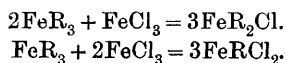


XXXIII.—*Action of Ferric Chloride on Ethereal Salts of Ketone Acids.*

By ROBERT SELBY MORRELL, M.A., Ph.D., and JAMES MURRAY CROFTS, B.A., B.Sc.

THE colour reactions between ferric chloride and organic substances, especially di-ketones and ethereal salts of ketone acids, have been investigated by Claisen, Traube, and Wislicenus, but the compounds formed have not as yet been isolated. Claisen (*Annalen*, 1894, **281**, 344) has observed that the red, crystalline ferriacetylacetone, $\text{Fe}(\text{C}_5\text{H}_8\text{O}_2)_3$, or ferribenzoylacetone, $\text{Fe}(\text{C}_{10}\text{H}_{10}\text{O}_2)_3$, dissolved in alcohol, gives a red solution, and on the addition of aqueous ferric chloride, a much deeper red coloration is produced, just as when aqueous ferric chloride is added to acetylacetone or benzoylacetone. A series of colour changes also occurs when alcoholic solutions of ferrioxymethylenecamphor are treated with aqueous ferric chloride.

The iron salts mentioned above are insoluble in water, but the alcoholic solutions, after treatment with ferric chloride, can be diluted with water to any extent, without separation of the insoluble iron salts. Claisen considers that the reaction with ferric chloride may be expressed by the following equations.



[R is the residue of acetylacetone or oxymethylenecamphor or benzoylacetone.]

The red or violet colorations which ferric chloride gives with alcoholic solutions of ketone ethereal salts may be due to the formation of soluble salts of the type FeR_2Cl or FeRCl_2 (Claisen).

Claisen, Traube, and Wislicenus consider that the colour reaction

with ferric chloride indicates the existence of an enolic grouping in di-ketones and ethereal salts of di-ketone acids.

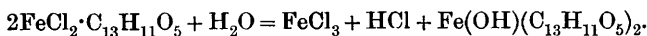
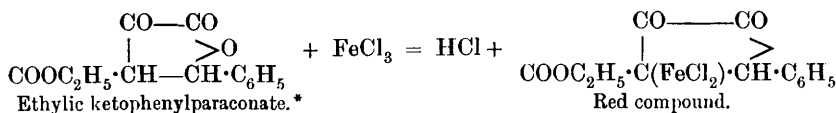
Traube (*Ber.*, 1896, **29**, 1718) points out that the shade and intensity of the colour depends on the solvent used, strongly associated solvents, such as water, methylic alcohol, and ethylic alcohol, favouring the production of the enolic form, whilst in non-associated solvents, such as benzene, chloroform, and carbon tetrachloride, the aldo-form is much more stable.

Knorr (*Ber.*, 1897, **30**, 2387) has isolated five tautomeric ethylic di-acetylsuccinates, two of the forms giving the ferric chloride reaction, and being considered to contain enolic groupings in the anti-position. The keto-forms, in solution, pass into the enolic forms, and *vice versa*, until equilibrium is attained.

We noticed that when ethylic acetoacetate was added to a solution of anhydrous ferric chloride in dry ether, a deep violet oil separated. The production of a coloured oil was also observed in the case of ethylic methylacetoacetate, ethylic ethylacetoacetate, ethylic benzilidenedi-acetoacetate, ethylic oxalacetate, ethylic ketophenylparaconate, and the lactone of ethylic oxalocitrate. In the last three cases, the oils were of a deep red colour. By washing with dry benzene or dry ether, and removing the excess of the benzene or ether in a vacuum, the purple oil from ethylic benzilidenedi-acetoacetate and the red oil from ethylic ketophenylparaconate became solid. Only in these two instances have we as yet been able to obtain solids almost free from ferrous iron, and we are inclined to consider the red substance from ethylic ketophenylparaconate as a derivative of ferric chloride, one chlorine atom of the FeCl_3 being replaced by the univalent residue of the ethereal salt, whilst the red oil from the lactone of ethylic oxalocitrate, may be regarded as an additive product of ferric chloride and the lactone salt.

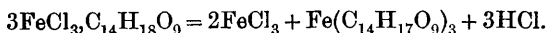
The evidence in support of these views may be summarised as follows.

