

LXXIII.—*Studies on Citrazinic acid.* Part I.

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IN 1884, Behrmann and Hofmann (*Ber.*, **17**, 2681) announced that, by the action of sulphuric acid on the citramides, a pyridine derivative had been obtained to which the name citrazinic acid was given. Since then, however, this interesting substance has been but little investigated. Ruhemann (*Trans.*, 1887, **51**, 403) has shown that the amide of citrazinic acid may be obtained from acetotriethylic citrate and also (*Ber.*, **20**, 3366) from ethylic aconitate by the action of strong aqueous ammonia; he has also described chloro- and bromo-derivatives of the amide and their reactions with aniline. Schneider (*Ber.*, **21**, 670) states that citrazinic acid is formed in the action of ammonia on methylic aconitate, but this is disputed by Ruhemann.

Lovén (*Ber.*, **22**, 3053) confirms Ruhemann's experimental results, but holds different views as to the probable mechanism of the reaction.

In a previous paper, we have shown (*Trans.*, 1892, **61**, 1008) that acetanhydrocitric acid* gives a good yield of citrazinic acid when

* In a recent note (this vol., 699), Klingemann draws attention to the fact that he had obtained acetanhydrocitric acid two years before the publication of our paper, and had described "at least" one of the reactions mentioned by us. He also asserts that we state the cause of the error in the melting point of citrodianilic acid given by Pebal to be "most probably" a misprint. As a matter of fact, we stated the error to be "possibly" due to a misprint, and did so willingly at the suggestion of the Editor of this Journal, wishing to give to Pebal all possible credit. Dr. Klingemann's note appears to us scarcely called for, since we had already expressed to him our intention of acknowledging in the present paper the priority of his claim.

treated with aqueous ammonia at 120—130°, and that the amides and ethereal salts of citric acid, as well as the anhydride of aconitic acid, yield the same product under the same circumstances.

Evidence has already been brought forward (*loc. cit.*) that the formation of citrazinic acid is intimately connected with the ethenoid linking of aconitic acid, and the authors consider, on the whole, that the formula $\text{COOH} \cdot \text{C} \begin{smallmatrix} \text{CH}_2 - \text{CO} \\ \text{CH} \cdot \text{C}(\text{OH}) \end{smallmatrix} \text{N}$ most simply explains the formation of the acid from aconitic derivatives. This formula is, of course, "tautomeric" with one of those suggested by Lovén, $\text{COOH} \cdot \text{C} \begin{smallmatrix} \text{CH} \cdot \text{C}(\text{OH}) \\ \text{CH} \cdot \text{C}(\text{OH}) \end{smallmatrix} \text{N}$, which might, of course, just as well be written centrically. The assumption of some such tautomerism is necessary in order to explain many of the reactions of citrazinic acid, and such an assumption is tacitly made by Ruhemann in the formula assigned by him to trichlocitrazinamide.

The present investigation was begun with the object of ascertaining the nature of the reaction which takes place between citrazinic acid and potassic nitrite, but the work has expanded in many directions and is by no means complete. In this paper, the following are the chief points dealt with:—

- 1.—Preparation of citrazinamide, its diacetyl derivative and alkali salts.
- 2.—The acid and normal alkali salts of citrazinic acid.
- 3.—Trichlorocitrazinic acid and its reaction with phenylhydrazine.
- 4.—The action of diazobenzene chloride on citrazinic acid to form a bright red hydrazone capable of yielding metallic salts.
- 5.—The reaction of citrazinic acid with nitrous acid under various conditions; a nitroso- (?) and isonitroso-compound are formed, the latter being an unstable substance easily converted into a beautiful yellow acid by oxidation. Both the isonitroso-compound and its oxidation product are easily converted into quinhydroketopyridine, the solution of which is intensely blue. The quinhydro-derivative is easily oxidised to the corresponding quinone, and the reverse change can be effected as in the case of benzoquinone.

It is to be distinctly understood that the constitutional formulæ assigned in this paper are not to be regarded as definitely settled. They express in the simplest manner the reactions and methods of formation of the various products so far as our present knowledge extends.

Preparation of Citrazinamide.

Though several of the methods above mentioned give a good yield of citrazinic acid, none of them, with the exception of that proposed

by Behrmann and Hofmann, are suitable for the production of large quantities of citrazinic derivatives, the use of strong ammonia at temperatures above 100° excluding those processes in which the best yield is obtainable.

Recognising the fact that citrazinic acid or its amide is produced in all ordinary cases where the opportunity is given for the formation of aconitamides, it seemed probable that by fusing citric acid with urea, citrazinic acid or its amide would be formed; this we have found to be the case. The details of the process are as follows:—

Dry citric acid (1 mol.) is well mixed with urea (3 mols.), and the mixture heated in a retort in an oil-bath at a temperature of $155\text{--}160^{\circ}$. Ammonium carbonate, carbamate, and water distil over, and the contents of the retort become almost solid in one to two hours. The light brown product is dissolved in water and acidified with acetic acid; this produces a precipitate which consists chiefly of citrazinamide. The amide is most readily purified by dissolving it in sodium carbonate, filtering, and reprecipitating by acetic acid. Upon the filter there remains a small quantity of a humus-like substance which dissolves easily in caustic alkalis, giving a strongly fluorescent, greenish-red solution. The yield of analytically pure citrazinamide obtained by this method is about 25 per cent. of the citric acid taken.

