The reaction is easily explained by the assumption of an intermediate addition compound similar to the aldehyde ammonias.

6. Unstable nitric acid addition products of benzoyl "nitroso-thymol" and benzoyl "nitroso-carvacrol" are described for the first time.

7. Thymoquinone-dioxime can be prepared more conveniently from nitroso-carvacrol than from nitroso-thymol; the former yielding 70% of the calculated quantity of dioxime whereas the latter yields only 10%.

8. The dibenzoic ester of thymoquinone-dioxime is described for the first time. The compound is of value for the identification of the dioxime.

AMES, IOWA

THE SALTS OF MALEIC, FUMARIC AND INACTIVE MALIC ACIDS

BY JOHN MORRIS WEISS AND CHARLES RAYMOND DOWNS

RECEIVED MARCH 27, 1923

In various investigations which had for their purpose the development of analytical methods for mixtures of maleic, fumaric and malic acids, a number of salts of these three acids were prepared and studied. The results are admittedly incomplete and in certain instances the compounds deserve further study. We are presenting here the results obtained, regretting that we did not have the time to study all the compounds thoroughly but hoping that others will do so. We wish to express our thanks to Dr. G. C. Bailey, Dr. H. E. Williams and Dr. Wolesensky for the careful work which they carried on under our direction in preparing and determining the formulas and solubilities of a number of the compounds described, and to Mr. E. C. Buck for the very careful preliminary search of the literature which he made in this connection.

Ammonium Salts

Analysis.—These salts were analyzed by distilling the material with an excess of standard sodium hydroxide solution and collecting the distillate in an excess of standard sulfuric acid. The distillate, titrated back with methyl orange as indicator, gave the ammonia content; and the flask residue, titrated back with phenolphthalein as indicator, gave the acid radical content.

Ammonium Fumarate.[1]—The product was best prepared by treating fumaric acid suspended in water with concd. ammonium hydroxide in slight excess of the calculated amount, concentrating in a vacuum at not over 60°, adding a little ammonium hydroxide to make up for losses in concentration and allowing the substance to crystallize. The crystals were filtered and washed with alcohol.

Analyses. Calc. for $(NH_4)_2C_4H_2O_4$: NH_3, 22.67; $C_4H_4O_4$, 77.33. Found: NH_3, 22.55; $C_4H_4O_4$, 77.40.

The aqueous solution of the salt is stable at 60° but when boiled it loses ammonia; 4.5506 g. of salt was dissolved in 200 cc. of water and the solution distilled, the distillate

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[1] Keiser and McMaster, *Am. Chem. J.*, **49**, 84 (1913).

being collected in standard acid. In 50 minutes 0.08148 g. of ammonia distilled with 150 cc. water, representing 7.9% decomposition. On the addition and distillation of 150 cc. more water, 0.03933 g. of ammonia was volatilized (3.8%). The final limit of this decomposition or the product formed was not determined.

Ammonium Acid Fumarate.[2]—Fumaric acid was neutralized by two molecules of ammonium hydroxide with litmus as indicator and a second portion of fumaric acid equal to the first added. The mixture was fractionally crystallized into two lots of crystals, each equivalent to slightly more than $^1/_3$ of the whole, the balance in the mother liquor being discarded.

Analyses. Calc. for $NH_4C_4H_3O_4$: NH_3, 12.78; $C_4H_4O_4$, 87.21. Found: Fraction 1: NH_3, 11.70; $C_4H_4O_4$. 87.70; Fraction 2: NH_3, 12.70; $C_4H_4O_6$, 87.40.

Ammonium Maleate.[1,3]—We were not able to obtain crystalline material by the same method as that used for ammonium fumarate. Under ordinary pressure, the solution does not lose ammonia by evaporation. Only a thick sirup results which cannot be crystallized. When the solution is evaporated in a vacuum, the solid obtained is ammonium acid maleate. This salt deserves attention by future investigators.

Ammonium Acid Maleate.[3]—This salt was obtained by the same method as described under the corresponding fumarate.

