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SUCCINIMID.

By Edmund H. Miller.

PART I.

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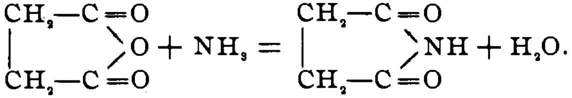
SUCCINIMID was discovered in the year 1835 by Felix d' Arcet,[1] who prepared it by acting on succinic anhydride with ammonia gas, according to the reaction.



He noticed that when the two bodies were allowed to react, there was a great elevation of temperature, that a considerable amount of water was evolved, and that a compound much more fusible than succinic acid resulted; by aiding the reaction with heat, a white substance was sublimed which had none of the properties of succinic acid.

D' Arcet found that this substance which he called succinamid, crystallized in regular rhombs from ether and alcohol and contained one molecule of water when crystallized from that solvent, also it gave off ammonia when treated with hot caustic potash. He considered the formula as $C_8H_6NO_2$ from his analysis which would correspond to $C_4H_5NO_2$, according to the atomic weights now in use.

Bisuccinimid. This compound is identical with that prepared by D' Arcet and was so named by Fehling[2] who prepared it by conducting dry ammonia-gas over melted succinic acid, and recrystallizing the sublimate. He announced the melting point to be 210° C. Fehling also prepared this compound by

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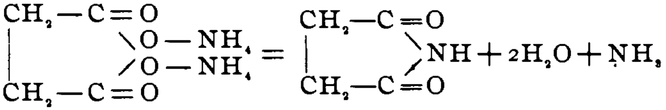
[1] *Ann. chim. phys.*, [2] 58, 282–300, *1835*.

[2] *Ann. Chem.*, (Liebig), 49, 98, *1844*.

neutralizing a solution of succinic acid with ammonia, evaporating to dryness, and then distilling; ammonia and water go off first and then bisuccinimid and a little succinic acid are sublimed.



Bisuccinimid was also obtained similarly from acid ammonium succinate by the splitting off of water.

Fehling found that an aqueous solution of bisuccinimid dissolved lead oxide in great quantities giving the lead salt containing fifty-eight per cent. of lead. He also announced that barium gave a similar compound.

The name succinimid was given to the compound by Laurent and Gerhardt[1] who devoted considerable time to its investigation, and first prepared the silver salt.

Trisuccinimid was prepared by Gerhardt and Chiozza[2] by the action of succinyl chloride on silver succinimid as follows: $C_2H_4(CO)_2Cl_2+2AgN\ (CO)_2\ C_2H_4=N_2(C_4H_4O_2)_3+2AgCl$. Teuchert,[3] in his experiments on succinamic acid, gives the following statements concerning succinimid:

1. By treating succinimid with barium hydroxide the barium salt of succinamic acid is obtained.

2. On decomposing salts of succinamic acid by acids with the aid of heat, ammonium succinate is formed, not succinimid, as stated by Laurent and Gerhardt.

3. The compound called silver succinamate by Laurent and Gerhardt must not be considered as this compound, but as a silver hydroxide succinimid.

Teuchert also prepared the potassium, magnesium, manganese, cadmium, zinc, and copper salts of succinimid.

In 1869 Erlenmeyer[4] redetermined the melting point of succinimid and found that instead of being 210° as stated by both Fehling and Teuchert, it was 125°-126°. Erlenmeyer denied the

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[1] *Compt. rend.*, *1847*, 291, and *1849*, 108.

[2] *Ann. Chem.*, (Liebig), **134**, 136, *1865*.

[3] *Ann. Chem.*, (Liebig), **134**, 136, *1865*.

[4] *Ztschr. fur Chemie*, **12**, 174, *1869*.

conjecture made by Mendelejeff that succinimid might be identical with the isomeric compound, cyanpropionic acid on account of its formation from succinic anhydride, and from succinamid by the decomposition of two NH_2 groups into NH and NH_3: he ascribed its acid properties to the fact that the hydrogen is combined with a nitrogen attached to the rest of the molecule by two CO groups, and further states that it is an imid, and, therefore, plays the part of a monobasic acid.

Bunge,[1] in 1870, confirmed the melting point of succinimid obtained by Erlenmeyer; he found that it crystallized free from water when acetone was used as a solvent and obtained rhombic octahedra, whose axes were as follows: brachydiag.: makrodiag.: vertic. a : b : c = 0.7888 : 1 : 1.3655.

Bunge first replaced the hydrogen of the NH group by a nonmetallic element when he formed iodine succinimid by treating silver succinimid with iodine dissolved in acetone or ether. The iodine succinimid reacted with silver nitrate and formed succinimid again. Menshutkin,[2] in 1872, found that there existed two silver compounds with succinimid, one containing no water of crystallization and the other one-half a molecule. He also states that the hydrogen of the NH group can be replaced by mercury, but that the lead, barium or calcium oxides convert it into the corresponding salt of succinamic acid, thus confirming Teuchert's results.

Succinimid may be converted into the amide by alcoholic ammonia at the temperature of the room, or more quickly by heating them together in a sealed tube at 100° C.

Menshutkin prepared succinimid by distilling succinic acid with acetamide. $C_4H_6O_4 + C_2H_3ONH_2 = C_4H_4O_2NH + C_2H_4O_2 + H_2O$.

He also gave the following definition of an imid: "The imid is that acid amide, which, by the taking up of water, gives the amic acid, and by absorption of ammonia gives the amide." To Menshutkin[3] belongs the distinction of first preparing an organic compound of succinimid; he accomplished this by distilling succinic acid and ethylamine and also by their solution in

[1] *Ann. Chem.*, (Liebig), Suppl., 7, 118, *1870*.

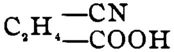
[2] *Ann. Chem.*, (Liebig), 162, 166, *1872*.

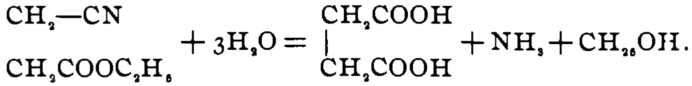
[3] *Ann. Chem.*, (Liebig), 182, 90, *1876*.

the proper proportions. Ethyl succinimid melts at 26° and boils at 234°, has a vapor density of 4.61 (compared to air) and is easily soluble in water, alcohol or ether. It is entirely decomposed into ethylamine and succinic acid by treating with caustic potash, and by gentle warming with barium hydroxide, gives the characteristic conversion into ethyl succinamic acid. Methyl succinimid, was similarly prepared.

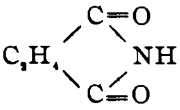
The first evidence of the symmetrical formula of succinimid is found in the statement of Bell[1] that succinimid by distillation with zinc dust, or on reducing its vapor by hydrogen, yields pyrrol; the presence of pyrrol is shown by the reaction with pine moistened with hydrochloric acid.

