

cyanurate 71). He used brom-cyanogen instead of chlor-cyanogen in his experiments and found to his astonishment that the presence of much water in the sodium ethylate used exercised no influence, but led to the same product. Mulder sums up his results as follows:

1) The product of the action of brom-cyanogen on sodium ethylate contains substances which are soluble in water, among which urethane can easily be detected.

2) The portion insoluble in water — Cloëz's substance — consists at first of C_2H_5OCN , C_2H_5OH and gives only after long standing over sulphuric acid in a vacuum analytical figures for C_2H_5OCN . The product contains much ethyl cyanurate, but also another body, perhaps ethyl cyanate.

Ponomareff 72) undertook to study the action of brom-cyanogen on sodium ethylate almost at the same time as Mulder. He found that brom-cyanogen acts very energetically on sodium ethylate (free from alcohol) in ethereal suspension.

On distilling off the ether he obtained an oil which had the odor of an amine base (no one had previously mentioned this), and which boiled between 90° and 200° . When heated for a long time in an evaporating dish on the water bath the amine odor disappeared completely. Ponomareff, therefore, assumes that a volatile body boiling at about 100° is present, which he thinks may possibly be ethyl cyanate. He was strengthened in this opinion by finding that the oil was for the most part soluble in water; the aqueous solution on standing with dilute hydrochloric acid gave urethane. The part insoluble in water on the other hand he ~~considers~~ believes to be ethyl cyanurate.

~~experiments~~ The subject was in this somewhat confused state when I undertook further experiments.

It was first determined that pure brom-cyanogen and sodium ethylate do not act at all on each other in ethereal suspension when the sodium ethylate is prepared with the utmost possible care, is perfectly free from alcohol and is used at once. Even when digested for a long time under a condenser on a water bath heated to 50° no interaction takes place. Chlor-cyanogen shows the same behavior when allowed to stand for many days with sodium ethylate.

If to a solution of brom- or chlor-cyanogen in absolute alcohol, cooled

71) Rec. d. trav. chim. d. Pays. Bas. 1, 81 and 191; 2, 133; 3, 287.

72) Ber. d. Chem. Ges. 15, 1515.

1) The product of the action of bromine on sodium ethylate contains a substance which is soluble in water, and which can easily be detected. 2) The product is soluble in water - (this substance - consists of first of C_2H_5OCN , C_2H_5OH and gives only after long standing over sulphuric acid in a vacuum analytical figures for C_2H_5OCN . The product contains much ethyl cyanurate, but also another body, perhaps ethyl cyanurate. Pomeroy 12) undertook to study the action of bromine on sodium ethylate about the same time as Huber. He found that bromine acts very energetically on sodium ethylate (free from alcohol) in ethereal suspension. On distilling off the ether he obtained an oil which had the odor of an amine base (as one had previously mentioned this), and which boiled between 90° and 100°. When tested for a long time in an evaporating dish in the water bath the amine odor disappeared completely. Pomeroy, therefore, assumes that a volatile body boiling at about 100° is present, which he thinks may possibly be ethyl cyanurate. He was strengthened in this opinion by finding that the oil was for the most part soluble in water; the aqueous solution on standing with dilute hydrochloric acid gave no reaction. The part insoluble in water on the other hand he believes to be ethyl cyanurate. The subject was in the somewhat confused state when I undertook further experiments. It was first determined that pure bromine and sodium ethylate do not act at all on each other in ethereal suspension when the sodium ethylate is prepared with the utmost possible care, is perfectly free from alcohol and is used as such. Even when subjected for a long time under a condenser on a water bath heated to 50° no interaction takes place. Chloroform shows the same behavior when allowed to stand for many days with sodium ethylate. If to a solution of bromine or chloroform in absolute alcohol, cooled

to -8° or -10° ; an alcoholic solution of sodium ethylate is slowly added interaction begins at once with a considerable evolution of heat. There is formed quantitatively imido-ethyl carbonate and sodium chloride or bromide, but not a trace of any other compound. Much water and sodic hydrate are added and the solution is extracted six to eight times with ether; the ethereal solution is washed three times with dilute sodic hydrate, in order to remove alcohol, and dried with caustic potash. After distilling off the ether the substance is dried once more with caustic potash and then distilled, first under reduced then at ordinary pressure. It is a colorless, strongly basic smelling oil boiling at $138-140^{\circ}$; identical in every respect with the imido-carbonic ether described above. The yield from 18 grams of chlor-cyanogen is 26 grams of pure imido-ether; from 41 grams of brom-cyanogen 30 grams of imido-ether.