If a smaller proportion of urea be taken than that indicated above, both the yield and purity of the product will be affected. The amide is then contaminated with a small quantity of a substance which dissolves in alkalis with blue fluorescence and reduces the percentage of nitrogen in the compound. This is probably citrazinic acid, but was not isolated; the amide can readily be purified from this substance by a third precipitation by acetic acid from a solution in excess of alkaline carbonate, as a test experiment taught us that though a small excess of acetic acid at once precipitates citrazinamide from its solutions in excess of carbonate of soda, citrazinic acid is not usually precipitated until a mineral acid has been added. The amide gave the following results when analysed.

0.156 gave 0.0567 H_2O and 0.2718 CO_2 . $\text{C} = 46.72$; $\text{H} = 3.97$.

0.0672 gave 58.87 c.c. dry CO_2 and 9.81 c.c. dry nitrogen, corrected to 0° and 760 mm. (vacuum process). $\text{C} = 47.08$; $\text{N} = 18.13$.

$\text{C}_6\text{H}_6\text{N}_2\text{O}_3$ requires $\text{C} = 46.75$; $\text{H} = 3.90$; $\text{N} = 18.18$ per cent.

The identity of the amide with that described by Ruhemann was proved by a comparison of the barium salts. Ruhemann describes the barium salt as containing 2 mols. H_2O , but apparently this description applies to the salt dried at 100° or in a vacuum. We find that the air-dried barium salt prepared through Ruhemann's

amide, or through our own, contains $6\text{H}_2\text{O}$; 4 of these are rapidly given up in a vacuum or at 100° ; but in a vacuum the salt does not become constant in weight until nearly the whole of the water has been expelled.

Analysis of the air-dried barium salts.

α , from amide from acetyl derivative.

0.5265 gave 0.2142 BaSO_4 . $\text{Ba} = 24.87$.

0.2270 „ 0.0824 H_2O and 0.2208 CO_2 . $\text{C} = 26.52$; $\text{H} = 4.03$.

β , from urea process.

0.5814 gave 0.2432 BaSO_4 . $\text{Ba} = 24.59$.

0.1822 „ 0.0663 H_2O and 0.1785 CO_2 . $\text{C} = 26.66$; $\text{H} = 4.04$.

0.9617 „ 85 c.c. dry nitrogen at 11.7° and 750 mm. $\text{N} = 10.3$.

$\text{Ba}(\text{C}_6\text{H}_5\text{N}_2\text{O}_2)_2 \cdot 6\text{H}_2\text{O}$ requires $\text{C} = 26.11$; $\text{H} = 3.99$; $\text{Ba} = 24.82$; $\text{N} = 10.16$ per cent.

When the amide was boiled with strong hydrochloric acid or preferably warmed on the water-bath with an excess of caustic alkali, it was converted into ordinary citrazinic acid. In passing, we may mention that an aqueous solution of citrazinic acid is not fluorescent, but becomes so on the addition of an alkali or alkali carbonate.

Diacetylcitrazinamide.

Ten grams of citrazinamide were boiled with 50 grams of acetic anhydride until complete dissolution took place; the crystals which separated on cooling, after being washed with ether and recrystallised from alcohol with the addition of animal charcoal, were obtained as colourless prisms melting at 183 — 185° with decomposition. The compound is very stable (quite different in this respect from diacetylcitrazinic acid, which cannot be recrystallised), and when recrystallised from water or alcohol, showed no change in melting point.

0.1606 gave 0.0595 H_2O and 0.2983 CO_2 . $\text{C} = 50.65$; $\text{H} = 4.14$.

0.2272 „ 23.45 c.c. dry nitrogen at 18° and 767 mm. $\text{N} = 11.92$.

$\text{C}_6\text{H}_4(\text{C}_2\text{H}_3\text{O})_2\text{N}_2\text{O}_5$ requires $\text{C} = 50.42$; $\text{H} = 4.20$; $\text{N} = 11.76$ p. c.

Citrazinate of Citrazinamide.—From an alkaline solution containing equal quantities of citrazinic acid and citrazinamide, acetic acid at once precipitated citrazinamide contaminated with some citrazinic acid. (The precipitate contained 16 per cent. nitrogen; citrazinic acid contains 9 per cent., the amide 18 per cent.) The mother liquor, on standing, yielded a feathery mass of nearly colourless needles which, on analysis, gave numbers agreeing with the formula $\text{C}_6\text{H}_5\text{NO}_4$, $\text{C}_6\text{H}_5\text{N}_2\text{O}_3$.

0.1572 gave 0.0535 H_2O and 0.2675 CO_2 . $\text{C} = 46.40$; $\text{H} = 3.77$.
 0.1446 „ 17 c.c. dry nitrogen at 15° and 749 mm. $\text{N} = 13.61$.
 $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_6$ requires $\text{C} = 46.60$; $\text{H} = 3.56$; $\text{N} = 13.59$ per cent.

Alkali Salts of Citrazinamide.

The ammonium salt of citrazinamide is comparatively sparingly soluble, and in strong ammonia very sparingly soluble. 1 c.c. of strong ammonia diluted with 6 c.c. of water was added to 1 gram of citrazinamide and solution effected by boiling the liquid. When the filtered solution was cooled, about 0.5 gram of ammonium salt was deposited in the form of minute, yellow, shining crystals, which were washed with strong ammonia, then with absolute alcohol, and finally dried in a current of air.

0.1022 gave 0.0510 H_2O and 0.1598 CO_2 . $\text{C} = 42.64$; $\text{H} = 5.54$.