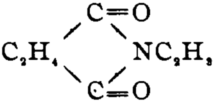
This fact is confirmed by Bernthsen[2] who repeated the experiments, and who also investigated the action of phosphorus trichloride on succinimid, and announced that it gave a fluid chloride. Erlenmeyer's statement that succinimid was not identical with cyanpropionic acid was confirmed in 1882 by Landsberg[3] who, besides preparing a number of metallic salts of succinimid, found that ethyl succinimid when decomposed gave ethylamine and not ethyl alcohol. (This fact was first observed by Menshutkin, but he drew no conclusions from it.) Landsberg made the following statement of the matter:

If succinimid is  $C_2H_4{<}^{\text{—CN}}_{\text{—COOH}}$ then the ethyl ester is  $C_2H_4{<}^{\text{—CN}}_{\text{—COOC}_2\text{H}_5}$; this body by treatment with either bases or acids would give



$$\begin{matrix} CH_2\text{—}CN \\ CH_2COOC_2H_5 \end{matrix} + 3H_2O = \begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix} + NH_3 + CH_{25}OH.$$

But if succinimid is  the ethyl ester is

 and such a body would give

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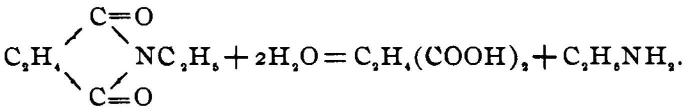
[1] *Ber. d. chem. Ges.*, 13, 877, *1880*.

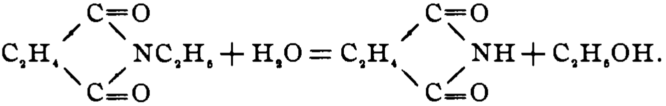
[2] *Ber. d. chem. Ges.*, 13, 1047, *1880*.

[3] *Ann. Chem.*, (Liebig), 215, 172, *1882*.



$$C_2H_4\left\langle\begin{matrix}C=O\\ \\ C=O\end{matrix}\right\rangle NC_2H_5 + 2H_2O = C_2H_4(COOH)_2 + C_2H_6NH_2.$$

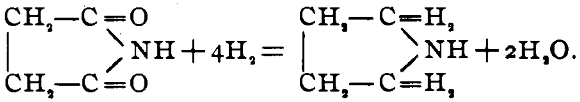
The fact that Menshutkin obtained succinimid and alcohol when he treated silver succinimid with ethyl iodide instead of ethyl succinimid and silver iodide, is explained by the water of crystallization present in some silver succinimid which decomposes the ethyl ester of succinimid first formed as follows:



$$C_2H_4\left\langle\begin{matrix}C=O\\ \\ C=O\end{matrix}\right\rangle NC_2H_6 + H_2O = C_2H_4\left\langle\begin{matrix}C=O\\ \\ C=O\end{matrix}\right\rangle NH + C_2H_6OH.$$

Cimian and Silber[1] investigated the action of bromine on succinimid. They found that the hydrogen of the imid group was not attacked but that when a calculated amount of bromine was dropped into a flask containing succinimid heated to 160° C., that hydrobromic acid was given off, and bibrommaleicimid $(CBr)_2(CO)_2NH$ was formed (M. P. 225° C). This imid when treated with aqueous caustic potash gave bibrommaleic acid. The corresponding anhydride, and the barium and silver results were also made. Bender[2] treated succinimid with calcium chloride in acetic-acid solution and obtained chlorine succinimid $C_2H_4(CO)_2NCl$, which crystallizes in large colorless crystals from boiling benzene, melts at 148° C. without decomposition, and by treatment with hydrochloric acid or alkalies forms succinimid again.

Ladenburg[3] found that by reducing succinimid by sodium, in an alcoholic solution, he obtained pyrrolidin.



$$\begin{matrix}CH_2-C=O\\ |\\ CH_2-C=O\end{matrix}\Big\rangle NH + 4H_2 = \begin{matrix}CH_2-C=H_2\\ |\\ CH_2-C=H_2\end{matrix}\Big\rangle NH + 2H_2O.$$

A curious body was made by Strache[4] by heating together two molecules of succinic anhydride and one of propylene diamine, called propylene succinimid. Its melting point is 98°–100° C. and has the formula

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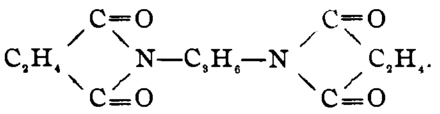
[1] *Ber. d. chem. Ges.*, 17, 556, *1884*.

[2] *Ber. d. chem. Ges.*, 19, 2273, *1886*.

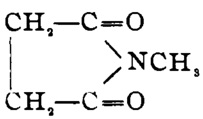
[3] *Ber. d. chem. Ges.*, 20, 215, *1887*.

[4] *Ber. d. chem. Ges.*, 21, 2360, *1888*.

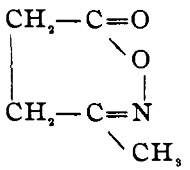


A most extraordinary method of making methyl succinimid was announced by Bredt and Boeddinghous[1] in 1889. They found that the valeroximidolacton of Rischbieth, which is made by treating isonitrosovalerianic acid (made from levulinic acid and hydroxylamine) with concentrated sulphuric acid, to be identical with methyl succinimid, both in melting and boiling points and to give succinic acid and methylamine on treatment with caustic potash.

Methyl Succinimid.



γvaleroximidolacton.



The only conclusions that can be drawn from this remarkable reaction are that either the formula given above for methyl succinimid is wrong or, as is more probable, that the compound must undergo an elaborate molecular rearrangement.

The substitution of a bromine in one of the CH_2 groups of succinimid, was accomplished by Kusserow[2] in 1889. He formed bromsuccinimid $C_2H_3Br(CO)_2NH$ by heating water-free succinimid and bromine dissolved in chloroform in a sealed tube at 120°–130° C. After heating for two or three hours the bromine disappears and the substitution product is seen as a brown oil under the chloroform. $C_2H_4(CO)_2NH + 2Br = C_2H_3Br(CO)_2NH + HBr$.

If water is present and the tube is heated to 160° a mass of white crystals results and scarcely any pressure. The bromsuccinimid is attacked by the hydrobromic acid and water as follows:

$$C_2H_3Br(CO)_2NH + 2H_2O + HBr = C_2H_3Br(COOH)_2 + NH_4Br.$$

Anilidosuccinimid, $C_2H_3(NH\ C_6H_5)(CO)_2NH$, is formed by warming monobromsuccinimid with an excess of anilin on the

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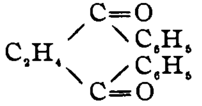
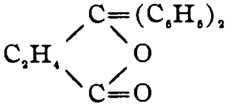
[1] *Ann. Chem.*, (Liebig), **251**, 316, *1889*.

[2] *Ann. Chem.*, (Liebig), **252**, 158, *1889*.

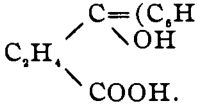
water-bath; from this the following compounds have been made: nitrosoanilidosuccinimid $C_2H_3(N\text{-}NOC_6H_5)(CO)_2NH$ and acetylanilidosuccinimid $C_2H_3(NC_2H_3OC_6H_5)(CO)_2NH$.

Anilido succinanil $C_2H_3(NHC_6H_5)$ $(CO)_2NC_6H_5$ is formed by warming monobromsuccinic acid with an excess of anilin and recrystallizing the product from alcohol. The corresponding nitroso-compound and the amic acid have also been prepared.