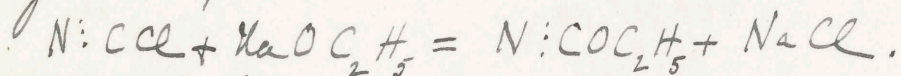
The same result is of course obtained by filtering the reaction product from the sodium salt and distilling directly; but ~~the~~ much imido-ether is carried over with the alcohol. The oil remaining, after the alcohol is distilled off always dissolves completely in water. Since Cloëz, Hofmann and Olshausen, Mulder and Ponomareff in analogous experiments always obtained a compound insoluble in water, this discrepancy was puzzling; at length it was found that the temperature is an important factor in the reaction. If the interaction is allowed to go on, not as above below 0° ; but at the ordinary or better ~~at~~ yet at a somewhat higher temperature there is formed besides imido-carbonic ether, which is also here the chief product, a small quantity of an oil little soluble in water; this oil boils at 155° at 18 mm pressure and consists of ethyl cyanurate. It was found too that a little methane is formed in the reaction when the alcohol used contains water.

Now since imido-carbonic ester forms a hydrate with water (see above) and ethyl cyanurate, as Mulder has shown 73), gives with water a hydrate of the formula $[C_2H_5OCN] + 12H_2O$ as well as with alcohol an alcoholate, $[C_2H_5OCN] + 3C_2H_5OH$, the earlier observations concerning this reaction are fully explained. ³ In whatever way the experiment is carried out (addition of chlor-cyanogen to alcoholic

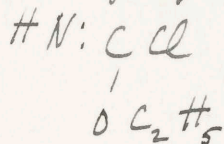
(47)

sodium ethylate or vice versa, with or without cooling, imido-carbonic ether is always formed as the chief product of the reaction; this substance was overlooked by all the earlier workers and only mentioned by Ponomareff as a volatile product having the odor of an amine base.

It was formerly assumed as self evident that chlor-cyanogen could react with sodium ethylate only by direct replacement of the chlorine atom according to the equation



The idea that the chlor-cyanogen molecule might, in the presence of sodium ethylate, simply add alcohol to the cyanogen group forming the intermediate product



was never taken into consideration; regarded from the standpoint of the substitution theory such a reaction would be inconceivable and a priori it seems somewhat extraordinary. — Nevertheless the reaction actually takes place in this way, as is proved by the following experiments.

On adding to a well cooled ($-5 - 10^\circ$) mixture of chlor-cyanogen (or brom-cyanogen), water (five parts) and alcohol (2 parts), an excess of sodic hydrate (or potassic hydrate), care being taken that the temperature never rises above 0° , the odor of chlor-cyanogen soon disappears. The solution is repeatedly extracted with ether and the ether extract worked up precisely as in the above experiment with sodium ethylate. Imido-carbonic ester is obtained as the chief product and urethane as a by-product (about in the proportion of 8:1). The urethane obtained in this way boiled at 181° and melted at 52° .

0.1738 grams gave 24.6 ccm nitrogen at 18° and 750 mm pressure.

Theory for
 $\text{C}_3\text{H}_7\text{NIO}_2$

Found

16.12

C 15.73

The yield of imido-carbonic ether in the above reaction is excellent — almost as good as when sodium ethylate is used. The same result is obtained whether the caustic potash added is very dilute or concentrated, the quantity of alcohol

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It was formerly assumed as self-evident that chloro-cyanogen would react with sodium ethylate only by direct replacement of the chlorine atom according to the equation

$$N:C\dot{C}l + NaOC_2H_5 = N:CO_2C_2H_5 + NaCl$$

The view that the chloro-cyanogen molecule might, in the presence of sodium ethylate, simply add ethyl to the cyanogen group forming the intermediate product

$$N:C\dot{C}l + C_2H_5 \rightarrow N:C(C_2H_5)\dot{C}l$$

was never taken into consideration; regarded from the standpoint of the substitution theory such a reaction would be inconceivable and a priori it seems somewhat extraordinary. Nevertheless the reaction actually takes place in this way, as is proved by the following experiments.

In adding to a well cooled (-5 - 10°) mixture of chloro-cyanogen (or bromo-cyanogen), water (five parts) and alcohol (2 parts), an excess of sodium ethylate (or potassium hydroxide), care being taken that the temperature never rises above 0°, the color of chloro-cyanogen soon disappears. The solution is repeatedly extracted with ether and the color extract worked up precisely as in the above experiment with sodium ethylate. Methyl-carbonic ether is obtained as the chief product and water as a by-product (about in the proportion of 8:1). The water obtained in this way boiled at 181° and melted at 52°.

0.1788 grams gave 24.6 c.c.m nitrogen at 18° and 750 mm pressure.