Analyses. Calc. for $NH_4C_4H_3O_4$: NH_3, 12.78; $C_4H_4O_4$, 87.21. Found: NH_3, 12.72; $C_4H_4O_4$, 87.16.

Sodium Salts

The sodium acid maleate[3,4], sodium maleate[3,4], sodium acid fumarate[5] and sodium fumarate[2,5,6] were prepared by mixing the acids with the proper amounts of sodium hydroxide in water solution, allowing the salt to crystallize and drying it at room temperature.

The data on water of crystallization as given in the literature were confirmed by ignition to sodium carbonate. In the case of the sodium acid fumarate, where there are no data, we found the crystalline material to be anhydrous.

Barium and Strontium Salts

Barium acid maleate,[3] barium maleate,[3,7,8], barium fumarate[2] and barium *i*-malate[9,10],[11] have been described. We did not isolate these but observed that a heavy white precipitate of slight solubility was obtained when a 10% solution of barium chloride was added to a 10% solution of either sodium maleate or fumarate. With sodium *i*-malate only a slight precipitate was formed.

[2] Rieckher, *Ann.*, **49**, 31 (1844).

[3] Buechner, *Ann.*, **49**, 57 (1844).

[4] Bodewig, *Z. Kryst.*, **5**, 558 (1881).

[5] Chandler, THIS JOURNAL, **30**, 694 (1908).

[6] Kannonikov, *J. prakt. Chem.*, [2] **31**, 321 (1885).

[7] Kekulé and Strecker, *Ann.*, **223**, 170 (1884).

[8] Vorlaender. *Ann.*, **280**, 177 (1894).

[9] Kekulé, *Ann.*, **117**, 120 (1861).

[10] Buisine, *Compt. rend.*, **106**, 1426 (1888).

[11] Duboux and Cuttat, *Helvetica Chim. Acta*, **4**, 735 (1921).

Strontium acid maleate and strontium maleate[3] and strontium *i*-malate[11] have been prepared.

Strontium fumarate[2] has been described as containing three molecules of water of crystallization.

We prepared this salt by mixing strontium nitrate and sodium fumarate in water solution in equimolecular proportions, filtering off the precipitate and drying at 100° at which temperature it was anhydrous.

Analyses. Calc. for $SrC_4H_2O_4$: Sr, 43.45; H, 0.99. Found: Sr, 43.25; H, 1.13.

Calcium Salts

The compositions were determined by igniting the salts to calcium oxide.

Calcium Acid Maleate[3] was prepared and found to correspond with the formula as given for 5 molecules of water of crystallization. With the neutral salt[3] the same coincidence was observed, this salt containing one molecule of water.

Analysis. Calc. for $CaC_4H_2O_4.H_2O$: Ca, 23.25. Found: 23.28.

Calcium Fumarate[2,7,12] was prepared by precipitating a sodium fumarate solution with calcium chloride, and filtering, washing and air-drying the product. Our material corresponded to the trihydrate described in the literature.

Analyses. Calc. for $CaC_4H_2O_4.3H_2O$: Ca, 19.23; H, 3.84. Found: Ca, 19.47; H, 4.01.

Calcium Acid Fumarate is not described in the literature. When a solution of sodium acid fumarate was mixed with a molecular equivalent of calcium chloride and evaporated, crystals were obtained which were separated and air-dried.

Analysis. Calc. for $CaC_8H_6O_8.2H_2O$: Ca, 13.06. Found: 13.22.

Calcium Acid *i*-Malate[13] is stated to contain one molecule of water of crystallization. Our preparation was made by heating 52.8 g. of *i*-malic acid with 20 g. of calcium carbonate, filtering the solution, allowing it to crystallize, and separating and air-drying the crystals; yield, 64 g. The substance was found to be the anhydrous salt.

Analysis. Calc. for $CaC_8H_{10}O_{10}$: Ca, 13.06. Found: 12.85.