0.1385 „ 29 c.c. moist nitrogen at 18° and 770 mm. $\text{N} = 24.49$.
 $\text{C}_6\text{H}_6\text{N}_2\text{O}_3\cdot\text{NH}_3$ requires $\text{C} = 42.10$; $\text{H} = 5.26$; $\text{N} = 24.50$ per cent.

Ruhemann (Trans., 1887, 51, 405) noticed that during the formation of citrazinamide from acetylic ethylic citrate, a small quantity of minute, yellow crystals was deposited which he believed to be citrazinamide. On preparing citrazinamide by his method, we were struck by the resemblance of the small crystals in question to the ammonium salt of citrazinamide. The crude substance contained 3 per cent. less nitrogen than is required by theory, but it at once gave off ammonia when treated with cold, dilute potash, and its filtered aqueous solution deposited very pure citrazinamide when acidified with acetic acid. The citrazinamide was analysed with the following results.

0.077 gave 0.0297 H_2O and 0.1315 CO_2 . $\text{C} = 46.57$; $\text{H} = 4.28$.

0.0948 „ 14.6 c.c. dry nitrogen at 15° and 771 mm. $\text{N} = 18.29$.

$\text{C}_6\text{H}_6\text{N}_2\text{O}_3$ requires $\text{C} = 46.75$; $\text{H} = 3.90$; $\text{N} = 18.18$ per cent.

Potassium Salt of Citrazinamide, $\text{C}_6\text{H}_5\text{KN}_2\text{O}_3$.—This was prepared by dissolving the amide in a slight excess of strong potash, and adding alcohol until the liquid became turbid. The filtrate was then allowed to remain for four hours, when it had set to a mass of needle-shaped crystals; these were washed with alcohol, dried in a vacuum, and analysed.

0.1115 gave 0.0514 K_2SO_4 . $\text{K} = 20.69$.

$\text{C}_6\text{H}_5\text{KN}_2\text{O}_3$ requires $\text{K} = 20.36$ per cent.

Sodium salt, $\text{C}_6\text{H}_5\text{NaNO}_3\cdot 2\text{H}_2\text{O}$, was slowly precipitated in granular crystals on adding alcohol to a solution of the amide in dilute caustic soda.

0.4260 lost 0.0720 H_2O at 120° , then gave 0.1400 Na_2SO_4 . $\text{H}_2\text{O} = 16.90$; $\text{Na} = 10.64$.

$\text{C}_6\text{H}_5\text{NaNO}_3 \cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 16.98$; $\text{Na} = 10.84$ per cent.

The Alkali Salts of Citrazinic acid.

Behrmann and Hofmann (*loc. cit.*) point out that the metallic salts described by them leave much to be desired; indeed up to the present no well defined metallic salt of citrazinic acid has been analysed, and no acid salts have been described. As a matter of fact, the acid sodium and ammonium salts are comparatively sparingly soluble, and the normal alkali salts, though very soluble in water, are easily precipitated from their concentrated solutions by the addition of alcohol.

The Diammonium Salt, $\text{C}_6\text{H}_5\text{NO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$.—This was precipitated by means of alcohol. Since the ammoniacal solution of the acid rapidly becomes dark blue on standing, it is advisable to perform the precipitation with a large excess of alcohol, otherwise the slowly formed crystals will be of a greenish-blue colour. The air-dried salt was analysed.

0.1338 gave 0.0764 H_2O and 0.1709 CO_2 . $\text{C} = 34.83$; $\text{H} = 6.34$.

0.0882 „ 15.5 c.c. moist nitrogen at 16° and 754 mm. $\text{N} = 20.30$.

$\text{C}_6\text{H}_5\text{NO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ requires $\text{C} = 34.78$; $\text{H} = 6.28$; $\text{N} = 20.28$ p. c.

The Acid Ammonium Salt, $\text{C}_6\text{H}_5\text{NO}_4 \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$.—Behrmann and Hofmann state that, on evaporating an ammoniacal solution of citrazinic acid, the acid is regenerated. We found, however, that the residue left on boiling off the water, though resembling citrazinic acid in appearance, was completely soluble in hot water, from which it readily crystallised on cooling. The experiment was performed in an atmosphere of hydrogen on account of the ease with which the ammoniacal solution absorbs oxygen from the air. The residue, after boiling off the water, was heated to 120° , and then recrystallised; it proved to be the hydrated monammonium salt.

0.125 gave 0.0580 H_2O and 0.1757 CO_2 . $\text{C} = 38.32$; $\text{H} = 5.15$.

0.1292 „ 16.5 c.c. dry nitrogen at 16° and 760 mm. $\text{N} = 14.9$.

Calculated, $\text{C} = 37.90$; $\text{H} = 5.26$; $\text{N} = 14.70$ per cent.

The normal potassium salt, $\text{C}_6\text{H}_5\text{K}_2\text{NO}_4$, is precipitated by alcohol as yellowish-white needles. Analysis was made of a specimen dried at 100° .

0.1540 gave 0.1165 K_2SO_4 . $\text{K} = 33.97$.

0.1279 „ 6.6 c.c. dry nitrogen at 17° and 756 mm. $\text{N} = 5.96$.

Calculated, $\text{K} = 33.82$; $\text{N} = 6.06$ per cent.

The normal sodium salt, $C_6H_3Na_2NO_4$, was prepared in a similar manner to the corresponding potassium salt. When dried in a vacuum, it was anhydrous.

0.1515 gave 0.1065 Na_2SO_4 . Na = 22.77 per cent.

Calculated, Na = 23.11 per cent.