Found

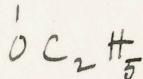
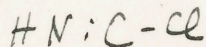
$C_2H_5N_2O$

Calcd for

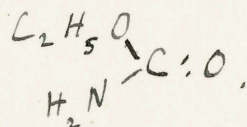
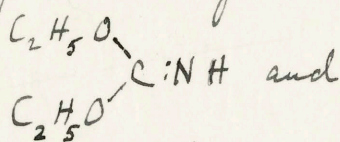
$C_2H_5N_2O$

The yield of methyl-carbonic ether in the above reaction is excellent — almost as good as when sodium ethylate is used. The same result is obtained when the caustic potash added is very dilute or concentrated, the quantity of alcohol

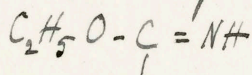
small or large, whether the reaction is carried out at low or at ordinary temperatures; at low temperatures, however, the formation of ethyl cyanurate was never observed. Since as is well known chlor- and brom- cyanogen are converted by dilute caustic potash into cyanate and into potassium chloride or bromide, and since, as I have verified by special experiment, potassium cyanate in the presence of alcohol, water and potassic hydrate can under no conditions be converted into imido-carbonic ester or urethane, the reaction in question can only be explained on the basis of an addition of alcohol to the triple bond present in chlor- cyanogen. The intermediate product thus formed



is then simply converted by alcohol or water present into

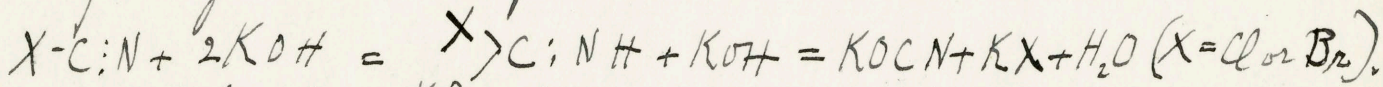


The formation of ethyl cyanurate at higher temperatures is then also easily explained: a small portion of the intermediate product



before it can be acted upon by the alcohol present loses hydrochloric acid forming $\text{C}_2\text{H}_5\text{O} - \text{C} = \text{N}$, which in the nascent state polymerizes to ethyl cyanurate.

It follows, moreover, from the facts just stated that when chlor- and brom- cyanogen are converted by means of potassic hydrate into potassium cyanate the following reaction takes place:



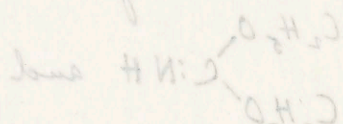
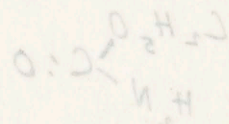
It has long been known ^{KO} that toward many substances (water, alcohol etc.)

chlor- cyanogen shows a greater reactivity than brom- cyanogen and that cyanogen iodide is the least reactive of the cyan haloids. This fact was justly regarded as remarkable as long as it was assumed that in the reactions of these bodies substitution processes took place. It now becomes self evident since it has been established that

small or large, whether the reaction is exothermic or endothermic, at low temperatures, however, the formation of ethyl cyanurate is more favored. This is well known also - and brown - cyanogen is converted to ethyl cyanate faster in the presence of water. Potassium cyanate in the presence of alcohol, water, and other substances can be converted into nitrile - carbonic ester or urethane, the reaction in question can only be explained on the basis of an addition of alcohol to the triple bond present in ethyl - cyanogen. The intermediate product thus formed



is then simply converted to alcohol or water present in

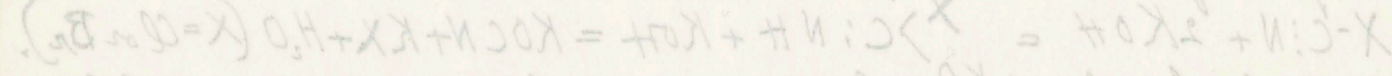


The formation of ethyl cyanurate at higher temperatures is then easily explained. A small portion of the intermediate product



before it can be acted upon by the alcohol present has hydrolyzed and forming $H_2N-C \equiv O$, which in the present state polymerizes to ethyl cyanurate.

It follows, moreover, from the facts just stated that when ethyl - cyanogen is converted by means of potassium cyanate into potassium cyanate the following reaction takes place:



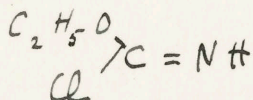
It has long been known that many substances (water, alcohol, etc.)

ethyl - cyanogen shows a greater reactivity than brown - cyanogen and that cyanogen is the best reagent of the cyanohydrin. This fact is justly regarded as remarkable as long as it was assumed that in the reaction of the triple bond with cyanogen took place. It is now known that cyanogen is not a simple substance but a mixture of ethyl cyanogen and ethyl cyanate.