The only investigation pointing towards the existence of an unsymmetrical as well as a symmetrical succinimid is that of Auger.[1] He succeeded in preparing two succinimids by the reaction of ammonia on succinyl chloride in the proportion of eight of the unsymmetrical to one hundred of the symmetrical. He also formed the silver salt corresponding to the silver salt of symmetrical succinimid, but failed to make the unsymmetrical succinimid. Auger's investigation on the imid is very imcomplete so that to draw any inference as to the molecular arrangement of succinimid, we must consider his work on succinyl chloride and phtalimid. Succinyl chloride when acted on by benzene and aluminum chloride in the cold for five hours, gives a mixture of a symmetrical and unsymmetrical compound.


and


The unsymmetrical compound melts at 90° C., is insoluble in water and cold alkalies, and has a neutral reaction. When treated with potash on the water-bath and then made acid with hydrochloric acid γdiphenyloxbutyric acid separated out,



as we would expect from the lactone formula, this body melts at 145° and gives water and the unsymmetrical lactone, M. P. 90° C.

The symmetrical body, separated from the unsymmetrical by fractional distillation, is formed in much smaller quantity. It melts at 134° C. and is unacted on by alkalies. Its symmetrical constitution is shown by the formation of a dioxime,

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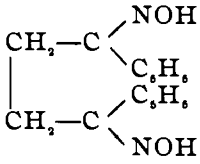
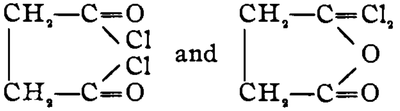
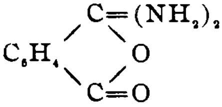
[1] *Ann. chim. phys.*, [6] 22, 289-368, *1891.*



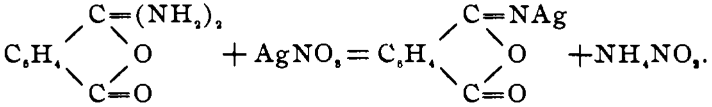
These results show that succinyl chloride is a mixture of the symmetrical and the unsymmetrical.

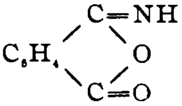
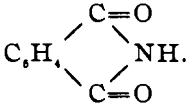


If there are two succinyl chlorides, it would seem that there should be two succinimids and the probability of the existence of the unsymmetrical, at present unknown, is more evident by Auger's research on the amids of phtalic acid.

Unsymmetrical phtalamid  is formed by dropping phtalyl chloride into a large excess of aqueous ammonia, then evaporating, drying, and extracting with ninety-nine per cent. alcohol and recrystallizing. It begins to melt at 90° C. and is soluble in water while the symmetrical phtalamid is not.

The unsymmetrical compound gives a silver salt having the composition $C_8H_4O_2NAg$ which is the silver salt of the unsymmetrical phtalimid.

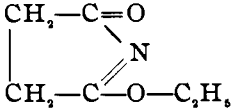


The unsymmetrical phtalimid  is made as follows: To a seven per cent. aqueous solution of the unsymmetrical phtalamid add, in the cold, a quantity of hydrochloric acid calculated to remove one NH_3. A voluminous white precipitate is the immediate result, which, when recrystallized from ninety-five per cent. alcohol, gives a compound which has the same percentage composition as phtalimid, the same appearance, the same solubility in water, the same acid reaction, and if heated very gently, has the same melting point. But if it is heated rapidly, to about 145° C., it melts, giving a perfectly limpid liquid which in about half a minute, without the disengagement of any gas or vapor, solidifies completely and does not melt till 228° C. is reached, the melting point of the symmetrical phtalimid. It therefore seems that on heating it has undergone a molecular rearrangement and has been converted into the more stable symmetrical phtalimid 

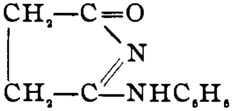
The unsymmetrical phtalimid, though similar to the symmetrical in most of its properties, is more easily decomposed by water giving first the amic acid and then the ammonium salt.

The oxygen ethers of succinimid isomeric with the nitrogen ethers previously described, have been prepared recently by Comstock and Wheeler,[1] as follows:

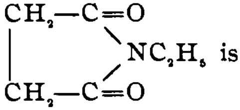
Oxygen ethyl-succinimid. Dry silver succinimid was allowed to stand for several weeks at the ordinary temperature with one molecule of ethyl iodide, diluted with three times its weight of dry chloroform; a dark oily residue was obtained which, when distilled under diminished pressure, gave the ether. It must have the composition



as it gives with anilin a base, having the composition



Some of the nitrogen ether



is formed at the same time, as is proved by allowing the mixture to stand for some time with water, which converts the oxygen ether into succinimid, and then distilling with caustic potash; the distillate showed the presence of primary amine by the isonitril reaction.

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[1] *Am. Chem. J.*, 13, 520, *1891*.

The nitrogen ether so obtained agrees in properties with that described by Menshutkin. Oxygen propyl-succinimid was made in the same way, also the isomeric nitrogen ether. The oxygen propyl ether as well as the ethyl ether gives with anilin the base $C_{10}H_{10}N_2O$, melting point 216° C.

Succinimid bromide has been made by Lengfeld and Steiglitz[1] by adding bromine to a solution of succinimid in sodium hydroxide cooled by ice; the yield is ninety to ninety-five per cent. of the theoretical. The melting point is 172 5°; acids instantly liberate bromine and regenerate succinimid; water decomposes it slowly; when pure and dry, it is stable. It is evidently analogous.to the succinimid iodide of Bunge, and the succinimid chloride of Bender.

The above compound sometimes called bromyl succinimid was made in the same year by Seliwanow[2] from succinimid and bromyl-acetamide; he gives its melting point as 161°-162° and states that it can also be made from succinimid and hypobromous acid; in the presence of water it acts like hypobromous acid, as does the corresponding chlorine compound. He regards the compound as an amide of hypobromous acid.

It only remains for me to describe here briefly, three new methods by which I have made succinimid.

No. 1. On heating together ethylene cyanide and acetic acid in a sealed tube for eight hours at a temperature of 180°-200° C. the following reaction takes place:

$$C_2H_4(CN)_2 + CH_3COOH = C_2H_4(CO)_2NH + CH_3CN.$$

No. 2. On heating under the same conditions succinic acid and acetonitril, succinimid is formed as follows:

$$C_2H_4(COOH)_2 + CH_3CN = C_2H_4(CO)_2NH + CH_3COOH.$$

No. 3. On heating in the same way equal molecules of succinic acid and ethylene cyanide, two molecules of succinimid are formed, the yield being nearly theoretical.

$$C_2H_4(COOH)_2 + C_2H_4(CN)_2 = 2C_2H_4(CO)_2NH.$$

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[1] *Am. Chem. J.*, 15, 215, *1893*.

[2] *Ber. d. chem. Ges.*, 25, 3623, *1892*, and *Ber. d. chem. Ges.*, 26, 423, *1893*.

PART II.

MY EXPERIMENTS ON SUCCINIMID.

First Method. Ethylene Cyanide and Acetic Acid.—Tube No. 1. Three grams of ethylene cyanide (one molecule) were dissolved in 2.25 grams of glacial acetic acid (one molecule) in a small thick glass tube, then a few drops of acetic anhydride were added to render the acid anhydrous; the tube was sealed and heated for two hours at 120°–130° C. and then as no change seemed to have taken place, for six hours at 200° C. On cooling, the tube contained a thick brown liquid.

When this tube was opened several months later, some pressure was observed but no colored flame; the contents were transferred to an evaporating dish and allowed to evaporate slowly. Crystals soon made their appearance, and the entire mass finally turned solid and smelled strongly of acetic acid. To determine a method of purification the solubility of the product was tested as follows:

Cold.	Hot.
Ether, partially soluble	same
Chloroform, partially soluble	same
Ethyl alcohol, soluble	very soluble
Methyl alcohol, very soluble	very soluble
Benzene, slightly soluble	soluble
Amyl acetate, slightly soluble	same
Carbon disulphide, readily soluble	same
Water, very soluble	same

The mass was dried and extracted with dry ether in a continuous extractor for several hours. On allowing the ether extract to cool, diamond-shaped crystals formed, which were removed and their melting point found to be 123°–124° C. (uncorrected). The ether solution was evaporated to dryness and recrystallized from methyl alcohol, giving white crystals melting at 122.5°–123° C.