The acid sodium salt, $C_6H_4NaNO_4 \cdot 2H_2O$, was prepared by adding to the acid, suspended in a small quantity of water, just sufficient soda to cause complete solution at the boiling temperature; the salt separated in the crystalline condition on cooling.

0.2310 lost 0.0385 H_2O at 110° , then gave 0.0775 Na_2SO_4 . H_2O = 16.66; Na = 10.87.

Calculated, H_2O = 16.98; Na = 10.86 per cent.

Trichlorocitrazinic acid.

If chlorine is passed through water in which freshly precipitated citrazinic acid is suspended, it dissolves completely, and the liquid becomes warm. The temperature should not be allowed to rise above 50° , or the product is liable to be dark coloured. The pale yellow solution begins almost immediately to deposit trichlorocitrazinic acid in beautiful rhombohedra which are already analytically pure, but may be recrystallised from alcohol or tepid water. The pale yellow substance contains $1H_2O$, which it loses at 100° ; it is then practically colourless.

0.3035 lost 0.0205 at 100° . H_2O = 6.75 per cent.

Calculated for 1 mol. H_2O = 6.50 per cent.

Of the dried substance

0.1400 gave 0.011 H_2O and 0.142 CO_2 . C = 27.66; H = 0.87.

0.2285 „ 11.2 c.c. dry nitrogen at 16° and 764 mm. N = 5.60.

0.1082 „ 0.1805 $AgCl$. Cl = 41.25.

$C_6H_2Cl_3NO_4$ requires C = 27.85; H = 0.77; N = 5.41; Cl = 41.20 p.c.

When boiled for some time with water, the whole of the chlorine is eliminated from the acid; the products have not been studied.

Action of Phenylhydrazine on the Trichlorinated Acid.—When an excess of alcoholic phenylhydrazine is mixed with an alcoholic solution of the trichlorinated acid and the liquid boiled, a bright scarlet precipitate gradually forms, consisting of well developed hexagonal plates; this substance is only sparingly soluble in the ordinary menstrua. Analysis indicates that 2 mols. of the hydrazine have reacted with 1 mol. of the acid, 2 mols. HCl being eliminated. Though the view is undoubtedly open to criticism, we regard the

substance as the phenylhydrazine salt of hydrazochlorocitrazinic acid, $C_6H_2(\cdot N \cdot NHC_6H_5) \cdot ClNO_4 \cdot C_6H_5 \cdot NH \cdot NH_2$. The following are the results of analysis:—

- I. 0.1383 gave 0.0515 H_2O and 0.2720 CO_2 . $C = 53.63$; $H = 4.13$.
 II. 0.1285 „ 0.0475 „ 0.2540 „ $C = 53.90$; $H = 4.10$.
 III. 0.1550 „ 23 c.c. dry nitrogen at 16° and 770 mm. $N = 17.5$.
 IV. 0.2000 „ 0.0704 $AgCl$. $Cl = 8.70$.
 $C_{18}H_{16}N_5ClO_4$ requires $C = 53.82$; $H = 3.98$; $N = 17.4$; $Cl = 8.84$ p.c.

We propose to investigate in detail the reactions of trichlorocitrazinic acid.

*Tribromocitrazinic Acid.**

A solution of bromine in acetic acid was added to warm water (at 40°), in which finely divided citrazinic acid was suspended. The citrazinic acid dissolved readily, yielding a dark red solution; this was bleached on the addition of a slight excess of bromine, and the filtered liquid at once began to deposit almost colourless crystals, which bore a striking resemblance to those of trichlorocitrazinic acid. Like the chlorinated acid, the substance is monohydrated. The following are the results of analysis:—

- Found, $H_2O = 4.21$; $C = 17.65$; $H = 1.07$; $N = 3.46$; $Br = 58.12$.
 $C_6H_2Br_3NO_4 \cdot H_2O$ requires $H_2O = 4.39$; $C = 17.56$; $H = 0.97$;
 $N = 3.41$; $Br = 58.53$.

The water was determined by heating at 90° in a vacuum. The substance decomposes slowly when exposed to moist air at ordinary temperatures, and its solutions decompose so readily that it cannot be conveniently recrystallised from ordinary menstrua.

Phenylhydrazocitrazinic acid.

Quite in accordance with the behaviour which citrazinic acid shows towards chlorine are the reactions which the acid exhibits when treated with diazobenzene chloride or with nitrous acid (see below); in the former case, a hydrazo-compound is produced, and in the latter, an isonitroso-derivative.

Citrazinic acid (1 mol.) was dissolved in excess of caustic soda solution, and the solution slightly acidified with acetic acid; to the

* Tribromocitrazinic acid was not described in the paper when read before the Society on June 15th, for though the substance was at that time in our hands, we had not completed the analysis. A notice by Ruhemann in the *Berichte* for June 26th, in which he proposes to brominate citrazinic acid, causes us to insert this description of the tribrom-acid, with the study of which we are still engaged.

ice-cold liquid, a solution containing diazobenzene chloride (1 mol.) and some free hydrochloric acid was added. A bright yellow precipitate was immediately formed, and this, when recrystallised from water, proved to be the acid sodium salt of the hydrazo-acid. It contained 6 mols. H_2O .

0.1305 lost 0.036 at 110° , then gave 0.0235 Na_2SO_4 . $\text{H}_2\text{O} = 27.58$;

$\text{Na} = 5.82$ per cent.

$\text{C}_{12}\text{H}_8\text{NaN}_3\text{O}_2 + 6\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 27.76$; $\text{Na} = 5.91$ per cent.