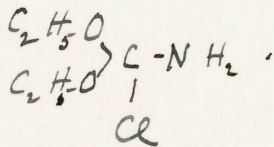
in many reactions the cyanogen ~~group~~ and not the halogen group present is the point of attack. The additive power of the cyanogen group in $X-C:N$ diminishes as the mass ⁷⁴ (atomic weight) of the halogen present increases.

Special attention should ^{here} be called ~~to the~~ to the interesting and long known fact that cyanogen iodide in contrast to both the other halogen cyanides breaks down when treated with caustic potash into potassium cyanide, potassium iodate and potassium iodide. The product first formed by an absorption of water $I-C:NH$ breaks down spontaneously, as shown above in the case of other ^{H'O} analogous substances, into its components, prussic acid $C:NH$, and hypoiodous acid, $H'OI$; the latter then gives at once iodic and hydroiodic acid.

Cyanogen chloride is readily decomposed by alcohol forming ethyl carbonate, urethane, ethyl chloride and ammonium chloride ⁷⁵. This reaction becomes intelligible on the basis of an absorption of alcohol by the cyanogen group: the intermediate product



thus formed being an acid chloride is at once converted by the alcohol into the hydrochloride of imido-carbonic ester,



This salt is very easily decomposed ⁷⁶ at ordinary temperatures giving urethane and ethyl chloride; in the presence of water, on the other hand it is split into ammonium chloride and ethyl carbonate.

The decomposition of cyanogen bromide by means of alcohol may be explained in a perfectly analogous manner; this reaction takes place much less readily than

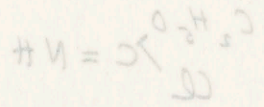
⁷⁴ Compare Liebig's Annalen 276, 237.

⁷⁵ Wirtz, Liebig's Ann. 79, 287.

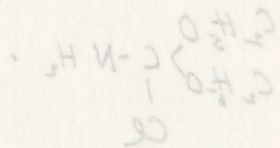
⁷⁶ Erdmeyer, Ber. d. Chem. Ges. 19, 864.

in many reactions the oxygen atom is the point of attack. The relative power of the oxygen group in X-C: N is considerable as the case of (butyramide) of the nitrogen group is shown. Special attention should be called to the interesting and long known fact that oxygen is in contrast to the other nitrogen compounds which when treated with caustic potash into potassium cyanide, potassium iodide and potassium iodate. The product first formed by an absorption of water I-C: N + H₂O breaks down spontaneously, as shown above in the case of other analogous substances, into its components, formic acid C: N + H₂O and hypobromous acid, HOI; the latter then gives at once iodine and hydrobromic acid.

Oxygen chloride is easily decomposed by alcohol forming ethyl carbonate, water, ethyl chloride and ammonium chloride (7). This reaction becomes intelligible on the basis of an absorption of alcohol by the oxygen group: the water molecule product



the former being an acid chloride is at once converted by the alcohol into the hydrochloride of imido-carbonic ester,

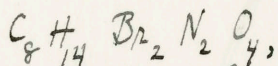


This salt is very easily decomposed by ordinary temperature giving water and ethyl chloride; in the presence of water, on the other hand it is split into ammonium chloride and ethyl carbonate.

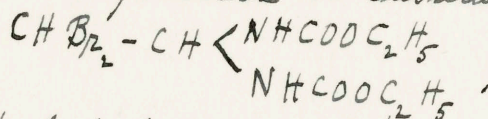
The decomposition of oxygen bromide by means of alcohol may be explained in a perfectly analogous manner; the reaction takes place much less readily than

74) Compare with 73) 75) 76) 77) 78) 79) 80) 81) 82) 83) 84) 85) 86) 87) 88) 89) 90) 91) 92) 93) 94) 95) 96) 97) 98) 99) 100)

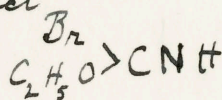
in the case of cyanogen chloride so that it is necessary to heat in a sealed tube. Ammonium bromide, carbon dioxide, urethane and ethyl bromide are formed as Mulder⁷⁷⁾ has shown: he also obtained in this reaction a substance having the formula



which melts at 121° and is soluble in hot water. This product is in all probability identical with the substance which Bischoff⁷⁸⁾ obtained by the action of bromine on alcoholic prussic acid, and which he proved possesses the constitution,

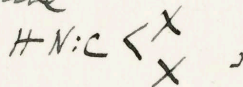


The formation of this product from cyanogen bromide and alcohol is to be explained on the basis of a splitting of the addition product

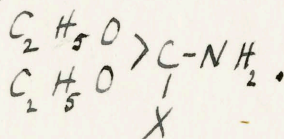


into prussic acid and ethyl hypobromite, C_2H_5OBr ; the latter then decomposes with the formation of dibrom-acet. aldehyde, which condenses with the urethane formed in the reaction.

