ON THE USE OF ORGANIC BASES IN THE PREPARATION OF BARIUM AND CALCIUM FERROCYANIDES.

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THE methods hitherto proposed for the preparation of ferrocyanides of barium and calcium are based either upon the decomposition of Prussian blue by the hydroxides of barium or calcium ; or upon double decomposition of barium or calcium salts on the one hand, and potassium ferrocyanide on the other.

It is very difficult to prepare Prussian blue free of potassium, and the double ferrocyanides of barium or calcium with potassium are formed more readily than the simple salts. Even when the simple salts are formed, if any potassium salt has been used in the preparation, it is almost impossible to remove the whole of the potassium by recrystallization.

After trying various other methods for the preparation of barium ferrocyanide, and having very poor success, I undertook, at the suggestion of Dr. Launcelot Andrews, to prepare it according to the following method:

This method depends upon the formation of the normal strychnine ferrocyanide, the decomposition of this with ammonia, and the decomposition of the ammonium ferrocyanide by means of barium hydroxide. Strychnine was converted into the acetate by gently heating with water and the calculated amount of acetic acid. This salt, though one of the most soluble salts of strychnine, readily separates in the crystalline form from comparatively dilute solutions when allowed to cool, so it is best to keep it warm. A solution of the calculated amount of potassium ferrocyanide was added to the strychnine acetate, allowed to stand in a warm place, stirred frequently, and the white crystalline strychnine ferrocyanide, filtered and washed. After washing, the strychnine ferrocyanide was thoroughly mixed with ammonia water in excess, which decomposed it forming ammonium ferrocyanide and precipitating strychnine, which was easily separated from the solution of ammonium ferrocyanide, and could be used over again.

The solution of ammonium ferrocyanide, with excess of ammonia, was then boiled with a solution of the calculated amount of barium hydroxide until no more ammonia was given off. The solution was allowed to cool, decanted from the crystals, and the mother liquid further evaporated. The crystals were dried in the air. They were found to contain a very slight amount of barium carbonate. On analysis, they gave 9.43 per cent. of iron and 46.98 per cent. of barium, which corresponds very closely to a salt of the composition represented by the formula $Ba_2Fe(CN)_6.6H_2O$, and which is described in Wurtz Dict. de Chim., p. 1090.

The barium ferrocyanide can be easily prepared by this method. The main objections to this method are the bulk of liquid required to dissolve the strychnine salt, and the chance for the formation of barium carbonate during the boiling of the ammonium ferrocyanide solution with barium hydroxide. This last objection can be largely avoided by boiling in a large flask, not with the direct flame, but by passing in a current of live steam. This latter method also has the advantage of inducing the formation of better crystals of barium ferrocyanide.

The following equations represent the reactions:

(1) $C_{21}H_{22}N_2O_2 + CH_3COOH = C_{21}H_{22}N_2O_2CH_3COOH$.
(2) $4C_{21}H_{22}N_2O_2CH_3COOH + K_4Fe(CN)_6$
$= (C_{21}H_{22}N_2O_2)_4H_4Fe(CN)_6 + 4CH_3COOK$.
(3) $(C_{21}H_{22}N_2O_2)_4H_4Fe(CN)_6 + 4NH_3$
$= 4C_{21}H_{22}N_2O_2 + (NH_4)_4Fe(CN)_6$.
(4) $(NH_4)_4Fe(CN)_6 + 2Ba(OH)_2$
$= 4NH_3 + 4H_2O + Ba_2Fe(CN)_6$.

Quinoline ferrocyanide was prepared in a similar manner, and this was treated directly with barium hydroxide solution, and the attempt made to get rid of the quinoline by distilling. A large amount of Prussian blue was formed, however, and the mass was thrown away. No other attempt was made using quinoline, as it was then thought that dimethylaniline would answer.

This latter method is the easiest tried and leaves little to be desired. Dimethylaniline is mixed with water, and hydrochloric acid added in slight excess. This solution then mixed with potassium ferrocyanide solution, the whole filtered and the precipitate washed with the least possible amount of water, then with alcohol, and finally with ether, and dried between pieces of filter-paper. As little water as possible must be used, as the salt is rather soluble.

ANALYSIS OF THE DIMETHYLANILINE SALT.

Into a beaker was put 0.2220 gram with about one gram pure calcium carbonate, titrated with standard silver nitrate (one cc. = 5.829 milligrams sodium chloride) using potassium chromate as indicator. Required 18.4 cc. The end reaction was not very sharp, and after standing over night the red color disappeared. Then added more of the silver solution, making a total of 19.5 cc. One cc. of the above silver nitrate solution would be equivalent to 11.26 milligrams di-acid dimethylaniline ferrocyanide. Therefore the 19.5 cc. would correspond to 0.21957 gram.

Taken, 0.1325 gram mixed with water and two cc. dilute sulphuric acid added. Then added 17.18 cc. silver nitrate solution and two cc. solution of iron alum, titrated back with solution of potassium thiocyanate corresponding to the silver nitrate solution. Required six and one-tenth cc. Therefore 11.08 cc. silver nitrate solution used up by salt. In this the end reaction was not sharp.

Taken, 0.1341 gram salt. Treated as above except filtered before titrating back silver nitrate. Sixteen cc. silver nitrate added, four and one-tenth cc. potassium thiocyanate required. Therefore 11.9 cc. silver nitrate solution used, which corresponds to 0.1340 gram of the di-acid salt.