The aqueous solution of the sodium salt gives crystalline precipitates with calcium and barium chlorides. The salt is much more readily soluble in dilute alkaline solutions than in water, being probably converted into a normal salt. The addition of dilute hydrochloric acid to the solution of the sodium salt in water, or indeed to the crude mother liquors obtained in the preparation, causes an immediate precipitation of the hydrazo-acid in yellowish-red flocks; the substance was recrystallised twice from hot alcohol, and then gave the following analytical data.

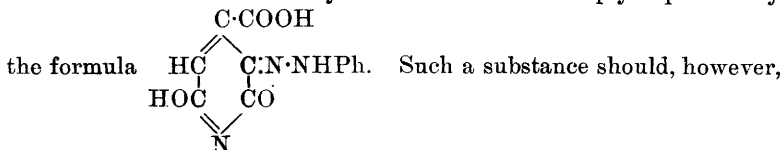
0.1243 gave 0.0411 H_2O and 0.2550 CO_2 . $\text{C} = 55.94$; $\text{H} = 3.67$.

0.097 „ 14.1 c.c. dry nitrogen at 19° and 768 mm. $\text{N} = 16.6$.

$\text{C}_{12}\text{H}_8\text{N}_3\text{O}_4$ requires $\text{C} = 55.60$; $\text{H} = 3.47$; $\text{N} = 16.2$ per cent.

The acid chars at 230° without melting.

The constitution of the hydrazo-acid is most simply expressed by



easily yield a pyrazolone by elimination of the elements of water; we have not yet succeeded in effecting this condensation.

ACTION OF NITROUS ACID ON CITRAZINIC ACID.

Behrmann and Hofmann have shown that the production of an intense blue colour when citrazinic acid is added to a warm, dilute neutral solution of potassium nitrite is a characteristic test for this acid. The nature of this blue colouring matter being hitherto unexplained, we decided to examine the reactions between citrazinic and nitrous acids. These reactions are by no means of a simple nature, and vary considerably with the experimental conditions.

Treatment with Potassic Nitrite in Acid Solution.

When citrazinic acid is added to cold, dilute solution of potassium nitrite, no change of colour takes place, but if the solution is warmed,

the above-mentioned deep blue colour is produced. Experiments made with standard solutions of nitrite and citrazinate of potassium in presence of acetic acid showed that the deepest coloration occurred when the ratio of citrazinic to nitrous acid was about 2 mols. to 1. The presence of mineral acids does not interfere with the colour reaction, but excess of nitrite must be carefully avoided.

If the deep blue solution prepared in the above manner be at once poured into excess of absolute alcohol, a dark blue, amorphous potassium salt separates; this salt dissolves readily in water yielding a blue solution, which, when acidified with dilute sulphuric acid, deposits magnificent, dark green crystals with metallic lustre not unlike the ordinary quinhydrone.

If dilute sulphuric acid be substituted for acetic acid in the nitrite reaction, the bronze-green substance just described begins to separate as soon as the temperature approaches 100° . It may be recrystallised from a very large quantity of boiling water, to which it gives a fine blue colour, and from which it separates on cooling sometimes as hair-like needles, sometimes in short prisms; when crystallisation is complete, the solvent remains practically colourless. The substance is insoluble in ordinary menstrua, but dissolves readily in caustic alkalis with an intense blue colour which is discharged on exposing the solution to the air. By acidifying the freshly made alkaline solution, the substance is obtained as a purple-red, finely divided powder; it may be obtained in the same condition by diluting its solution in strong sulphuric acid, in which it dissolves readily. The yield is about 20 per cent. of the citrazinic acid employed.

Analysis showed that the substance has the empirical formula $C_5H_3NO_3 \cdot H_2O$; it therefore contains 1 carbon atom less than the original citrazinic acid; indeed its production is attended by a continuous evolution of carbon dioxide. The following are the results of analysis:—

0.2042 lost 0.0267 H_2O at 120° = 13.0.

$C_5H_3NO_3 \cdot H_2O$ requires H_2O = 12.6 per cent.

Of the dry substance

0.1592 gave 0.0355 H_2O and 0.2779 CO_2 . C = 47.6; H = 2.47.

0.1707 „ 0.0372 „ 0.3005 „ C = 48.00; H = 2.42.

0.1614 „ 16.3 c.c. dry nitrogen at 19° and 757 mm. N = 11.5.

$C_5H_3NO_3$ requires C = 48.00; H = 2.40; N = 11.20 per cent.

Since it is only produced when the reaction takes place in a hot solution, it is highly probable that the substance is to be regarded as a decomposition product of an intermediate compound. Though the intermediate product could not be isolated in the above reaction, it

was readily obtained by the action of nitrous fumes on citrazinic acid. As shown below, the formation and reactions of the bronze-green derivative agree with the assumption that it is $\alpha\beta'$ -quinhydro- α' -ketopyridine, and it is to the formation of this substance that the characteristic nitrite reaction of citrazinic acid is due.

If an excess of nitrite is used in the above reaction, and the solution, after being acidified with sulphuric acid, is gradually raised to the boiling point and then allowed to cool, a yellow solution is obtained from which a considerable quantity of reddish-yellow crystals of the potassium salt of a new acid is deposited. These, after recrystallisation from boiling dilute hydrochloric acid with use of animal charcoal, became lemon-yellow. The salt is anhydrous.

0.1679 gave 0.0652 K_2SO_4 , corresponding to 17.40 per cent. K.

$C_6H \cdot KN_2O_5$ requires K = 17.72 per cent.