The processes which take place when chlorine or bromine is led into alcoholic prussic acid are also now easily intelligible. Chlor- or brom- cyanogen and halogen hydride are first formed; as the solution becomes richer in halogen hydride there is formed more and more of the imido derivative



($X = Cl$ or Br) which, combining with the alcohol, gives halogen hydride and the salt of imido-ethyl carbonate



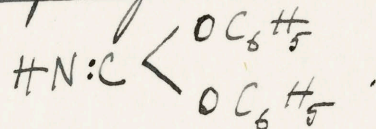
The latter is known to decompose easily into urethane and halogen ethyl. If more chlorine or bromine continue to be led into the solution a part of the alcohol is naturally oxidized to halogen-substituted aldehydes which then simply condense with the urethane present. That this explanation of the reaction is correct follows from the following experiments: chlor- or brom- cyanogen treated in alcoholic solution with dry hydrochloric or hydrobromic acid are all at once very energetically decomposed and urethane is formed in large quantities. It may incidentally be stated that when dry

⁷⁷⁾ Rec. trav. chim. d. Pays-Bas 5, 86.

⁷⁸⁾ Bischoff, Ber. d. Chem.-Ges. 5, 80; 7, 630.

hydrobromic acid is led into an absolute ethereal solution of cyanogen bromide a yellowish-white, very hygroscopic precipitate of imido-carbonyl bromide, $\text{HN}:\text{C} \begin{smallmatrix} \text{Br} \\ \text{Br} \end{smallmatrix}$, or of its hydrobromic acid salt is formed. This salt fumes strongly in moist air and breaks down into carbon dioxide and ammonium bromide; in the absence of moisture it readily loses hydrobromic acid regenerating cyanogen bromide.

Imidophenyl Carbonate,



On leading chlor-cyanogen into an alcoholic solution of sodium phenolate and subsequently distilling the oily reaction product Hofmann and Olshausen ⁷⁹ obtained, together with much phenol, phenyl cyanurate ($\text{C}_6\text{H}_5\text{OCN}$)₃ melting at 225. They concluded that phenyl cyanate is the first product of the reaction, and that on distilling it simply polymerizes. This assumption is incorrect: not a trace of phenyl cyanate nor of of phenyl cyanurate is formed, as is shown by the following experiments.

If a solution of 80 grams phenol (two molecules) and 48.6 grams caustic potash in 300 ccm water is added slowly, with constant shaking, to a cold solution (20°) of 46 grams brom-cyanogen in two and one half liters of water reaction sets in at once; the solution becomes turbid, gives an alkaline reaction and a yellowish oil separates out. As soon as the odor of brom-cyanogen has disappeared the oil solidifies. The precipitate is dissolved in ether, washed with dilute sodic hydrate and ~~the solution evaporated~~ after drying with ~~titrate~~ calcium chloride the solution is evaporated. The yield is about 67 grams of almost perfectly pure imido-phenyl carbonate. For the purpose of analysis a portion was recrystallized from lukewarm ligroin (bpt. 70-80°); in this way were obtained colorless needles melting at 54° and possessing a faint odor similar to that of phenol.

Triphenyl Carbamate



On heating chloro-organogen into an alcoholic solution of sodium phenolate and subsequently distilling the oily reaction product Hoffman and Robinson (19) obtained, together with much phenol, phenyl cyanurate ($\text{C}_6\text{H}_5\text{OCN}$) melting at 115°. They concluded that phenyl cyanate is the first product of the reaction, and that on distilling it simply polymerizes. This assumption is incorrect; but a trace of phenyl cyanate or of phenyl isocyanate is formed, as is shown by the following experiments.

If a solution of 80 grams phenol (two molecules) and 48.8 grams caustic potash in 300 c.c. water is added slowly, with constant shaking, to a cold solution (20°) of 40 grams trim-organogen in two and one half liters of water reaction sets in at once; the solution becomes turbid, gives an alkaline reaction and a yellowish oil separates out. As soon as the odor of trim-organogen has disappeared the oil solidifies. The precipitate is dissolved in ether, washed with dilute sodium hydroxide and the solution evaporated after drying with calcium chloride the solution is evaporated. The yield is about 20 grams of almost perfectly pure triphenyl carbamate. For the purpose of analysis a portion was recrystallized from absolute ligroin (b.p. 70-80°); in the way were obtained colorless needles melting at 34° and possessing a faint odor similar to that of phenol.