Magnesium Salts

Magnesium acid maleate, magnesium maleate,[3,14] magnesium fumarate[2] and magnesium *i*-malate[11] have been described. These salts were not prepared but note was made that none of the three acids is precipitated from its sodium salt solutions (10%) by soluble magnesium compounds. In an attempt to produce the *i*-malate, magnesium oxide was dissolved in *i*-malic acid. On concentrating the filtered solution a sirup was obtained which did not crystallize but solidified on standing to a hard white mass.

Cobalt Salts

Cobalt Maleate is not described in the literature.

Cobalt was precipitated as carbonate from a solution of its nitrate and the latter filtered, washed and suspended in water. An equivalent quantity of maleic acid was added and the solution filtered and evaporated.

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[12] Carius, *Ann.*, **142,** 129 (1867).

[13] Bremer, *Ber.*, **8,** 863 (1875).

[14] Walden. *Z. physik. Chem.*, **1,** 529 (1887).

Analysis. Calc. for $CoC_4H_2O_4.11H_2O$: Co, 15.90. Found:[15] 15.80.

Cobalt Fumarate[2] is stated to correspond to the formula $CoC_4H_2O_4.3H_2O$; this we were unable to confirm. Using concentrated solutions of cobalt nitrate and sodium fumarate, a copious, crystalline, pink precipitate was obtained. This was washed and air-dried.

Analyses. Calc. for $CoC_4H_2O_4.4H_2O$: C, 19.59; H, 4.08; Co, 24.07. Found: C, 20.36; H, 3.86; Co, 23.93.

When the pink compound was dried at 100° it became somewhat bluish from loss of water.

Analysis. Calc. for $CoC_4H_2O_4.2H_2O$: Co, 28.23. Found: 28.62.

Cobalt *i*-Malate.—This is not described in the literature. It was prepared by treating cobalt carbonate suspended in water with the calculated amount of *i*-malic acid and evaporating the mixture to dryness at 100°. The formula seems to be that of a trihydrate.

Analyses. Calc. for $CoC_4H_4O_5.3H_2O$: C, 4.08; H, 24.07; Co, 19.59. Found: C, 4.15; H, 23.40; Co, 19.28.

Nickel Salts

The nickel was determined by digesting a sample with concentrated ammonium hydroxide, adding water, a small amount of sodium iodide (0.02–0.05 g.), a few drops of standard silver nitrate solution and an excess of standard sodium cyanide solution. The excess was titrated back with silver nitrate to a slight permanent precipitate.

Nickel Fumarate[2] is stated to contain 4 molecules of water of crystallization. The salt was prepared by mixing dilute solutions of nickel nitrate and sodium fumarate and concentrating until a green crystalline precipitate was formed, and removing soluble materials by repeated boiling with water.

Analyses. Calc. for $NiC_4H_2O_4.4H_2O$: Ni, 24.08; calc. for $NiC_4H_2O_4.5H_2O$: 22.43. Found: 23.42.

If the precipitation of the nickel fumarate is carried on in concentrated solution, a different product seems to be formed.

Analyses. Calc. for $NiC_4H_2O_4.5H_2O$: C, 18.27; H, 4.56; Ni, 22.43. Found: C, 18.44; H, 4.06; Ni, 22.30.

Nickel Maleate[3] resembles the fumarate in general properties but appears to be more soluble. This compound was not analyzed.

Nickel *i*-Malate is not described in the literature. It is extremely soluble in water and, therefore, cannot be precipitated. If nickel carbonate is dissolved in malic acid a green solution is obtained which on concentration forms a jelly. On long standing at room temperature, the sample lost water and crystals began to appear. This compound was isolated but not analyzed.

Manganous Salts

Manganous Acid Maleate.—This compound has not been previously described; 69.6 g. of maleic acid was dissolved in the minimum amount of water at 30° and to this was added 34.6 g. of manganese carbonate. A solid separated which was dissolved by warming it. As the solution was cooled in ice water, a granular pink precipitate was formed which was filtered, washed, recrystallized from water and dried at room temperature; yield, 32.5 g.