(a) The red solid from ethylic ketophenylparaconate is decomposed by excess of water into ferric chloride and a basic iron salt of ethylic ketophenylparaconate. The analysis of the red substance shows the presence of both chlorine and iron, nearly in the proportions required for $\text{FeCl}_2 \cdot \text{C}_{12}\text{H}_{11}\text{O}_5$; the red colour is more stable in aqueous solution towards ether, and in ethereal solution towards chloroform, than in the case of the purple colorations, as when ferric chloride solution is added to ethylic acetoacetate, hydrochloric acid is produced in the reaction, without any oxidation by the ferric chloride occurring. The formation of the red compound from ethylic ketophenylparaconate, and its decomposition by water, may probably be expressed by the following equations,



The hydrochloric acid formed decomposes some of the red compound into ferric chloride and the original ethylic ketophenylparaconate.

(b) The red oil from ferric chloride and the lactone of ethylic oxalocitrate is either an additive product of ferric chloride with the lactone of the ethereal salt, or an FeCl_2X compound (where X is the acid radicle of the lactone of the ethereal salt). It does not contain the FeX_3 salt, since it is insoluble in benzene, whilst the iron salt is easily soluble. Moreover, with water, it undergoes a similar decomposition to that in the case of the ketophenylparaconic substance, giving ferric chloride and the normal ferric salt of the organic acid. This decomposition may be expressed by the equation,



The formation of coloured oils with ethereal ferric chloride and the ethereal salts of ketonic acids may lead to the separation of the enolic from the ketonic forms. It is our intention to examine this, and to endeavour to isolate the tautomeric modifications.

EXPERIMENTAL PART.

Action of Anhydrous Ferric Chloride on Ethylic Ketophenylparaconate.

Ethylic ketophenylparaconate was prepared from benzaldehyde and ethylic oxalacetate (Wislicenus, *Ber.*, 1892, 25, 3448), and recrystallised several times from alcohol. Ferric chloride, dissolved in dry ether, and ethylic ketophenylparaconate were mixed in exact molecular proportions, the red oil which separated was washed by decantation with anhydrous ether, and excess of the latter removed in a vacuum. Hydrochloric acid was given off, but no ferrous iron could be detected. After the removal of the acid in a vacuum over soda-lime, and the addition of more dry ether, a dark red, crystalline powder separated, which was washed on the filter with more dry ether and then dried in a vacuum. Analyses

	Oil freed from HCl in a vacuum.	Red powder.
Fe.....	15.56	15.28, 15.81.
Cl.....	19.5	21.8, 21.5, 19.55.
$\text{FeCl}_2 \cdot \text{C}_{13}\text{H}_{11}\text{O}_5$ requires Fe = 14.97 ; Cl = 19.0 per cent.		
$\text{FeCl}_3 \cdot \text{C}_{13}\text{H}_{12}\text{O}_5$ „ Fe = 13.6 ; Cl = 25.94 „		

* Wislicenus and Hjensen (*Ber.*, 26, 2144).

The red oil, if left for some weeks under dry ether, becomes crystalline (long rhombic needles). These crystals were washed with ether until the washings gave only a trace of iron and chlorine.

Melting point, 146—147° with decomposition. On analysis, it gave Fe = 13.29; Cl = 15.52; C = 41.9, 41.22, 39.4; H = 4.2, 4.19, 4.16.

This substance could not be purified further; it is probably some of the FeCl_2X compound which has undergone decomposition.

Action of Water on the Red Compound.

Cold water removed 11 per cent. of iron and 21.4 per cent. of the chlorine, that is, all the chlorine, from the red powder. The dark red solid left was dried on a tile and added to hot methylic alcohol; on rapidly filtering, an orange, crystalline substance was deposited, which could not be redissolved in the same solvent. The analysis showed it to be a basic ferric salt of ethylic ketophenylparaconate, identical with that obtained by the addition of aqueous ferric chloride to ethylic ketophenylparaconate dissolved in alcohol, and subsequently diluting with much water. Analysis.

	Fe.	C.	H.
I.	10.32	54.93	4.7.
II.	9.94	55.00	4.3.

$\text{Fe}(\text{OH})(\text{C}_{13}\text{H}_{11}\text{O}_5)$ requires Fe = 9.87; C = 55.0; H = 4.05 per cent.

The iron salt crystallises in aggregates of needles, and melts at 202° with decomposition. It is different from the basic salt obtained by the addition of ferric acetate to ethylic ketophenylparaconate, being orange, not buff brown, and containing much less iron. In the decomposition of the red powder by cold water, some of the ethylic ketophenylparaconate was always produced, and could be isolated from the alcoholic mother liquor of the basic salt.

Action of Ferric Chloride on the Lactone of Ethylic Oxalocitrate.

Ethylic oxalocitrate was prepared from ethylic oxalacetoacetate by the action of aqueous potassium acetate, according to the directions given by Claisen and Hori (*Ber.*, 1891, 24, 120); it was purified by converting it into the barium salt, and decomposing the latter by dilute sulphuric acid.