Mixed 0.1350 gram with water and titrated with tenth normal sodium hydroxide, using phenolphthalein as indicator.

Required twelve cc. which corresponds to 0.1351 gram of the di-acid salt.

The compound is, therefore, the di-acid dimethylaniline ferrocyanide $[C_6H_5N(CH_3)_2H]_2H_2Fe(CN)_6$, a white crystalline salt, which is somewhat soluble in water.

PREPARATION OF BARIUM FERROCYANIDE BY THE DIMETHYLANILINE FERROCYANIDE METHOD.

30.5 grams di-acid dimethylaniline ferrocyanide is mixed with barium hydroxide solution containing 22.5 grams barium hydroxide and shaken violently for some time in a flask or separatory funnel. Most of the barium ferrocyanide crystallizes out directly and can be filtered from the liquid. The dimethylaniline is recovered by shaking the liquid with ether, which also causes more of the barium ferrocyanide to separate.

The crystals of barium ferrocyanide should be well washed, first with a little water and then with alcohol. The following equations express the reactions taking place:

(1) $C_6H_5N(CH_3)_2+HCl=C_6H_6N(CH_3)_2HCl.$

(2) $2C_6H_5N(CH_3)_2HCl+K_4Fe(CN)_6+2HCl$
$=4KCl+[C_6H_5N(CH_3)_2H]_2H_2Fe(CN)_6.$

(3) $[C_6H_5N(CH_3)_2H]_2H_2Fe(CN)_6+2Ba(OH)_2$
$=2C_8H_6N(CH_3)_2+4H_2O+Ba_2Fe(CN)_6.$

Barium ferrocyanide $[Ba_2Fe(CN)_6.6H_2O]$ crystallizes in oblique rectangular prisms belonging to the monoclinic system. The crystals are unaltered in the air at ordinary temperature, lose eleven-twelfths of their water at 40° C., the rest of the water is not driven off until the salt begins to decompose. The solubility varies from one in 584 parts cold water to one in 116 parts boiling water.[1] Dammer gives the solubility as varying from one in 1000 parts water at 15° to one in 100 at 75°.

SOLUBILITY OF BARIUM FERROCYANIDE.

Some solubility determinations were made on the salt prepared as above. The apparatus used was, I believe, devised by Dr. Launcelet Andrews. The apparatus consists of two Woulff bottles, *A* and *B*. *A* has three necks. The middle neck contains a perforated stopper holding a thermometer, the bulb of which goes nearly to the bottom of the bottle. The left hand neck has a stopper carrying a short glass tube which can be connected with the suction pump. The right hand neck has a stopper with a tube passing through and reaching to the bottom of the bottle; in fact, it is better to have the tube touch the bottom. This tube is connected to a tube passing through one of the necks of *B*, the other neck of *B* has a tube passing nearly to the bottom of the bottle. Water is put in the two Woulff bottles, and in *A* a larger amount of the salt to be tested than can be dissolved by the water. The whole apparatus is then put in a vessel of water, and air drawn through for several hours. The water in *B* preventing any evaporation from *A*. The current of air is then

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[1] *Wurtz Dict. de Chim.*, *p. 1091*.

stopped long enough to allow the undissolved portion to settle. A measured amount of the clear liquid taken out, noting the temperature, evaporated and residue weighed.

	Amount solution.	Temperature.	Residue. grams.	Parts water.	
I.	5 cc.	18° C.	0.0194	257.7	
II.	5 cc.	18° C.	0.0198	252.5	
III.	30 cc.	18° C.	0.1190	252.1	Added 50 cc. Water to *A*.
IV.	25 cc.	17° C.	0.0936	267.0	
V	25 cc.	19° C.	0.0930	268.8	
VI.	25 cc.	16° C.	0.0924	270.5	

These results fall within the limits as given by Wurtz.

PREPARATION OF CALCIUM FERROCYANIDE.

Twenty-three grams of di-acid dimethylaniline ferrocyanide mixed with water and milk of lime prepared from six grams pure lime. The mixture shaken violently in a flask, allowed to stand some time, filtered, shaken with ether to separate the dimethylaniline, separated from ethereal solution with separatory funnel, evaporated down in flask, carbon dioxide passed through, again boiled, filtered, and evaporated to about fifty cc. Alcohol then added, which causes crystals to separate. Then crystals dried between filter-paper. The crystals are of a pale yellow color and are very soluble in water. When a saturated solution is allowed to stand for a long time at the temperature of the laboratory, large flat crystals are deposited.

NOTE ON THE SEPARATION OF IRON AND ALUMINUM.

Since strychnine ferrocyanide is almost insoluble and is easily filtered, it may possibly be used to separate iron and aluminum in the following manner:

The solution containing ferric and aluminum salts is treated with excess of strychnine ferrocyanide. The Prussian blue thus formed can be filtered with ordinary filter-paper and the aluminum precipitated by ammonia from the filtrate. By this method I have easily gotten perfectly white aluminum oxide ; but have not as yet gotten the conditions for a complete quantitative separation.

I wish in conclusion to express my thanks to Dr. Launcelot Andrews, who, by his advice and assistance, rendered this work possible.

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