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[15] Cobalt was determined by ignition to cobaltous cobaltic oxide, Co_3O_4.

Analyses. Calc. for $MnC_8H_6O_8.4^1/_2H_2O$: C, 25.60; H, 4.20; Mn, 15.02. Found: C, 25.37; H, 3.91; Mn, 15.19.

From examination of the crystals microscopically, it appears that the salt is stable in the air and in a vacuum over sulfuric acid.

Manganous Maleate has not been previously described. It was prepared in the same manner as the acid salt except that twice as much manganese carbonate was used. It appears to be stable at 100°. In dil. water solution it decomposes with the formation of manganese dioxide.

Analyses. Calc. for $MnC_4H_2O_4.3H_2O$: C, 21.53; H, 3.58; Mn, 24.64. Found: C, 21.01; H, 3.31; Mn, 24.48.

Manganous Fumarate[2] has been stated to have the formula $MnC_4H_2O_4.3H_2O$. Our results did not confirm this. To 11.55 g. of manganese carbonate we added 11.6 g. of fumaric acid. The slight excess of carbonate was filtered off and the filtrate evaporated until a precipitate appeared, at first flocculent and then granular. This was filtered off and dried at room temperature.

Analyses. Calc. for $MnC_4H_2O_4$: C, 28.41; H, 1.18; Mn, 32.54. Found: C, 27.55; H, 1.42; Mn, 32.02.

Zinc Salts

Zinc was determined by ignition to zinc oxide.

Zinc Acid Maleate[16] was not prepared.

Zinc Maleate[3] was made by quickly mixing a saturated maleic acid solution with zinc carbonate as a paste in a mortar and filtering before the zinc maleate separated. Zinc maleate formed as a white, granular precipitate which was washed and dried at room temperature.

Analyses. Calc. for $ZnC_4H_2O_4.2H_2O$: C, 22.80; H, 2.78; Zn, 30.42. Found: C, 21.78; H, 2.78; Zn, 30.68.

When a solution of zinc maleate is heated, it decomposes giving a flocculent precipitate.

Zinc Fumarate[2] has been described in two modifications with 3 and 4 molecules of water, respectively. Our product was made by treating a suspension of fumaric acid with an excess of zinc carbonate in a mortar, filtering the mixture and evaporating the filtrate until crystallization began. Colorless crystals were obtained and dried at room temperature.

Analyses. Calc. for $ZnC_4H_2O_4.5H_2O$: C, 17.81; H, 4.45; Zn, 24.26. Found: C, 17.24; H, 4.25; Zn, 24.42.

Iron Salts

Ferric Maleate[3] has been described as an indeterminate smear. On evaporation of a mixture of two molecular equivalents of ferric hydroxide and three molecular equivalents of maleic acid a dark, nearly black, amorphous mass was obtained which was dried at 100°. When analyzed this showed approximately the composition of the dihydrate.

Analyses. Calc. for $Fe_2(C_4H_2O_4)_3.2H_2O$: C, 29.4; H, 2.04; Fe, 22.88. Found: C, 27.34; H, 2.59; Fe, 22.90.

In solution this material seems to be able to hold an excess of ferric hydroxide.

Ferric Fumarate[2] could not be prepared from ferric hydroxide and fumaric acid.

Ferric *i*-Malate[17] was not prepared, but considerable work was carried on with

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[16] Richter, *Z. Chem.*, **11,** 449 (1868).

[17] Pickering, *J. Chem. Soc.*, **103,** 1358 (1914).

ferric ammonium *i*-malate. One molecular equivalent of ferric hydroxide (precipitated cold because when precipitated hot it did not dissolve properly) was mixed with a clear solution of 2 molecular equivalents of malic acid and the mixture was heated to 60°. One molecular equivalent of ammonium hydroxide was then added and the mixture heated rapidly to boiling. The work was carried on in semi-darkness as the material is light sensitive. A clear, red-brown solution resulted which was cooled rapidly in an ice-bath. It showed no ferrous iron when tested with ferricyanide solution. The solution was not stable even in the dark, as ferrous iron appeared on standing and gradually increased. When a thick solution was painted on glass and dried in a dark closet at room temperature a solid similar to ferric ammonium citrate was produced which contained no ferrous iron. When it was dried between 30° and 40° some reduction took place.