These crystals were tested for nitrogen by the prussian-blue reaction, which showed that it was present without doubt. They were also tested with methyl orange in aqueous solution and gave a very light pink, showing that it was neither strongly acid nor alkaline. Comparative tests were made with both cyanacetic acid and succinimid, and the color was found to be almost identical with the latter.

Combustions for carbon, hydrogen and nitrogen were made on some of the best crystals as follows: Nitrogen combustion: weight of substance 0.1211 gram gave 15.15 cc. of nitrogen at a temperature of 23.5°, barometer 769.5 mm.; 14.23 per cent. Carbon and hydrogen determination: weight of substance, 0.1509 gram; weight CO_2, 0.2554; weight H_2O, 0.0760, equivalent to 45.98 per cent. carbon and 5.59 per cent. hydrogen.

As the amount of the recrystallized substance was very small, these combustions could not be checked but some more of the substance had to be prepared as is described later.

Tube No. 2 contained three grams of ethylene cyanide, 4.5 grams of glacial acetic acid and a few drops of acetic anhydride, or one molecule of the cyanide to two of the acid. This tube was treated exactly like No. 1, and the only noticeable difference was that its contents, on evaporation, smelled more strongly of acetic acid, and required longer heating before they solidified, owing to the presence of the greater excess of acetic acid.

The melting point of the crystals from this tube, when purified by crystallization from methyl alcohol, was found to be 123° C. (uncorrected).

A nitrogen determination on crystals from tube No. 2 gave the following figures: Weight substance, 0.2026 gram; volume of nitrogen, 25.5 cc. at 22° C., and 772.5 mm., 14.44 per cent.

The carbon and hydrogen were determined as follows: Weight substance, 0.3303 gram; weight CO_2, 0.5857 gram; weight H_2O, 0.16055 gram, equivalent to carbon 48.36 per cent., and hydrogen 5.39 per cent.

I considered that this substance was identical with that obtained from tube No. 1 and that it was probably succinimid.

The following table shows a comparison of my first results with the calculated percentage of succinimid:

	Tube No. 1.	Tube No. 2.	Succinimid.
C....................	45.98	48.36	48.48
H....................	5.59	5.39	5.05
N....................	14.23	14.44	14.14
M. P.............	123°–124°	123°	124°—125°
	(uncorrected.)	(uncorrected.)	(according to different authorities.)

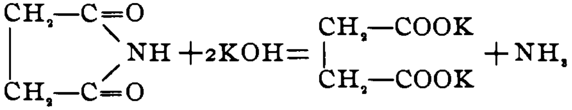
As the yield from tube No. 2 was slightly larger than from tube No. 1, some more of the substance was made for further investigation by using two molecules of acetic acid to one of ethylene cyanide.

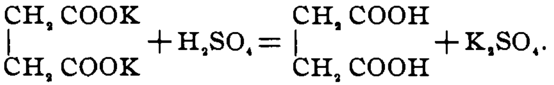
Tube No. 3 contained ethylene cyanide, twelve grams, acetic acid, sixteen grams, acetic anhydride, five drops, and was heated for three hours at 170°–180° C. and then for six hours at about 200° C. The appearance of the tube on cooling was the same as Nos. 1 and 2.

Thinking that, if succinimid was produced, acetonitril must also be formed, an endeavor was made to separate by distillation the more volatile contents of the tube before transferring them to an evaporating dish; and by using a paraffin bath, a few cubic centimeters of a liquid which smelled of acetic acid and acetonitril, were obtained.

The contents of tube No. 3, after evaporating, were extracted with dry ether for five hours and yielded twelve grams of good dry crystals (theory, 14.85 grams). A portion of these crystals was purified by crystallization from methyl alcohol and combustions were made on it as follows: Nitrogen determination: Weight substance, 0.1923 gram; volume of nitrogen, 24.6 cc.; temperature, 25° C.; pressure, 771 mm.; 14.34 per cent. nitrogen. Carbon and hydrogen determination: Weight substance, 0.2948 gram; weight CO_2, 0.5264 gram; weight H_2O, 0.1416 gram; 48.69 per cent. carbon; 5.33 per cent. hydrogen.

These figures agree closely with the percentage composition of succinimid, but to confirm them some of the crystals were treated with boiling aqueous caustic potash; ammonia was given off and succinic acid was formed, which was obtained by extracting with ether, and its melting point determined. This agreed with the established melting point of succinic acid. The reactions are as follows:

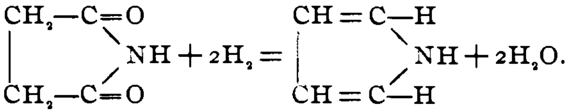




$$\begin{array}{l}CH_2\,COOK\\ |\\ CH_2\,COOK\end{array} + H_2SO_4 = \begin{array}{l}CH_2\,COOH\\ |\\ CH_2\,COOH\end{array} + K_2SO_4.$$

Another portion of the pure crystals was tested for reduction to pyrrol as follows: A small portion of the crystals was ground fine with zinc dust in an agate mortar, and the mixture then transferred to a very small distilling flask and heated over a Bunsen burner; the distillate was but a few drops, but the fumes turned a piece of pine moistened with hydrochloric acid bright red, showing unmistakably the presence of pyrrol.

Reaction is



Some of the crystals obtained from tubes 1, 2, and 3 are large and diamond-shaped when crystallized from ether and retain this characteristic diamond form even when recrystallized from methyl alcohol.

The lack of agreement in the melting points of succinimid and my crystals is explained by the length of the column of mercury outside the liquid in which the melting point was determined. The correction for this was found to be 1.8°, which would make my results agree with the accepted melting point of succinimid. To make sure that there was no mistake in this determination the melting point of some succinimid, made by the distillation of ammonium succinate, was found by my thermometer under the same conditions as obtained in the previous determination, to be 123° C.

Second Method. Acetonitril and Succinic Acid.—This method was tried to see whether the position of the COOH and CN groups had any effect on the reaction.

Tube No. 4. Succinic acid, 17.7 grams (one molecule), acetonitril, 12.3 grams (two molecules), and acetic anhydride four drops, were heating in a sealed tube for eight hours as described under tube No. 3. On cooling, this tube contained a black liquid but not as thick as the preceding. The contents were evaporated and extracted as before. Crystals were obtained which melted at 123° but were not entirely diamond-shaped. The yield in this case was nine grams but would probably have been larger had the tube been heated longer.

The pure crystals from this tube were treated with hot KOH and gave ammonia and succinic acid which was identified by its melting point. They also gave pyrrol when distilled with zinc dust as in the previous case. Combustions for carbon, hydrogen and nitrogen were made with the following results:

Carbon and hydrogen: Weight substance, 0.2857 gram; weight CO_2, 0.5080; weight H_2O; 0.1382; equivalent to carbon, 48.49 per cent.; hydrogen, 5.37 per cent. Nitrogen: weight substance, 0.2787 gram; volume of nitrogen, 36.45 cc. at 27° C. and 766 mm.; pressure, equivalent to 14.54 per cent. nitrogen. (This figure is too high as NaOH was used to absorb the CO_2 because the KOH had given out.)