When the potassium salt is dissolved in cold, strong sulphuric acid and poured into an equal volume of water, the corresponding acid is precipitated in silky needles of a sulphur-yellow colour. Analysis agrees with the formula $C_6H_2N_2O_5 \cdot 4H_2O$.

0.8371 lost 0.2378 at $130^\circ = 28.40 H_2O$.

Calculated for 4 mols. $H_2O = 28.34$ per cent.

Of the dried acid

0.2535 gave 0.027 H_2O and 0.3673 CO_2 . C = 39.48; H = 1.18.

0.1763 „ 0.0197 „ 0.2555 „ C = 39.52; H = 1.20.

0.1095 „ 14 c.c. dry nitrogen at 12° and 761 mm. N = 15.67.

$C_6H_2N_2O_5$ requires C = 39.56; H = 1.09; N = 15.38 per cent.

Treatment with Nitric Oxide in presence of Air.

A slow current of nitric oxide evolved from copper and nitric acid (sp. gr. 1.2) was passed through water in which citrazinic acid was suspended, free access of air being allowed. The dark brown solution was filtered before the whole of the citrazinic acid had dissolved, and in a few hours the solution became light yellow, and deposited a large crop of yellow, leafy crystals of micaceous appearance. A second crop was obtained by spontaneous evaporation of the mother liquor. The substance can be recrystallised from hot, very dilute hydrochloric acid, from which, according as the temperature is high or low, it is deposited in spherical masses or glistening plates, the two forms being mutually convertible by recrystallisation. It is decomposed by prolonged heating with water, but is more stable in dilute acid solution. Analysis agrees with the formula $C_6H_4N_2O_5 \cdot H_2O$.

0.1555 (1st crop) lost 0.014 at 105°. $\text{H}_2\text{O} = 9.00$.

0.1792 (2nd „) „ 0.016 „ 100°. $\text{H}_2\text{O} = 8.93$.

Calculated for 1 mol. $\text{H}_2\text{O} = 8.91$ per cent.

Of the dried preparations

0.1302 gave 0.027 H_2O and 0.185 CO_2 . $\text{C} = 38.94$; $\text{H} = 2.30$.

0.1224 „ 0.0255 H_2O and 0.1777 CO_2 . $\text{C} = 39.54$; $\text{H} = 2.31$.

0.1085 „ 13.5 c.c. dry nitrogen at 13° and 772 mm. $\text{N} = 14.93$.

0.1185 „ 15.3 c.c. „ 15° and 761 mm. $\text{N} = 15.37$.

$\text{C}_6\text{H}_4\text{N}_2\text{O}_5$ requires $\text{C} = 39.13$; $\text{H} = 2.17$; $\text{N} = 15.21$ per cent.

The reactions of the substance have not been studied; it is readily decomposed by dilute sulphuric acid with formation of ammonium oxalate; but other products of the change have been isolated, and will be described in a later paper. Provisionally, we assume that it is a nitroso-compound isomeric with the isonitroso-compound described below.

After the mother liquor from the nitric oxide treatment had ceased to deposit the above-mentioned micaceous scales, crystals of quite a different character, and having a fungoid appearance, separated. These, on examination, proved to be the ammonium salt of the yellow acid $\text{C}_6\text{H}_2\text{N}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$, previously obtained by the potassic nitrite treatment; the salt is anhydrous.

0.1265 gave 0.029 H_2O and 0.1668 CO_2 . $\text{C} = 35.96$; $\text{H} = 2.56$.

0.1755 „ 32.5 c.c. dry nitrogen at 755 mm and 21°. $\text{N} = 20.94$.

$\text{C}_6\text{H}_2\text{NH}_3\text{N}_2\text{O}_5$ requires $\text{C} = 36.18$; $\text{H} = 2.51$; $\text{N} = 21.10$ per cent.

The aqueous solution of the ammonium salt deposited the characteristic yellow needles of the free acid when acidified with an excess of hydrochloric acid. For analysis they were dried at 120°.

0.1587 gave 0.0175 H_2O and 0.229 CO_2 . $\text{C} = 39.33$; $\text{H} = 1.23$.

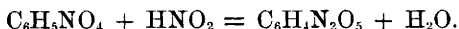
0.1454 „ 19.4 c.c. dry nitrogen at 15° and 761 mm. $\text{N} = 15.88$.

$\text{C}_6\text{H}_2\text{N}_2\text{O}_5$ requires $\text{C} = 39.56$; $\text{H} = 1.09$; $\text{N} = 15.38$ per cent.

Treatment with Nitrous Fumes from Arsenious Oxide.

When nitrous fumes evolved from arsenious oxide are bubbled through water containing a large proportion of suspended citrazinic acid (10 grams in 50 c.c. water), a crystalline precipitate is rapidly formed. The action is stopped as soon as the change appears to be complete, and the crystals are drained with the aid of a filter pump. It dissolves readily in cold alcohol, from which it separates on spontaneous evaporation in greyish crystals; when washed with ether containing a little alcohol, most of the colour is removed, and the substance is sufficiently pure for analysis. The formula of the com-

pound is $C_6H_4N_2O_5, H_2O$, and its formation may be represented by the following equation



Analysis of two different preparations gave the following results.

0.169 lost 0.0145 at 110° . $H_2O = 8.58$.

0.3693 lost 0.0328 at 110° . $H_2O = 8.88$.

0.1236 gave 0.0348 H_2O and 0.1642 CO_2 . $C = 36.23$; $H = 3.12$.

0.1685 „ 0.046 H_2O and 0.2240 CO_2 . $C = 35.99$; $H = 3.01$.