0.3195 grams, dried in a vacuum over H_2SO_4 , gave 19 cc nitrogen at 18° and 748 mm pressure.
 0.1402 grams, dried in a vacuum over H_2SO_4 , gave 0.3747 CO_2 and 0.0672 H_2O .

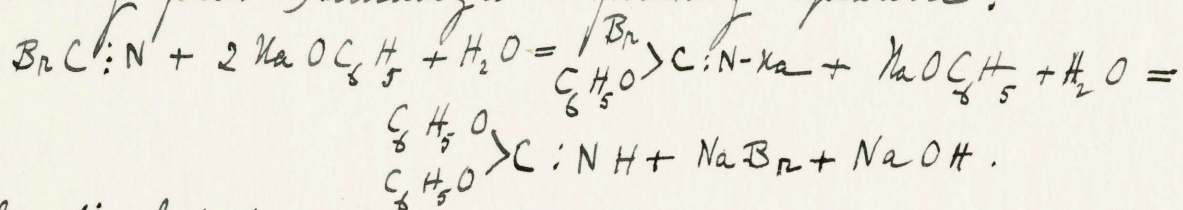
Theory for

	$C_{13}H_{11}NO_2$
C	73.24
H	5.16
N	6.57

Found

72.89
5.33
6.76

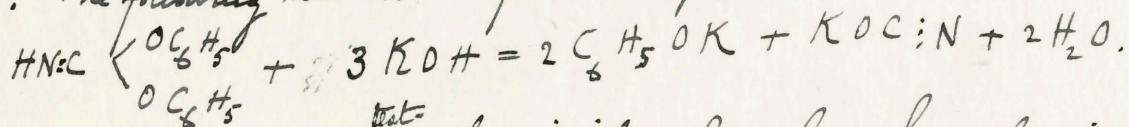
Imido-phenyl carbonate is, therefore, formed (73% of the quantity theoretically possible) according to the following equation:



The sodic hydrate formed in the reaction converts a small portion of the bromocyanogen into cyanate.

Imido-phenyl carbonate is very easily soluble in all organic solvents with the exception of cold ligroin; it is perfectly insoluble in water.

In its chemical behavior it resembles in every respect the corresponding imido-ethyl carbonate: ^{cold} dilute hydrochloric acid converts it in the cold completely into phenyl carbonate (mpt. 88° , from alcohol) and ammonium chloride. When 10 grams of the substance are heated for 20 minutes with three molecules of alcoholic potash 1.7 grams almost perfectly pure potassium cyanate separate out as fine crystals. The salt gave on treatment with 2 grams ammonium sulphate 0.9 grams pure urea melting at 132° . The following reaction therefore takes place:



On heating in a ^{test} tube imido-phenyl carbonate is completely decomposed giving phenol and phenyl cyanurate according to the equation:

$$3 \begin{matrix} C_6H_5O \\ | \\ C_6H_5O \end{matrix} C:NH = 3C_6H_5OH + 3 \begin{matrix} C_6H_5O \\ | \\ C_6H_5O \end{matrix} C:N = 3C_6H_5OH + [C_6H_5OCN]_3.$$

The phenyl cyanurate formed being very difficultly soluble in alcohol was recrystallized from glacial acetic acid; it melts at 225° and is in every respect identical with the product obtained by Hofmann and Olschansen.

On treating brom- or chlorocyanogen in alcoholic solution either with aqueous

0.3192 g. dried in a vacuum at 18° and 748 mm pressure
 0.1402 g. dried in a vacuum over H_2SO_4 at 18° and 748 mm pressure
 Found
 C 73.24
 H 5.16
 N 6.57
 C 73.24
 H 5.16
 N 6.57

Triethyl phenyl carbonate is, therefore, formed (73% of the quantity the-
 thetically possible) according to the following equation:

$$3\text{C}_6\text{H}_5\text{N} + 2\text{NaOC}_2\text{H}_5 + \text{H}_2\text{O} = 3\text{C}_6\text{H}_5\text{N} + \text{NaOC}_2\text{H}_5 + \text{H}_2\text{O}$$

The solid hydrate formed in the reaction consists of a small portion of the tri-
 ethyl phenyl carbonate which is very easily soluble in all organic solvents with the exception
 of cold ligroin; it is perfectly insoluble in water.