The crystals from this tube are undoubtedly identical with those obtained from Nos. 1, 2, and 3, and are formed according to the following reaction:

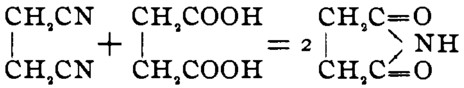
$$CH_3CN + (CH_2COOH)_2 = (CH_2)_2(CO)_2NH + CH_3COOH.$$

The second molecule of acetonitril plays no part in the reaction but was used to make the experiment as far as possible the reverse of No. 3.

I had hoped that these experiments might throw some light on the molecular arrangement of succinimid, but think they have not. Though the succinimid produced is undoubtedly identical with that formed by the distillation of ammonium succinate, and is probably symmetrical on account of its reduction to pyrrol, and is formed invariably to whichever radical the cyanogen group is attached, still I think, considering the analogy of phtalimid, that if an unsymmetrical succinimid were produced at first, that under the conditions of heat and pressure it would be converted into the more stable symmetrical compound.

Third Method. Ethylene Cyanide and Succinic Acid.—Tube No. 5 contained ethylene cyanide, eight grams, (one molecule); succinic acid, 11.8 grams, (one molecule); acetic anhydride, two drops. This tube was heated for six hours at a temperature of about 200° C. On opening, considerable pressure was observed and the contents were solid and semi-crystalline. The hard mass was extracted with ether as before; the crystals were partly diamond-shaped and partly rhombic octahedra; some had flat, diamond-shaped bases, and a pyramid on top, showing that the diamond-shaped crystals were but modifications of the rhombic octahedra, the ordinary crystalline form of succinimid.

According to the reaction



$$\begin{array}{l}CH_2CN\\ |\\ CH_2CN\end{array} + \begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array} = 2\begin{array}{l}CH_2C{=}O\\ |\\ CH_2C{=}O\end{array}\!\!>NH$$

the theoretical yield would be 19.8 grams. 16.2 grams, or 81.8 per cent. of the theoretical were obtained. The residue of carbon weighed 1.7 grams, which would be equivalent to 3.5 grams of succinimid, so that the loss due to manipulation was only 0.1 gram.

Two determinations of the melting point of the succinimid from this tube gave 122° C., or corrected, 123.8° C. The crystals also gave on distillation with zinc dust, pyrrol as before. Prof. Moses, of the School of Mines, very kindly measured the crystals obtained. The results were as follows:

$$a:b:c = 0.8044:1:1.471.$$

Some allowances must be made on account of the hollow faces of these crystals in comparing these figures with those of Bunge:[1]

$$a:b:c = 0.7888:1:1.3655.$$

Molecular Weight Determinations.—In order to determine that the molecular weight of succinimid was not a multiple of that ascribed to it (99), it was determined by Raoult's method, using water and glacial acetic acid as solvents. The method pursued was that given in Wiedermann and Ebert's Physikalisches Praktikum, Braunschweig, 1890.

First determination. In this experiment water was used as a solvent; the freezing mixture was snow and hydrochloric acid; the substance used was made by the action of acetonitril on succinic acid (tube No. 4).

The thermometer was set for water by changing the amount of mercury in the column, and then the freezing point of distilled water was determined twice. Both determinations gave 2.40 on the Beckman thermometer. 8.0449 grams of water were used which filled the portion of the tube in the freezing mixture; after the second determination the ice was allowed to melt and 0.1146 grams of the substance introduced through the side tube; when this had dissolved completely, which required an hour and a half, the mixture was again chilled; the mercury went down gradually to 0.8° and then rose rapidly to 2.12° where it remained

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[1] *Ann. Chem.*, (Leibig), Suppl., 7, 118, *1870*.

stationary for some time; after making sure that this was the correct reading, the mixture was allowed to melt and a second addition of 0.1153 gram of substance introduced as before. The process was repeated and the freezing point found to be 1.84°; using for water the value 18.5, the calculation is as follows:

$M = \frac{\Gamma}{e}$ or M, the molecular weight, is equal to the constant determined for water by use of known substances divided by e the depression in degrees centigrade produced by one gram of the substance dissolved in 100 grams of water. To obtain e we have the following proportions for the first addition:

$$0.1146 : 8.0449 :: X : 100.$$

X, number of grams per hundred grams of solvent in the solution used, 1.424.

$$1.4245 : 1 :: 0.28 : e \qquad e = 0.1965^\circ$$

Substituting in formula $M = \frac{\Gamma}{e} = \frac{18.5}{0.1965}$ or $M = 94.1$. For the second addition:

$$0.2299 : 8.0449 :: X : 100 \qquad X = 2.8577$$

$$2.8577 : 1 :: 0.56 : e \qquad e = 0.1959^\circ \quad M = 94.4$$

Though the results were sufficiently accurate to show that the formula of succinimid was not a multiple of ninety-nine, further experiments were made to confirm them and to obtain results with some other solvent as a check.

Benzene was tried but though a much smaller amount of substance was used, it was not sufficiently soluble to give any satisfactory results. On chilling the mixture, the succinimid gradually separated out and the thermometer did not go down regularly below the freezing point and then rise to and remain at a definite place, but went down continually by jerks. In determining the freezing point of benzene, snow and a little salt was used and it was found inadvisable to have the freezing mixture more than 10° below the freezing point of the solvent.

Ethylene bromide was next tried but exactly the same difficulty was encountered as with benzene. Water was again used as a solvent and the following figures were obtained with crystals from tube No. 3.

Weight of solvent, 9.6352; freezing point, 4.72°.

First addition: Weight substance, 0.0536; freezing point, 4.626°; e = 0.1689; M = 109.4.

Second addition: Weight substance, 0.0536 + 0.0568 = 0.1104; freezing point, 4.55°; e = 0.1485; M = 124.6.

Third addition: Weight substance, 0.0536 + 0.0568 + 0.0586 = 0.1690; freezing point, 4.395°; e = 0.1853; M = 99.8.

Fourth addition: Weight substance, 0.2224; freezing point, 4.22°; e = 0.2168; M = 85.3

Determinations Using Acetic Acid.—99.5 per cent. acetic acid was used in this work and the figure 38.6 (taken from Ostwald on Solution, page 229) was employed. A new difficulty was encountered in these determinations, which was that the acetic acid froze at a lower temperature each time; successive determinations gave the following figures: 2.17°, 2.13°, 2.105°, 2.08°. The explanation of this is that the acetic acid is constantly becoming weaker and the greater proportion of water gives a lower freezing point. In making the determination it was therefore necessary to estimate the probable depression due to evaporation and subtract it from that observed.

The determination was made substantially as before except that cold water was used instead of the freezing mixture.. As the lowering of the freezing point of the acetic acid seemed to grow slightly less on successive freezings, the probable freezing points for the next three determinations were estimated at 2.055°, 2.035°, and 2.015°, respectively. Weight of acetic acid, 12.1795 grams; weight of substance (succinimid from tube No. 3), 0.0700.

Second determination on first addition: Freezing point 1.81°; e = 0.3893; M = 99.1. Second addition: Weight solvent, 12.1795 grams; weight of substance, 0.0700 + 0.0965 = 0.1665; freezing point, 1.50°; depression, 0.515; e = 0.3840; M = 100.5.