0.1200 „ 14.2 c.c. dry nitrogen at 15° and 754 mm. $N = 13.78$.

$C_6H_4N_2O_5, H_2O$ requires $H_2O = 8.911$; $C = 35.64$; $H = 2.96$;

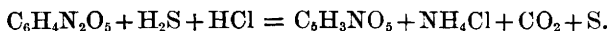
$N = 13.86$ per cent.

The substance is slightly explosive; its solutions are exceedingly unstable, so much so that the recrystallisation of the crude substance is a matter of some difficulty. The mother liquors from the recrystallisation become black on standing, and deposit a small quantity of the bronze-green substance $C_5H_3NO_3, H_2O$ after a few days' exposure. The same decomposition is at once brought about by warming the pure product with dilute sulphuric acid; much carbon dioxide and a little nitrogen are evolved, and about 20 per cent. of the bronze-green substance is formed.

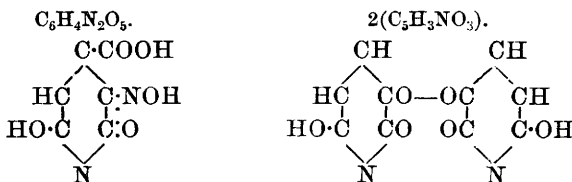
0.2195 gave 19 c.c. dry nitrogen at 19° and 757 mm. $N = 9.9$.

$C_5H_2NO_2, H_2O$ requires $N = 9.7$ per cent.

Sulphuretted hydrogen causes a similar change, sulphur being deposited and ammonia produced, probably according to the equation

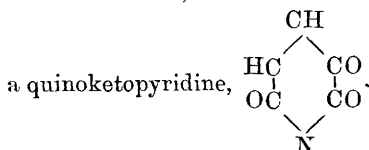


If we assume that the substance $C_6H_4N_2O_5, H_2O$ is isonitrosocitrazinic acid, its change to the bronze-green derivative is easily understood, their relationships being indicated in the following manner.



The latter substance is, in fact, a ketoquinhydrone, and illustrates in a remarkable manner that analogy, first pointed out by Dewar in 1871, between the benzene and pyridine derivatives. It is reduced by aluminium and hydrochloric acid or by hydrogen sulphide (in

boiling solution) to a colourless compound soluble in ether not yet obtained in an analytically pure state, as it passes rapidly back to the quinhydro-compound on exposure to the air. Nitric acid at once oxidises the quinhydro-compound to the corresponding quinone, a pale yellow substance easily isolated on account of its sparing solubility. The quinone becomes reddish-brown when exposed to light, and when boiled with water it darkens; if placed on the skin, it produces a dirty blue stain, a faint foetid odour being developed. Dried in a vacuum at 100° , it has the formula $C_5H_2NO_3$, and must be regarded as



0.1095 gave 0.0185 H_2O and 0.1923 CO_2 . C = 47.96; H = 1.71.

0.1104 „ 0.0170 „ „ 0.1945 „ C = 48.04; H = 1.87.

0.1570 „ 14.3 c.c. dry nitrogen at 16° and 773 mm. N = 10.9.

$C_5H_2NO_3$ requires C = 48.38; H = 1.61; N = 11.28 per cent.

Reducing agents such as sulphurous acid or ordinary hydroquinone at once reconvert the quinone to the quinhydrone, a sample of which, prepared by the latter of these methods and dried at 100° , contained 11.22 per cent. of nitrogen.

Calculated for the quinhydrone = 11.2 per cent. nitrogen.

Similarly, when a solution of the colourless reduction product of the quinhydrone is mixed with a solution of the quinone in dilute hydrochloric acid, splendid crystals of the quinhydrone are deposited.

The presence of a hydroxyl group in the quinhydrone is shown by the fact that when boiled with acetic anhydride, a monacetyl derivative is formed. It crystallises from the anhydride on cooling in well-formed rhomboidal plates having the composition $C_5H_2(C_2H_3O)NO_3$.

0.1251 gave 0.0363 H_2O and 0.2313 CO_2 . C = 50.42; H = 3.22.

$C_7H_5NO_4$ requires C = 50.30; H = 2.99 per cent.

Oxidation of Isonitrosocitrazinic acid.—The isonitroso-acid is readily oxidised by nitric acid, much nitric oxide being evolved and 2 atoms of hydrogen being eliminated. The product was found to be the yellow acid $C_6H_2N_2O_5 \cdot 4H_2O$, already mentioned in our account of the action both of nitrite and of nitric oxide on citrazinic acid. It is also produced if the action of nitrous fumes (from arsenious oxide) on citrazinic acid be continued long enough to dissolve the isonitroso-compound first formed; the latter is, in that case, largely converted

into the ammonium salt of the yellow acid. The conclusion that the acid obtained by these methods was identical with that found by those previously described was confirmed by a determination of the water of crystallisation.

In specimen by excess N_2O_3 on citrazinic acid, H_2O = 28.05 per cent.
 „ „ HNO_3 on nitroso-compound „ = 28.45 „
 Calculated for 4 mols. „ = 28.34 „

Since the action of a small quantity of potassium nitrite in acid solution gives rise to a blue colour owing to the production of the quinhydro-derivative, whereas excess of nitrite gives the yellow acid now under consideration, and since isonitrosocitraziinic acid decomposes readily in acid solution into the bronze-green quinhydrone, but is oxidised by nitric or nitrous acid to the yellow acid, we are forced to the conclusion that in the well-known nitrite colour reaction the isonitroso-compound is first formed, and that the subsequent phenomena are due to its decomposition.