To compare the sensitivity of ferric ammonium malate and citrate, dilute solutions of each, free from ferrous iron, were placed in sunlight and tested for ferrous iron. After 5 minutes the malate showed a faint test for ferrous iron and after 10 minutes a very positive test, while the citrate was negative at 24 minutes and showed a positive test only after 39 minutes. In the dark at 100° after 5 minutes the malate showed ferrous iron, while after 20 minutes the citrate still tested negatively.

Attempts to produce ferric ammonium maleate or fumarate in the same way were unsuccessful.

Copper Salts

Copper was estimated volumetrically in acetic acid solution by means of sodium iodide and thiosulfate.

Copper Fumarate[2,12,13] has been described both as a dihydrate and trihydrate. We obtained our material by precipitating fumaric acid with copper sulfate. The pale blue precipitate was washed and dried at 100°.

Analyses. Calc. for $CuC_4H_2O_4.2H_2O$: C, 22.47; H, 2.80; Cu, 29.78. Found: C, 21.70; H, 3.06; Cu, 29.45.

Copper Maleate[3,18] was prepared by precipitating a solution of equimolecular equivalents of copper sulfate and maleic acid with sodium carbonate. A deep blue crystalline precipitate formed which, as stated by the previous investigators, is the monohydrate.

Analyses. Calc. for $CuC_4H_2O_4.H_2O$: C, 24.54; H, 2.04; Cu, 32.50. Found: C, 24.05; H, 2.39; Cu, 32.22.

Copper *i*-Malate has not been described. When equivalent quantities of copper carbonate and *i*-malic acid solutions are mixed and the mixture is evaporated, a hard vitreous blue mass is formed which after several weeks becomes crystalline. It contains at this stage 25.02% of copper, which indicates a trihydrate (25.49% of copper). On continued exposure, the mass becomes paler blue and shows the presence of 25.70% of copper.

Analyses. Calc. for $CuC_4H_4O_5.2H_2O$: C, 20.72; H, 3.45; Cu, 27.28. Found: C, 20.86; H, 3.16; Cu, 25.70.

This formula is quite doubtful and further work is indicated.

Cadmium Salts

Cadmium salts of maleic and fumaric acids have not been described in the literature. Cadmium was determined by igniting the salt to the oxide, CdO, in a stream of oxygen.

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[18] Pickering, *J. Chem. Soc.*, **101**, 174 (1912).

Cadmium Fumarate.—Prepared by precipitating sodium fumarate with cadmium chloride in concentrated solutions this forms a copious, finely divided, white precipitate. It was filtered, washed and dried at 100°.

Analyses. Calc. for $CdC_4H_2O_4$: C, 21.20; H, 0.88; Cd, 49.57. Found: C, 21.63; H, 1.18; Cd, 49.29.

Cadmium Maleate.—This was made by mixing equimolecular proportions of cadmium chloride and sodium maleate in solution and evaporating to crystallization. The salt was washed repeatedly with hot water and dried at room temperature.

Analyses. Calc. for $CdC_4H_2O_4.2H_2O$: C, 18.29; H, 2.28; Cd, 42.75. Found: C, 17.76; H, 2.27; Cd, 42.50.

The salt retains sodium chloride tenaciously and needs exhaustive washing to purify it.

