, however, have been obtained by the present author, nor by other investigators. The difficulty is that these organic salts, just like the inorganic ferric salts, are capable of dissolving excess of ferric hydroxide, and, being uncrystallisable, evidence as to their true composition is hard to obtain. In the manufacture of them, the hydroxide and acid are taken in calculated proportions, and the product of the reaction is evaporated to a point when it will solidify when poured out on porcelain slabs.

As bearing on the behaviour of these substances, certain facts as to the inorganic salts must be notified. The chloride, nitrate and sulphate, when digested in the cold with freshly precipitated ferric hydroxide, gradually dissolve considerable quantities of it, but, after a time, the clear, dark solutions thus obtained deposit a precipitate either of ferric hydroxide in another form, or of a basic salt. With the chloride, the proportion of hydroxide which can be dissolved may reach about $20Fe_2O_3$ to each Fe_2Cl_6 , as established by previous investigators (Maus, *Pogg. Ann.*, 1827, **11**, 77; Phillips, *Phil. Mag.*, 1830, [iii], **8**, 406; Ordway, *Amer. J. Sci.*, 1868, [ii], **26**, 197; Béchamp, *Ann. Chim. Phys.*, 1859, [iii], **56**, 306; **57**, 296; Scheurer-Kestner, *Ann. Chim. Phys.*, 1862, [iii], **65**, 110; Hausmann, *Annalen*, 1854, **89**, 109; Scharizer, *Zeitsch. Kryst. Min.*, 1900, **32**, 338), but no definite limit has been obtained, and in the present experiments deposition of the insoluble hydroxide generally began long before this proportion had been reached. When, after several months, the deposition had apparently ceased, the precipitate was found to consist of pure ferric hydroxide, and the solution contained only a very small excess of iron, having the composition $33Fe_2O_3 + Fe_2Cl_6$.

By dialysing the original solution, liquids containing up to $47Fe_2O_3 + Fe_2Cl_6$ were obtained.

With the nitrate, the proportion of hydroxide dissolved reached nearly $20Fe_2O_3$ to $Fe_2(NO_3)_6$. The deposit eventually forming could not be separated satisfactorily by filtration, and was completely soluble in water. Dialysis increased the proportion to $33Fe_2O_3$ to $Fe_2(NO_3)_6$.

With the sulphate, the composition of the liquid left after deposition of the basic salt had become complete showed it to consist of $Fe_2(SO_4)_3, Fe_2O_3$ (ratio found, $Fe : SO_3 = 1 : 1.052$. Maus obtained the same ratio), but the precipitate was a basic salt of, probably,

indefinite composition, $\text{Fe}:\text{SO}_3=11:9$. On dilution of the solution, a still more basic salt, $\text{Fe}:\text{SO}_3=10:2\cdot04$, was precipitated.

In order to examine the behaviour of organic ferric salts, precipitated ferric hydroxide was digested with the acid in various proportions at 20° until the action was complete; the quantity of hydroxide which had dissolved was then determined. The mean results of several series are given in the accompanying table, "equivalent" being used as meaning the proportion required to form a normal salt.

Ferric Hydroxide Digested with Acids.

Equivalents of Fe_2O_3 taken to 1 equivalent of acid.	Equivalents of Fe_2O_3 dissolved.		
	Tartaric acid.	Malic acid.	Citric acid.
1·0	1·00	1·00	1·00
1·1	1·009	1·088	1·098
1·25	0·857	1·184	1·230
1·5	0·632	1·248	1·180
2·0	0·406	1·264	1·086
3·0	0·153	0·861	0·744

In all three cases quantities up to one equivalent of hydroxide dissolved completely—generally in one to four days—forming dark solutions which remained permanently clear; but beyond this point, although some of the excess of hydroxide dissolved, its dissolution was accompanied by the formation of an insoluble basic salt, which, unlike the hydroxide originally taken, was pale yellow, and filtered badly. The proportion of equal equivalents of hydroxide and acid is, therefore, a point at which the character of the reaction changes, thus affording evidence of the existence of compounds of this composition. As the proportion of hydroxide taken is increased beyond our equivalent, that dissolving increases at first (although very slightly so with the tartrate), but subsequently diminishes, so much so in the case of the tartrate, that when three equivalents of hydroxide are taken, only 0·15 equivalent remains in solution. What happens is that the excess of hydroxide, or part of it, first dissolves, forming an unstable compound, which gradually changes into the metameric basic salt. The change is shown by the following determinations, wherein two equivalents of hydroxide were digested with one of tartaric acid, and gave:

After $\frac{1}{2}$ day	0·94 equivalent in solution.
„ 1 „	0·89 „ „ „
„ 2 days	0·74 „ „ „
„ 3 „	0·55 „ „ „
„ 6 to 16 days	0·20 „ „ „

An analysis of the precipitate in this case did not, however,

yield satisfactory results, due, no doubt, to there being particles of unchanged ferric hydroxide enclosed in those of the basic salt.

The results with the malate and citrate are evidently similar to those with the tartrate, but the ferri-compounds of these acids are more stable than the ferritartrate, and, consequently, more of them remains in solution. In their case an examination of the solution at various intervals of time did not give any evidence that the deposition of the basic salt was subsequent to the dissolution of the hydroxide; the two actions may, of course, follow each other so rapidly that such evidence would be unattainable. In the case of the citrate, when two equivalents of hydroxide were taken, a condition of equilibrium was reached within two days; with the malate, about twenty days were necessary.

Temperature, apparently, has little effect on the final condition of equilibrium; in all three cases, mixtures with three equivalents of hydroxide which had attained equilibrium at 20° , were heated for two hours at 100° without that condition being sensibly modified.

The behaviour of the organic ferric salts in dissolving excess of ferric hydroxide, and subsequently depositing a basic salt, is similar to that of the inorganic salts, but the excess of hydroxide which dissolves is much smaller, and it is possible that the action in the two cases may be fundamentally different, for the hydroxide dissolving in the inorganic salts is in the colloidal condition, and it is doubtful whether this is so in the case of the organic salts. The matter is being investigated; certainly, where no excess of ferric hydroxide is present, the iron in the organic salts dialyses freely, even from very dilute solutions. This dialysis, however, must be conducted in the dark, or a ferrous salt may be formed in some cases.

Ferric hydroxide was digested with acetic acid in the same way as with the other acids, but the behaviour in that case appeared to resemble that of the inorganic acids. The hydroxide dissolved in considerable quantities (2.7 equivalents), but the action was not followed to its completion, and no deposit had begun to form within ten days.

Under the heading of salts of the type R'_6Fe_2 may be mentioned the salicylate, which is represented by this formula after drying at 100° . It is insoluble, and is doubtless a ferric salt, not a ferri-compound.

Behaviour with Alkalis.

When an alkali is added to the ferri-compounds, $[R''_3R'''_2]Fe_2$, no precipitate is formed, and a considerable amount may be added before alkalinity is obtained. Using dilute solutions, and phenol-

phthalein as indicator, the proportion of potassium hydroxide required for alkalinity represented:

With the citrate.....	4.16K for each Fe_2 present.
„ „ malate	5.56 „ „ „ „
„ „ tartrate	4.80 „ „ „ „
„ „ acetate	6.26 „ „ „ „

With these highly coloured solutions the reaction point cannot be determined with any certainty, but the results are not sufficiently concordant to indicate a simple and identical action in all cases. If the potassium compounds formed were analogous to the compounds $\text{R}''_3\text{Fe}_2\text{Fe}_2\text{O}_3$, the potassium hydroxide required would = 6K; this is approximately the value with the acetate and malate, but in the other cases the values are much lower. The commercial preparations of so-called potassio-ferric citrate, and analogous compounds containing ammonia or alkaloids, are of indefinite composition.

Ferric oxalate behaves differently from the ferri-compounds, an alkali causing precipitation.

Attempts to Prepare Other Ferri-compounds.

Most organic copper salts dissolve in alkalis to form cupri-compounds, and if a similar reaction occurred with ferrous salts, the ferri-compound formed should contain quadrivalent iron, although such compounds would not be the same as those discussed above, with $\text{R}''_3 : \text{Fe}_2$, which could not be formed from ferrous salts without oxidation.