Anhydrous ferric chloride, dissolved in ether (which had been dried over sodium), was freed from hydrochloric acid by shaking with iron filings, and added to the calculated quantity of the lactone of ethylic oxalocitrate. The ferric chloride used was always analysed, and the ratio of iron to chlorine agreed very nearly with that for FeCl_3 ; the red oil which separated was washed thoroughly with ether, dried over sodium,

by pouring from one separating funnel to another. The last traces of ether were removed in a vacuum over sulphuric acid; at the same time, acid fumes began to be evolved, although no ferrous iron could be detected. The oil became viscid, and a few crystals were visible. As we could not obtain the substance in crystals, the oil was analysed directly. The values for the iron were those for an additive product of ferric chloride and the lactone of ethylic oxalocitrate.

Fe = (1) 11.23; (2) 11.82; (3) 13.03; (4) 12.28 (12 days in a vacuum).

Cl = (1) 23.88; (2) 22.30; (3) 21.98; (4) 21.72 (14 , ,).

$\text{FeCl}_3 \cdot \text{C}_{14}\text{H}_{18}\text{O}_9$ requires Fe = 11.37; Cl = 21.62 per cent.

$\text{FeCl}_2 \cdot \text{C}_{14}\text{H}_{17}\text{O}_9$ requires Fe = 12.28; Cl = 15.57 ,

It seemed as if the chemical behaviour of the compound would give more information regarding its composition than analyses of a substance which has, up to now, resisted all attempts to purify it completely.

The red oil is insoluble in benzene, carbon tetrachloride and light petroleum, sparingly soluble in ether, but readily so in alcohol and acetone.

The decomposition with water is similar to that in the case of the iron compound with ethylic ketophenylparaconate. Nine grams of the red oil, freed from ether in a vacuum, were washed rapidly with cold water, and then with warm water, until the washings were free from iron and chlorine; the oily residue became solid on being stirred with a glass rod. The solid can be dissolved in ether and precipitated as a red solid, by the addition of light petroleum, or it may be dissolved in methylic alcohol and precipitated by water. To obtain this solid pure, it may be redissolved in methylic alcohol and precipitated with water, or crystallised from benzene, in which it is easily soluble, separating out on evaporation in stout, rhombic prisms.

Analysis showed that this red substance was the iron salt of the lactone of ethylic oxalocitrate.

C = 48.35; H = 5.22; Fe = 5.30.

$\text{Fe}(\text{C}_{14}\text{H}_{17}\text{O}_9)_3$ requires C = 48.32; H = 4.89; Fe = 5.37 per cent.

The iron salt melts at 163° with decomposition. In order to investigate the decomposition by water, the amounts of iron and chlorine washed out by water, and the weight of iron salt left, were estimated.

2.1243 grams of the oil, which had been standing several days in a vacuum over sulphuric acid, were washed, first with cold and then with hot water, about 500 c.c. of water being necessary to remove all the chlorine from the oil. The iron in the washings was estimated volumetrically by stannous chloride and potassium dichromate, the

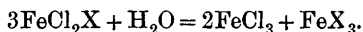
350 RUHEMANN : FORMATION OF *aa'*-DIHYDROXYPYRIDINE.

chlorine by titration with excess of silver nitrate and ammonium thiocyanate.

$$\text{Fe} = 10.52; \text{Cl} = 22.56 \text{ per cent.}$$

The oil which was treated with water was part of the sample containing 13.03 per cent. of Fe and 23.88 per cent. of Cl, but had stood for a longer time in a vacuum over sulphuric acid.

The weight of the iron salt left was 0.7013 gram. If the substance were an additive product, then water would decompose it, and at the same time some free hydrochloric acid, produced by the action of excess of water on the ferric chloride, would act on the iron salt, with the production of the soluble basic ferric chloride and the lactone ethereal salt. If, on the other hand, the compound FeCl_2X existed, then it would undergo decomposition according to the equation



That the iron salt itself exists in the oil is unlikely, for benzene does not take up the oil, whilst the iron salt is very easily soluble in that solvent.

In the case of the sodium salt of the lactone of ethylic oxalocitrate dissolved in dry benzene, a red solution was produced, without any separation of oil, when dry ethereal ferric chloride was added in the proportions to give FeCl_2X or FeX_3 . This points to the formation of an iron salt of the type FeX_3 , since the latter substance is soluble in benzene, whereas the additive product, or the FeCl_2X compound, is insoluble.

Further attempts are being made to obtain other similar red and violet ferric chloride compounds in a purer form.

GONVILLE AND CAIUS COLLEGE LABORATORY,
CAMBRIDGE.