The average of two determinations on substance from tube No. 4 is 94.25, using water as the solvent.

The average of four determinations on substance from tube No. 3 is 104.8 (solvent water).

The average of two determinations on same, using acetic acid as the solvent, is 99.8.

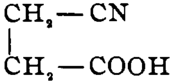
General average, 99.61.

Conclusions.—Succinimid has been made as follows:

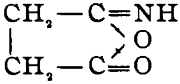
1. By the action of ammonia on succinic anhydride. (D'Arcet.)
2. By passing ammonia over melted succinic acid. (Fehling.)
3. By the distillation of ammonium succinate. (Fehling.)
4. By the distillation of acid ammonium succinate. (Fehling.)
5. By the distillation of succinic acid and acetamide. (Menshutkin.)
6. By heating ethylene cyanide and acetic acid in a sealed tube.
7. By heating in the same way acetonitril and succinic acid.
8. By heating, as above, ethylene cyanide and succinic acid.
9. Methyl succinimid has been made by the action of sulphuric acid on isonitrosovalerianic acid.

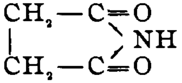
There seems to be no doubt that the succinimid produced by all these methods is identical. Its molecular weight and percentage composition show that the formula must be $C_4H_6NO_2$.

For its molecular arrangement, we have to choose between the following graphic formulae:



$$\begin{array}{l} CH_2-CN \\ | \\ CH_2-COOH \end{array}$$





The first is inadmissible as it is shown by Landsberg that the ethyl ether on decomposition gives ethylamine, while the ethyl ether of β cyanpropionic acid would give ethyl alcohol; it also seems to me that β cyanpropionic acid would turn methyl-orange pink as cyanacetic acid does, but as succinimid does not.

Between the last two, the facts that succinimid on reduction with zinc dust gives pyrrol and with alcohol and sodium pyrrolidin and that succinimid is formed invariably to whichever radicle the CN and COOH groups are attached, are the most important evidences in favor of the symmetrical arrangement. We would also expect that the symmetrical would be the more stable compound. This is borne out by the well-known stability of succinimid, which can be distilled without decomposition.

I believe that succinimid is symmetrical as all the facts observed point to that conclusion; but I think it cannot be proved absolutely until its specific refractive power is determined, which will show in connection with the specific refractive powers of the other elements and with that of nitrogen when joined in different ways, whether, in the case of succinimid, it is attached to one or two carbon atoms.

If β cyanpropionic acid could be isolated, it might on heating be converted into the isomeric unsymmetrical succinimid, and it was with a view to this that the attempts to make this acid, described in part third, were undertaken.

PART III.

ATTEMPTS TO MAKE AND ISOLATE β CYANPROPIONIC ACID BY THE ACTION OF POTASSIUM CYANIDE ON β IODOPROPIONIC ACID.

No. 1. Seventy-five grams of β iodopropionic acid were dissolved in ninety cc. of hot water and neutralized with thirty-four grams of potassium carbonate, then thirty-five grams of finely pulverized potassium cyanide were added and the solution stirred till it dissolved. It was next evaporated and stirred continuously with a thermometer till the temperature reached 132° C. During this time some hydrocyanic acid was given off; the mass was dissolved in a little hot water and neutralized with hydrochloric acid, then evaporated on a water-bath to a syrupy mass and shaken with ether. The ether extract on evaporation yielded nothing.

Before the experiment could be repeated, it was necessary for a new supply of β iodopropionic acid to be made from glyceric acid, and as no phosphorous di-iodide was to be obtained, that had to be prepared also.

After having secured a supply of the iodo acid, the attempts to convert it into the cyan acid were resumed.

No. 2. Fifty grams of β iodopropionic acid were dissolved in a little hot water and 22.8 grams of finely pulverized potassium carbonate added and the carbonic acid boiled out; 21.66 grams of potassium cyanide were dissolved in as little hot water as possible and added to the solution now containing the potassium salt of β iodopropionic acid. The solution was allowed to stand over night and then boiled with a return condenser for five hours, in an endeavor to ensure the formation of KI and cyanpropionic acid. The liquid was then put in an evaporating dish and neutralized with a calculated quantity of normal sulphuric acid and shaken with ether many times, the ether being recovered and used repeatedly, the residues from which the ether was distilled, were dissolved in water and shaken with lead carbonate separately. This gave an effervescence showing the formation of the lead salt of an acid and also of some lead sulphate. These several mixtures were each filtered and then saturated with hydrogen sulphide to precipitate the lead and set free the cyan acid. The lead sulphide was filtered out and the solution evaporated as far as possible on a water-bath. It was then put in a desiccator under diminished pressure over sulphuric acid and left for twenty-four hours. At the end of that time needle-like crystals appeared; they were left there for several days longer and the crystals were subsequently removed and dried between filter paper.

The crystals were white and small and not over 0.100 gram in weight. This method seemed an improvement over the use of hydrochloric acid but the yield was so extremely small as to be rather discouraging.

No. 3. Twenty-five grams of β iodopropionic acid were dissolved in hot water and potassium carbonate added until the solution was alkaline. It was then warmed on a water-bath till the effervescence ceased when nine grams of freshly pulverized potassium cyanide were added and the mixture heated till it was dissolved. In this way the amount of water present was reduced to a minimum. It was evaporated to a syrup on a water-bath and heated over a flame until the temperature reached 125° C. It was next transferred to a beaker and made acid by the addition of three cc. of concentrated sulphuric acid previously diluted with water. Carbon dioxide was given off as before. It was then shaken with large quantities of ether to extract the free acid and let stand for four weeks before the ether was distilled off. The residue was similar to that obtained by No. 2, but the quantity was very small.

No. 4. Twenty-five grams of β iodopropionic acid were dissolved in hot water and potassium carbonate was added until the reaction was alkaline, which required 19.75 grams owing to the poor quality of the iodo acid used. 11.4 grams of finely ground potassium cyanide were added and the solution warmed till it dissolved. The solution was at this time straw colored and was heated to boiling and boiled for about a minute, when it became dark reddish brown and smelled of hydrocyanic acid. The heating was stopped here, as the destruction of the compound by overheating was feared.

8.12 cc. of concentrated sulphuric acid diluted with thirty cc. of water were added which gave a lively effervescence of hydrocyanic acid. It was evaporated carefully over a flame and the sticky mass put in a continuous extractor and extracted for several hours. The ether was finally evaporated and the yellowish crystalline residue was dissolved in methyl alcohol which was put aside to crystallize. From this lot were obtained 0.200 gram of good crystals.

No. 5. The same method was tried again but the mass was heated to 135° instead of 125° and the acid was not added until after the evaporation. Twenty-five grams of β iodopropionic acid of good quality were dissolved in twenty-five cc. of hot water and neutralized with 10.15 grams of finely pulverized potassium carbonate; after it was warmed to drive out carbon dioxide, 11.35 grams of ground potassium cyanide were added. The mixture was placed on the water-bath to react for three hours. It was then heated over a flame until the temperature reached 135° after which it was allowed to cool and 4.17 cc. of concentrated sulphuric acid diluted with fifteen cc. of water were added. There was some smell of hydrocyanic acid but not so much as in No. 4. This was next evaporated rapidly over a flame till the mass was only slightly sticky, transferred to an extractor and extracted with ether for four hours. The residue was tested and found to be potassium cyanide and iodide. The ether solution was distilled and the residue recrystallized from methyl alcohol as before. The yield was small as usual.