In its chemical behavior it resembles in every respect the corresponding tri-
 ethyl carbonate: it is perfectly insoluble in water. When 10 grams of the
 carbonate (m.p. 88°, from alcohol) and ammonium chloride were heated for 20 minutes with three volumes of absolute alcohol, 1.7 grams
 almost perfectly pure triethyl phenyl carbonate separated out as fine crystals. The solid
 gave on treatment with 20% aqueous ammonium sulphate 0.9 grams of crystals melting at
 132°. The following reaction therefore takes place:

$$3\text{C}_6\text{H}_5\text{N} + 3\text{KOH} = 3\text{C}_6\text{H}_5\text{N} + 3\text{KOH} + 3\text{H}_2\text{O}$$

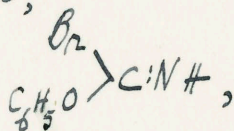
The reaction in other words triethyl carbonate is completely
 decomposed giving phenol and triethyl carbonate according to the equation:

The triethyl carbonate formed being very difficultly soluble in alcohol
 was recrystallized from phenol several times; it melts at 132° and is in every
 respect identical with the product obtained by Hoffmann and Robinson.
 On heating from 100° to 200° in absolute alcohol with aqueous

or with alcoholic sodium phenolate imido-phenyl carbonate is likewise formed as the chief product. In this case, however, imido-phenyl-ethyl carbonate,

$$\text{HN}:\text{C} \begin{matrix} \text{OC}_6\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{matrix},$$

is also formed as might be expected; the alcohol present, as well as the sodium ethylate or sodic hydrate arising from the reaction can act upon the intermediate product;



which is formed first. The oily reaction-product thus obtained contains not a trace of phenyl cyanurate, but on attempting to distill it under reduced pressure decomposition always occurs at 180° with formation of much phenol and phenyl cyanurate.

It is, therefore, ~~for~~ established that Hofmann and Olshausen's phenyl cyanurate did not result from the polymerization of phenyl cyanate but was formed from imido-phenyl carbonate during the process of distillation. The above mentioned imido-phenyl-ethyl carbonate boils at about 120° at 18 mm pressure; it was, however, not obtained perfectly pure.

or with alcoholic sodium hydroxide is likewise
formed as the chief product. In this case, however, methyl-ethyl-
carbonate, $\text{H.N.C}(\text{OCH}_3)_2$, is also formed as well as the

is also formed as might be expected; the chief product, as well as the
sodium ethylate or sodium hydroxide arising from the reaction can act upon the
intermediate product, $\text{C}_2\text{H}_5\text{O.C}(\text{OCH}_3)_2$, to form

which is formed first. The only reaction-product thus obtained contains
no trace of phenyl cyanurate, but on attempting to distill it under
reduced pressure decomposition always occurs at 180° with formation of
methyl phenyl and phenyl cyanurate.
It is therefore, established that Hoffman and Okamoto's
phenyl cyanurate did not result from the polymerization of phenyl
cyanurate but was formed from methyl-phenyl carbonate during the process
of distillation. The above mentioned methyl-phenyl-ethyl carbonate was
at about 120° at 18 mm pressure; it was, however, not obtained perfectly pure.

The Esters of Normal Cyanic Acid, $\text{RO}-\text{C}:\text{N}$.

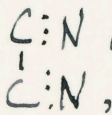
Up to the present time all attempts to prepare these still unknown esters have led only to negative results.

Ethyl hypochlorite does not act at low temperatures on dry silver cyanide, neither does it react with aqueous mercury cyanide, a neutral salt. On carefully adding aqueous potassium cyanide (1:1) to ethyl hypochlorite suspended in water at $+3^\circ$ energetic interaction takes place; besides much ethyl alcohol, however, only cyan-imido-carbonic ether was obtained. This leads to the conclusion that ethyl cyanate, $\text{C}_2\text{H}_5\text{OC}:\text{N}$, is at once decomposed by water. On treating silver cyanate, $\text{AgOC}:\text{N}$, with ethyl iodide much ethyl isocyanate was obtained — ^{hardly} a ~~not~~ surprising result, since now the great absorptive power of the cyanogen group has been shown. It is, however, not improbable that in this reaction normal ethyl cyanate is also formed to some extent; its presence having until now been overlooked ⁸⁰. The experiment will soon be repeated with larger quantities of silver cyanate. The possibility still exists that brom- or chlor-cyanogen may be converted into esters of normal cyanic acid by heating in a sealed tube with perfectly dry ~~alcohol~~ sodium ethylate or sodium phenolate free from alcohol; the success of such an experiment is, however, very problematic.

The esters of cyanic acid can certainly be prepared as soon as the esters of hypobromous acid, ^{ROBr} are accessible. Ethyl hypobromite for instance will react ~~at~~ with dry silver cyanide at -10° with formation of ethyl cyanate. Experiments in this direction are, therefore, being continued.

The Addition of Alcohol to Cyanogen.

In the presence of alkalis cyanogen,



^{easily} may be made to absorb either one or two molecules of alcohol giving

⁸⁰) Compare Ponomareff, Ber. d. Chem. Ges. 18, 3263.