Antimony Salts

No literature references were found to these salts and all attempts to form the maleate, fumarate or *i*-malate by dissolving antimony trioxide in the corresponding acid were unsuccessful. In the case of *i*-malate, some oxide is dissolved (never more than 21% of that calculated) but apparently an excess of acid is required to prevent hydrolysis so that the salt cannot be isolated.[19]

Sodium Antimonyl *i*-Malate.—Attempts were made to prepare this salt by heating 40 g. of sodium hydroxide, 144 g. of antimony trioxide and 134 g. of *i*-malic acid in water solution under a reflux condenser. After 15 hours, 82.8 g. of antimony trioxide remained undissolved. This was removed, dissolved in potassium acid tartrate and reprecipitated, washed and added again to the mixture. In this way all but 31 g. of the original quantity was finally dissolved and all attempts to increase this failed. The final solution was evaporated to a thick sirup which on seeding solidified to a white, hard mass. It can be powdered, and is apparently stable and very soluble in water. The problem of these complex salts is interesting and deserves further work.

Lead Salts

Lead was determined gravimetrically as the chromate or by titrating excess of dichromate with sodium iodide and thiosulfate.

Lead Fumarate[2] is stated to occur as the dihydrate. When equimolar quantities of lead nitrate and sodium fumarate were mixed in aqueous solution, fine crystalline flakes were obtained which were filtered and dried at 100°.

Analyses. Calc. for $PbC_4H_2O_4$: C, 14.91; H, 0.62; Pb, 64.48. Found: C, 14.48; H, 0.88; Pb, 64.22.

Lead Maleate[3,20] is stated to occur as the trihydrate. When we prepared it in a manner similar to that used for the fumarate, we obtained the anhydrous salt.

Analyses. Calc. for $PbC_4H_2O_4$: C, 14.91; H, 0.62; Pb, 64.47. Found: C, 14.94; H, 0.78; Pb, 64.20.

Lead *i*-Malate[21] is the subject of varying opinion, being reported as anhydrous,

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[19] Henderson and Barr, *J. Chem. Soc.*, **69**, 1451 (1896). Henderson and Prentice, *ibid.*, **67**, 1030 (1894).

[20] Pelouze, *Ann.*, **11**, 263 (1834).

[21] Lloydl, *Ann.*, **192**, 80 (1878). Kekulé, *Ann.*, **130**, 1 (1864). Pasteur, *Ann. chim.*, [3] **30**, 49 (1852). Werigo and Tanatar, *Ann.*, **174**, 367 (1874).

with 1$^1/_2$ molecules water and with 3 molecules water. This salt was obtained as a white precipitate by interaction of lead nitrate and sodium *i*-malate in aqueous solution. When heated to 100° it softens to a dough-like mass. Its formula is doubtful but seems to approach the composition $PbC_4H_4O_5.^1/_2H_2O$.

Analyses. Calc. for $PbC_4H_4O_5.^1/_2H_2O$: C, 13.78; H, 1.43; Pb, 59.48. Found: C, 11.91; H, 1.46; Pb, 59.42.

Silver Salts

Silver was determined as the chloride.

Silver Maleate[3,7].—This was formed by precipitating silver nitrate solution with sodium maleate and was obtained as a white precipitate which was dried at 100°.

Analysis. Calc. for $Ag_2C_4H_2O_4$: Ag, 65.42. Found: 65.44.

The compound deflagrated when heated during combustion (leaving metallic silver) and the carbon and hydrogen results are considered unreliable.

Silver Fumarate.—This compound has not been described. It was prepared in the same way as was the maleate and behaved similarly. Its silver content was 64.90%.

Solubilities

A number of the salts were tested for solubility in water. Samples were placed in 60cc. bottles with distilled water and securely stoppered. They were then held in a thermostat at the required temperature for 24 hours, 25-cc. portions of the clear solutions were withdrawn in a weighing bottle by means of a pipet with cotton filter, weighed, transferred to a platinum