No. 6. The effect of pressure as well as heat was tried in this and the following experiment:

Two lots of ten grams each of β iodopropionic acid were weighed out and mixed with 3.46 grams of fine potassium carbonate. To this, water was added and the whole warmed until it dissolved. Then 3.28 grams of potassium cyanide were dissolved in water and added to each, and the resulting solutions put in tubes. On standing, the solutions became dark colored; they were sealed and heated for three hours at 112° C., then allowed to cool. A black film appeared on the inside of the tubes similar to that deposited on the flask when boiled with a return condenser. They were heated three hours longer at the same temperature and examined; the contents seemed to be turning solid. The tubes were heated again for seven hours and when opened there was no perceptible pressure.

The contents of the two tubes were combined and evaporated on a water-bath to a syrup and enough sulphuric acid added to neutralize all the potassium carbonate. There was no effervescence whatever which was encouraging as it indicated that the potassium cyanide had been converted into iodide. It was replaced on the water-bath to evaporate, and when dry, extracted in a continuous extractor for six hours. The ether was then distilled and the residue of nearly white needle-shaped crystals dissolved in methyl alcohol and set aside to crystallize. After four days the crystals were dried and their melting point was found to be 165° The yield was 0.658 gram; theory, 5.1.

No. 7. This experiment differs from the preceding in that two molecules of potassium cyanide were used instead of potassium carbonate; one to form the potassium salt of the acid and the other to furnish the CN group.

Two portions of five grams each of β iodopropionic acid were weighed out, and to them were added 3.28 grams of potassium cyanide, dissolved in eight cc. of water. This produced an effervescence of hydrocyanic acid. It was transferred to tubes and allowed to stand for several hours, during which time the solution became dark reddish brown in color. These tubes were heated the same as No. 6 and appeared about the same. They were combined and evaporated as before, and enough of sulphuric acid added to satisfy one-half the potassium cyanide. The contents of the two tubes were extraced with ether as previously described, the crystals looked about the same as those obtained by No. 6 and melted at 162° C. The yield was 0.175 gram; theory, 2.9 grams.

ATTEMPTS TO MAKE β CYANPROPIONIC ACID FROM ETHYL ETHER OF β IODOPROPIONIC ACID.

No. 8. As the ethyl ether of chloracetic acid on treatment with potassium cyanide gives cyanacetic acid, it seemed probable that the ethyl ether of β iodopropionic acid would give β cyanpropionic acid. It was with this hope that the following experiments were undertaken.

The iodo acid had first to be converted into the ether which was done as follows: 200 grams of β iodopropionic acid, 100 grams of ethyl alcohol, and twenty grams of sulphuric acid were mixed in a round-bottomed flask and heated on a water-bath with a return condenser for five and a half hours. The liquid had then separated into two layers. It was transferred to a separator and washed, first with sodium carbonate solution and then with water. The ether, a dark, heavy liquid, was then separated and dried. The yield was 125 grams.

To convert the ether into the cyan acid I used an excess of potassium cyanide over the two molecules required by the reaction.

$$CH_2ICH_2COOC_2H_5 + 2KCN = CH_2CNCH_2COOK + \\ KI + C_2H_6CN.$$

To 145 grams of the ether were added ninety-three grams of potassium cyanide dissolved in 372 grams of water. This mixture was made in a round-bottomed flask in which it was left to stand for twenty hours, the ether forming a separate layer. It was then heated with a return condenser for ten hours; at the end of five hours the layers had mixed and the whole solution was a dark brown in color. On removing from the flask, a dark oil was seen floating on the liquid and to obtain this it was shaken with ether twice, the ether extracts separated, and the ether distilled off; the residue was a brown oil which was tested for nitrogen by the prussian blue reaction but none was found. It, however, gave a decisive test for iodine, and was the unaltered ether of β iodopropionic acid.

The solution from which the unaltered ether had been removed was made almost neutral with sulphuric acid and evaporated on a water-bath to dryness. It was then made acid with dilute (normal) sulphuric acid and shaken twice with liberal quantities of ether. The residue, a brown liquid, was made strongly acid with sulphuric acid and shaken with ether three times. The residue from this treatment was evaporated to dryness on a water-bath and extracted with ether three times more.

The three different ether solutions, supposed to contain the cyan acid, were distilled separately and the residues kept to convert into the lead salt of cyanpropionic acid as a means of purifying the product. To do this they were shaken with lead carbonate in excess and then the lead sulphate and carbonate filtered out. The formation of the lead salt gave a lively effervescence with the first two lots but failed to give any with the third, so I considered that none of the cyan acid was removed by the last extractions.

The filtrates described above were saturated separately with hydrogen sulphide, which gave a copious precipitate of lead sulphide. The solutions were filtered and the filtrates combined and evaporated on a water-bath to dryness. It was then found that the lead had not been entirely removed, so the mass was redissolved in hot water, and hydrogen sulphide passed in again. It was filtered and washed as before and evaporated on a water-bath. On cooling, the substance turned solid.

The solubility of this substance is as follows:

	Cold.	Warm.
Ether	insoluble	almost insoluble
Ethyl alcohol	slowly soluble	soluble
Chloroform	insoluble	insoluble
Carbon disulphide	insoluble	insoluble
Methyl alcohol	insoluble	soluble
Acetone	insoluble	insoluble
Benzene	insoluble	insoluble

Some of this product was recrystallized from both ethyl and methyl alcohol and the melting points determined. The results were as follows:

Ethyl alcohol	110°–111°
Methyl alcohol	109°–110°
Crude	154°

A small sample was recrystallized from methyl alcohol several times and its melting point determined. It began to melt at 117° but part remained solid until 144° was reached, when all melted, indicating in spite of repeated recrystallizations that the sample was a mixture.

No. 9. This method is a slight modification of the preceding.

Ninety grams of potassium cyanide were dissolved in 300 cc. of water and added to 142 grams of the ethyl ether of β iodopropionic acid in a round-bottomed flask as before. This was heated on a water-bath with a return condenser for twelve hours to try to ensure the entire conversion of the ether; it was then shaken with ether in a separator to recover the unaltered ether, and in spite of the increased time during which the mixture was heated thirty-five grams of the ether were obtained.

The under layer from the separator was neutralized with sulphuric acid and evaporated on a water-bath to a syrup. It was made acid with dilute sulphuric acid (one to one) and shaken with ether in a separator three times, using liberal amounts of ether each time.

(The object of first neutralizing and afterwards making acid was to avoid as far as possible, heating with acid which might form succinic acid.) The ether solutions were of a dark reddish color, much darker than those obtained in No. 8. The ether was distilled off, the residue diluted with water, shaken with lead carbonate, filtered, washed, the filtrate saturated with hydrogen sulphide as before, the lead sulphide filtered out and the solution evaporated on the water-bath.

The residue from the ether extraction was evaporated on a water-bath until on cooling it turned solid, and was then transferred to a separator and made much more strongly acid with dilute sulphuric acid, and was well mixed and shaken three times with ether. The ether solution was treated as before, and after removing the lead, was added to the first portion and evaporated to dryness with it. The solid mass was then crystallized twice from methyl alcohol.