That ferrous tartrate dissolves in alkalis is already known. When a strong solution of ferrous sulphate is mixed with one of sodium tartrate, the mixture gradually becomes semi-solid, owing to the formation of a white precipitate; this is minutely crystalline, moderately soluble in water, and redissolves in the liquid when warmed, being reprecipitated on cooling. If the clear, heated solution is boiled, a second white, but amorphous and denser, precipitate is thrown down. The latter is ferrous tartrate, which is anhydrous at 100° ; the first precipitate is a double tartrate with the formula $4\bar{\text{T}}\text{Fe}, \bar{\text{T}}\text{Na}_2$, after drying at 100° (Found, $\text{Fe} = 21.58$; $\text{Na} = 4.71$; ratio, 2 : 1.006. Calc., $\text{Fe}_2 = 22.13$; $\text{Na} = 4.56$ per cent.).

When either of these, or the liquid containing them in the freshly precipitated condition, is mixed with sodium hydroxide, they dissolve, forming a colourless, very viscid liquid. The proportion of alkali required for dissolving the precipitate being NaOH to each Fe, indicating the formation of a compound $\bar{\text{T}}\text{Fe}, \text{NaOH}$, or $\bar{\text{T}}_2\text{FeNa}_2, \text{NaOH}$. On the addition of alcohol, the whole of the iron is precipitated as a white, flocculent, sticky mass, and this precipita-

tion also occurs when the liquid, without the addition of alcohol, is kept in a sealed tube for several days. A direct analysis of the precipitate has not been possible. It is exceedingly oxidisable, and is best manipulated under a thick layer of benzene. It dissolves in water, forming a strongly alkaline liquid, but undergoes considerable decomposition at the same time, ferrous hydroxide being separated. On oxidation the solution becomes reddish-brown, the ferritartrate (so-called ferric tartrate) being formed. With suitable precautions against oxidation, it can be proved that the iron in it is still in the ferrous condition, and when it is electrolysed (under benzene) this iron is found to be entirely electropositive. Being colourless, the ferrous ion is not visible without the addition of ferricyanide to the gelatin, but in the alkaline liquid it does not react with the ferricyanide. Its presence, however, can be recognised by immersing the gelatin tube, after the electrolysis, in weak acid for a few minutes. This affords further argument in favour of copper in the cupri-compounds being quadrivalent, for when the metal, in the case of iron, does not become quadrivalent, we find none of the other changes which characterise the action in the case of copper, namely, intense coloration and transference to the electronegative position.

The nature of the compound formed by alkalis with ferrous tartrate can only be conjectured; it may be analogous to a hydrol, containing the group:

or the alkali metal may be present in substitution of H in a CH·OH group.

A similar compound is formed in the case of the racemate, but it is decomposed by water much more rapidly than the tartrate. Attempts to obtain analogous compounds in other cases have failed, the addition of alkali to the ferrous salt precipitating ferrous hydroxide at once; an appreciable amount of iron remained in solution, however, in the case of the citrate, but traces only in that of the malate, glycollate and lactate, and none in that of the acetate, oxalate, succinate, salicylate and phthalate.

Summary.

Evidence as to the definiteness of ferric organic salts of the type $\text{R}''_3\text{Fe}_2$ is given by the dissolution of ferric hydroxide in different proportions of acid. The oxalate is a normal salt, but the tartrate, malate and citrate are ferri-compounds closely resembling the cupri-compounds; the iron is in the electronegative ion, does not give the usual reactions of iron, and possesses great colour intensity. The compounds are very soluble, and solidify in scale form. The

corresponding normal ferric salts have not been obtained in these cases. Alcohol precipitates, from their solutions, emulsions consisting of a very soluble ferri-compound of the type R''_3Fe_2, Fe_2O_3 , which change into insoluble basic salts of a similar formula. Both these metamerides are obtained in succession when the acid is digested with excess of ferric hydroxide. Their exact composition in the case of the citrate is not certain. The benzoate, succinate and valerate are basic salts of the same type, of which no corresponding ferri-metamerides have been obtained.

Ferrous organic salts do not yield ferri-compounds, as cupric salts do, with an alkali.

HARPENDEN.