TABLE I

SOLUBILITIES OF FUMARATES, MALEATES AND MALATES

Compound	Formula	Solubilities in g. per 100 g. of water 25°	30°	40°	60°	100°
Cadmium fumarate	$CdC_4H_2O_4$	...	0.09	...	...	..
Cadmium maleate	$CdC_4H_2O_4.2H_2O$	...	0.66	...	...	..
Calcium acid fumarate	$Ca(C_4H_3O_4)_2.2H_2O$	...	5.19	...	...	..
Calcium fumarate	$CaC_4H_2O_4.3H_2O$	...	1.56	...	...	..
Calcium acid maleate	$Ca(C_4H_3O_4)_2.5H_2O$	21.13	...	41.89	94.78	..
Calcium maleate	$CaC_4H_2O_4.H_2O$	2.49	...	2.88	...	..
Cobalt fumarate	$CoC_4H_2O_4.4H_2O$	...	0.88	...	...	..
Copper fumarate	$CuC_4H_2O_4.2H_2O$	...	0.02	...	...	..
Copper maleate	$CuC_4H_2O_4.H_2O$	...	0.12	...	...	..
Lead fumarate	$PbC_4H_2O_4$	...	0.025	...	...	..
Lead *i*-malate	$PbC_4H_4O_5.^1/_2H_2O$	...	0.21	...	...	..
Lead maleate	$PbC_4H_2O_4$	...	0.052	...	...	..
Manganous fumarate	$MnC_4H_2O_4$	...	0.14	...	...	..
Nickel fumarate	$NiC_4H_2O_4.5H_2O$	...	0.36	...	...	..
Silver fumarate	$AgC_4H_2O_4$	...	0.013	...	...	..
Silver maleate	$AgC_4H_2O_4$	...	0.12	...	...	..
Sodium acid fumarate	$NaC_4H_3O_4$	6.87	...	10.74	18.15	30.2
Sodium fumarate	$Na_2C_4H_2O_4$	22.83	...	...	...	..
Sodium acid maleate	$NaC_4H_3O_4.3H_2O$	6.73	...	12.81	31.3	288.0
Sodium maleate	$Na_2C_4H_2O_4.^1/_2H_2O$	96.06	...	...	...	..
Strontium fumarate	$SrC_4H_2O_4$	...	0.29	...	...	..
Zinc fumarate	$ZnC_4H_2O_4.5H_2O$	...	1.96	...	...	..

dish, evaporated to dryness and heated to constant weight at 100°. With the acid salts, the amount of solute was determined by titration. The sampling of the solutions saturated at 60° and 100° was done entirely under the surface of the water in the thermostat with an apparatus described by Pawlewski.[22]

The solubility results are given in Table I.

Summary

The data in the literature regarding the salts of maleic, fumaric and *i*-malic acids have been reviewed and the water of crystallization of a number of these salts determined. In some cases the work agrees with that of past observers, but in others new numbers are apparently justified. Some 11 salts, not previously described, were prepared and the water of crystallization determined in certain cases definitely.

The solubilities in water of 22 salts were determined and tabulated. In general, fumarates are less soluble than the corresponding maleates.

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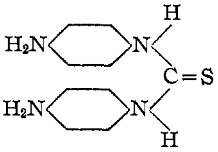
[Contribution from the Steele Chemical Laboratory, Dartmouth College]

THE REACTION OF CARBON DISULFIDE ON PARA-PHENYLENEDIAMINE

By C. Ernest Bolser and Elden B. Hartshorn

Received March 31, 1923

In the description of a patented process[1] for making symmetrical *p*-diamino-diphenyl-thio-urea, the statement is made that when carbon disulfide reacts on *p*-phenylenediamine in alcoholic solution two compounds are formed, symmetrical *p*-diamino-diphenyl-thio-urea, I, and phenylene-thio-urea, a compound insoluble in cold, dil. acids and all ordinary solvents. This compound was originally described by Lellmann[2] and given Formula II.



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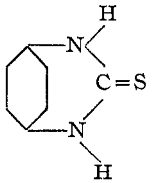

II

The description of the patented reaction is meager, and the formation by primary reaction of two substances to one of which is assigned Formula

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[22] Pawlewski, *Ber.*, **32**, 1040 (1899).

[1] Wm. Noetzel and Co., *Ber.*, **24**, 849 (1891).

[2] Lellmann, *Ann.*, **221**, 29 (1883). Gucci, *J. Chem. Soc. Abs.*, **64**, 588 (1893).