To the residue from the second ether extraction in the separator, water was added and the solution filtered, the residue was rejected, and to the filtrate, litharge and lead carbonate added until all the acid present which was mostly sulphuric was neutralized. It was next filtered and hydrogen sulphide passed in. A precipitate of a dark red brown color was obtained instead of the black lead sulphide. This precipitate was filtered out and was found to contain lead and sulphur, was soluble in hot dilute nitric acid and in concentrated hydrochloric acid, but insoluble in dilute sulphuric. This red precipitate sometimes forms at other times when the solution supposed to contain the lead salt of β cyanpropionic acid is saturated with hydrogen sulphide, but it was always either subsequently decomposed or obscured by the quantities of black sulphide which formed later.

This compound is apparently similar to the lead chlorosulphide described by Fresenius (page 173 Qual. Anal.), but in which some organic acid replaces the hydrochloric acid.

The filtrate from this precipitate was evaporated to dryness on the water-bath and extracted with ether four times. The ether was distilled off and the resulting crystals recrystallized from methyl alcohol.

Total yield, 2.6 grams, having a melting point of 124° C.

INVESTIGATION OF CRYSTALS MADE BY THE PRECEDING METHODS.

Combustions were made on the crystals obtained by methods 8 and 9. The amount of moisture was also determined by drying so as to calculate the percentage to the dry if possible. The results were as follows:

No. 8 gave—

Carbon	38.95 per cent.
Hydrogen	6.39 " "
Nitrogen	11.62 " "
Loss on drying for five hours at from 90° to 107°	12.31 " "
Nitrogen, on dried sample	8.07 " "

These results calculated to the dry measure gave—

Carbon	44.42 per cent.
Hydrogen	5.72 " "
Nitrogen	13.25 " "

These combustions were made very carefully and I believe them to be correct. The figures agree quite closely with the percentage composition of $C_8H_{12}N_2O_6$, which is

Carbon	44.44 per cent.
Hydrogen	5.55 " "
Nitrogen	12.97 " "

This might be formed by two molecules of β cyanpropionic acid taking up one molecule of water and combining, $2C_4H_5NO_2+$

$H_2O = C_8H_{12}N_2O_5$, or it may be written $C_4H_5NO_2 + \frac{1}{2}H_2O$. The melting point of crystals from No. 8, on which these combustions were made, was 110° C.

No. 9 gave—

Carbon	37.15	per cent.
"	37.27	" "
Nitrogen	6.34	" "
"	6.19	" "
Hydrogen	5.77	" "
"	5.79	" "

Loss on drying to constant weight for eighteen hours at 100°-110°, 13.22 per cent.

These determinations of the carbon, hydrogen, and nitrogen, calculated to the dry gave—

Carbon	42.88	per cent.
Hydrogen	4.96	" "
Nitrogen	7.22	" "

A nitrogen combustion was made on the crystals from Nos. 6 and 7, which gave further evidence of the loss of nitrogen by heating as the crystals obtained by these methods contained but 3.02 per cent. nitrogen.

The crystals from methods 8 and 9 were dissolved in water and tested with methyl orange to see whether they would give an acid reaction, but they did not. They only gave the color of a neutral solution. Succinimid (M. P. 124) was tried which gave the same color. Cyanacetic acid was also tried but this gave a bright pink. From this it was evident that the crystals could not be β cyanpropionic acid or they would turn the indicator like cyan acid.

The mother liquor from method No. 5, in which the crystals were slowly forming, was tested in the same way and it gave a decided pink color. To make sure this was not due to any mineral acid, I tested for sulphuric acid with barium nitrate but found none. (Sulphuric was the only acid used in the method.)

I now believe that β cyanpropionic acid is a liquid and is formed in many of the preceding methods, but that it decomposes very readily by heat or pressure, forming various complicated organic compounds, which are the crystals obtained. Another reason for my thinking so is that methods 6 and 7 which are heated in sealed tubes, on evaporating gave crystals direct, while in the methods which were not heated so much a syrupy liquid was left, which only deposited crystals after standing in some cases for weeks over sulphuric acid, showing the complete decomposition of the acid in the first case and but the partial in the second as it was there the acid reaction was obtained. The irregularity of the combustion is explained by the fact that the samples must have been in most cases, mixtures. The only combustions which agree very well are those made on the same day on a sample of No. 9 which had been recrystallized four times.

The diminished percentage of nitrogen in the methods where longer or higher heat was used, and also where the sample was afterwards dried, seems to be invariable and points to a decomposition in which nitrogen is lost.

The nearest approach to β cyanpropionic acid so far produced is its ethyl ether which has been made by L. Henry,[1] as follows:

Heat $CH_2ICH_2COOC_2H_5$ with potassium cyanide dissolved in alcohol in slight excess on a water-bath with a return condenser. The reaction takes place easily and potassium iodide is deposited abundantly; at the end the liquid turns brown. Drive out as much of the alcohol as possible by distilling on the water-bath and extract the cyan ether with ordinary ether. The distillation of the ether solution gives the pure cyanpropionic ether. The yield is almost theoretical.

The cyanpropionic ether is a colorless liquid, without odor, insoluble in and more dense than water, and boils at 228°. Caustic potash in aqueous alcohol transforms it easily into normal potassium succinate. With aqueous ammonia it gives cyanpropionic amide $CN(CH_2)_2CONH_2$.

The preceding facts were not known to me at the time I made my experiments on iodopropionic ethyl ether or I should have tried alcoholic cyanide, and so by the elimination of water, would have probably succeeded in obtaining the ethyl ether and amide of β cyanpropionic acid, if not the acid.

My experiments show that the β iodopropionic ethyl ether does not act with potassium cyanide like the ethyl ether of chloracetic, as by treating the latter with potassium cyanide as

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[1] L. Henry, *Bull d. l'acad. royal de Belgique*, [3] 18, 168, *1889*.

described under the first method in which the ether was used, I obtained a good yield of cyanacetic acid without difficulty.

The reactions between nitriles and both fatty and aromatic acids will be more fully developed in this laboratory.

ORGANIC LABORATORY, SCHOOL OF MINES,
COLUMBIA COLLEGE, MARCH, 1894.

THE DETERMINATION OF PHOSPHORIC ACID.

BY S. W. JOHNSON.

Received April 25, 1894.

THE papers on determination of phosphorus in steel by Messrs. Dudley and Pease, by Mr. Handy, and by Messrs. Doolittle and Eavenson, remind me of some work done at my instigation in the years 1880, 1889, and 1890, and published in the Annual Reports of the Connecticut Agricultural Experiment Station for those years.

In 1880, Mr. (now Professor) H. L. Wells, demonstrated that the citrate method for determining phosphoric acid may give good results under certain conditions, but that the results are correct because of a compensation of errors, the ammonium magnesium phosphate not carrying down quite all the phosphorus but containing enough impurities to counterbalance that loss. Over ninety determinations were made, many of them in duplicate, on forty different substances (fertilizers), after a large number of preliminary trials had indicated the effect of varying the several conditions which might influence the results. In most cases the percentages of phosphoric acid found in duplicate agreed well together and also agreed fairly with those given by the molybdate method. In a few cases, however, considerable discrepancies appeared and it was evident that further study was needful before the citrate method could be fully trusted for fertilizer work.

In 1889, in conjunction with Dr. T. B. Osborne, investigation of the citrate method was resumed. The German agricultural chemists were beginning to use it and J. H. Vogel had published details of procedure. We found that Vogel's process gave results too low and not closely agreeing with the molybdate method. By using more and stronger magnesium mixture and a larger quantity of concentrated ammonia, we overcame this discrepancy, and in sixty-seven determinations on bone-dust superphosphates, cotton-hull ashes, cotton-seed meal, tankage,