Turning now to the properties of the yellow crystalline acid, we find that, though it contains only 2 atoms of hydrogen, it is a strong bibasic acid and its salts crystallise well. With solutions of potassium and ammonium chlorides, it at once yields precipitates of the acid salts of these metals. The acid is slightly explosive, and this characteristic is intensified in the silver salts. It is very soluble in water and in alcohol, almost insoluble in concentrated hydrochloric acid, insoluble in benzene and ether. When treated with stannous chloride and the tin removed by sulphuretted hydrogen, it is apparently converted by reduction and loss of carbon dioxide into the hydroquinoneketopyridine, for, on exposing the solution to the air, it turns blue, and the quinhydrone is deposited.

0.0858 gram of the product, dried at 100° and burnt in a vacuum, gave 76.03 c.c. CO_2 and 7.96 c.c. dry nitrogen, both corrected to 0° and 760 mm. C = 47.56; N = 11.67.

The quinhydrone $\text{C}_6\text{H}_4\text{NO}_3$ requires C = 48.00; N = 11.2 per cent.

When the yellow acid is treated with excess of ammonia, its colour disappears, and it apparently takes up the elements of water, for, on evaporating the solution nearly to dryness, an ammonium salt separates in colourless, silky needles having the formula $\text{C}_6\text{H}_4\text{N}_2\text{O}_6 \cdot 2\text{NH}_3$, insoluble in alcohol. Analysis:—

0.124 gave 0.0485 H_2O and 0.1416 CO_2 . C = 31.13; H = 4.34.

0.1625 „ 0.0575 „ „ 0.1838 „ C = 30.84; H = 3.93.

0.1615 „ 33.4 c.c. dry nitrogen at 17° and 766 mm. N = 24.1.

$\text{C}_6\text{H}_{10}\text{N}_4\text{O}_6$ requires C = 30.76; H = 4.27; N = 23.9 per cent.

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This salt is quite different from the ammonium salt of the yellow acid. With barium chloride, it yielded a corresponding barium salt in colourless, silky needles.

0.2293 lost 0.0263 H_2O at 138° , then gave 0.1413 BaSO_4 . $\text{Ba} = 35.92$; $\text{H}_2\text{O} = 11.44$.

$\text{C}_6\text{H}_2\text{BaN}_2\text{O}_6 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 11.84$; $\text{Ba} = 36.05$ per cent.

An attempt to set free the new acid from its salts gave rise to a blood-red solution, from which nothing but ammonium oxalate could be obtained.

Salts of the Yellow Acid $\text{C}_6\text{H}_2\text{N}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$.

The ammonium and potassium salts of this acid have been described, for it was in the form of these sparingly soluble salts that our attention was first drawn to the acid itself.

The monargentate salt, $\text{C}_6\text{HAgN}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, was prepared by adding silver nitrate to a solution of the potassium salt in hot dilute nitric acid. On cooling, it separated in yellow, acicular plates.

0.2614 lost 0.0289 H_2O at 130° . $\text{H}_2\text{O} = 10.97$.

0.4203 gave 0.185 AgCl . $\text{Ag} = 33.11$.

$\text{C}_6\text{H}_2\text{N}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 11.06$; $\text{Ag} = 33.23$ per cent.

The diargentate salt, $\text{C}_6\text{Ag}_2\text{N}_2\text{O}_5$, was prepared by precipitating the hydrogen potassium salt with silver acetate; it forms a sulphur-yellow, highly explosive powder.

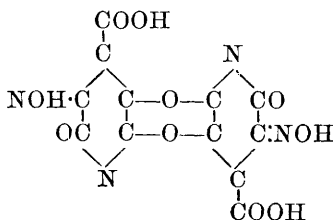
0.3792 gave 0.0042 H_2O and 0.2500 CO_2 . $\text{C} = 17.98$; $\text{H} = 0.12$.

0.587 „ 0.422 AgCl . $\text{Ag} = 54.13$.

$\text{C}_6\text{Ag}_2\text{N}_2\text{O}_5$ requires $\text{C} = 18.18$; $\text{H} = 0.00$; $\text{Ag} = 54.54$ per cent.

A crystalline barium salt was also obtained by precipitation of a hot solution of the acid potassium salt by barium acetate.

The constitution of the yellow salt is an open question; for the present, we shall represent it as derived from 2 mols. of the isonitroso-compound.



The reaction of the acid with ammonia we shall not at present attempt to explain.

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The reactions between nitrous acid and citrazinic acid may be conveniently tabulated as follows :—

Potassic nitrite in acid solution.	Nitric oxide in presence of air.	Nitrous fumes.
Isonitrosocitrazinic acid probably first formed; this decomposes into the blue quinhydrone if the nitrite be not in excess. In presence of excess of nitrite, a stable yellow bibasic acid is formed by direct oxidation.	Nitroso-? and isonitrosocitrazinic acids formed, the latter oxidising to the yellow bibasic acid.	Isonitrosocitrazinic acid formed; can be isolated. The mother liquors after a time deposit the ammonium salt of the yellow oxidation acid.

Several of the substances described in the present paper are isomeric with those obtained by Ost in his researches on meconic acid, and the relationship of these isomeric substances should form a fruitful field for future work. Encouraged by the success which has attended our attempts in the present investigation, we have acted on citrazinic acid with nitric and with fuming sulphuric acids, we have also tried the effect of reducing agents on citrazinamide in acid and in alkaline solution. In each case interesting results have been obtained, which will most suitably find a place in a subsequent communication.

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