The Nature of Normal Organic Acid, R-O-C-H.

Up to the present time all attempts to prepare these still unknown esters have led only to negative results. Ethyl hypochlorite does not act at low temperatures or dry ether yields neither here it reacts with organic bases, a neutral salt. On carefully adding organic potassium cyanide (1:1) to ethyl hypochlorite suspended in water at +8° temperature interaction takes place; besides much ethyl alcohol, however, only cyan-hydro-carbonic ester was obtained. This leads to the conclusion that ethyl cyanate, C_2H_5OCN , is at once decomposed by water. On treating silver cyanate, $AgOCN$, with ethyl iodide much ethyl cyanate was obtained. A most surprising result, since from the great absorptive power of the cyanogen group has been known. It is, however, not impossible that in this reaction normal ethyl cyanate is also formed to some extent, its presence having until now been overlooked. The experiment will now be repeated with larger quantities of silver cyanate. The possibility still exists that from or chlor-cyanogen may be converted into esters of normal organic acid by heating in a sealed tube with perfectly dry, ethyl sodium ethylate or sodium phenylate free from alcohol; the success of such an experiment is, however, very problematic.

The esters of organic acid and certainly be prepared as soon as the esters of hypochlorous acid are accessible. Ethyl hypochlorite for instance will react with dry silver cyanide at -10° with formation of ethyl cyanate. Experiments in this direction are therefore, being continued.

The Reaction of Alcohol to Cyanogen

In the presence of alkalis cyanogen, C_2N_2 , may be made to absorb either one or two molecules of alcohol giving

cyan-imido-carbonic ether,

$$\begin{array}{c} \text{C}_2\text{H}_5\text{O} \cdot \text{C} \cdot \text{N} \cdot \text{H} \\ | \\ \text{C} \cdot \text{N} \end{array}$$

or di-imido-oxalic ether,

$$\begin{array}{c} \text{C}_2\text{H}_5\text{O} \cdot \text{C} \cdot \text{N} \cdot \text{H} \\ | \\ \text{C}_2\text{H}_5\text{O} \cdot \text{C} \cdot \text{N} \cdot \text{H} \end{array}$$

The cyanogen used was prepared according to the method of Jacquemin 81) who states that 850 ccm of this gas are obtained from 10 grams of potassium cyanide.

On leading cyanogen (from 100 grams potassium cyanide) pretty rapidly into a solution, ^{cooled with ice,} of 10 grams potassium cyanide, 50 grams water and 70 grams alcohol a dark red coloration appears at once. As soon as the evolution of cyanogen ceases water is added and the solution extracted five times with ether; the ethereal solution is washed with water and dried with calcium chloride. 21 grams of the crude product were obtained. It consisted of much cyan-imido-carbonic ether and a little di-imido-oxalic ether. These substances may be easily separated by fractional distillation at reduced pressure.

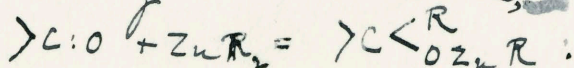
A corresponding experiment was carried out in which cyanogen gas (from 50 grams potassium cyanide) was led into a solution, cooled to 0°; of 6 grams sodium in 100 grams alcohol. A brown coloration appeared, and potassium carbonate and potassium cyanide separated out of the solution. 13.5 grams of oil were obtained. ~~It consisted~~ When distilled at reduced pressure almost all of this product (10 grams) boiled between 88 - 91° and consisted of pure di-imido-oxalic ether.

The Action of Zinc Ethyl on Cyanogen and its Derivatives.

It is known that the zinc alkyls react with acid chlorides, $\text{R} \cdot \text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{Cl} \end{array}$, acid ethers, $\text{R} \cdot \text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{O} \cdot \text{R}' \end{array}$,

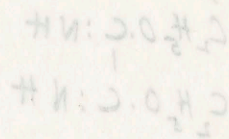
with aldehydes, $\text{R} \cdot \text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{H} \end{array}$ and ketones, $\text{R} \cdot \text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{R}' \end{array}$

with forming addition products in which the zinc alkyl is simply absorbed by the carbonyl group existing in these substances,



81) Annales de Chim. et de Phys. [6] 6, 140; the observation of Seuf, Journ. f. pract. Chem. [2] 35, 514, is probably due to an error.

oxygen - which - carbonic ether
or di-methyl - oxalic ether



The oxygen used was prepared according to the method of J. J. Berzelius. The gas was obtained from 10 grams of potassium superoxide. On heating oxygen (from 10 grams potassium superoxide) pretty rapidly with a solution of 10 grams potassium superoxide, 20 grams water and 70 grams alcohol a dark red coloration appeared at once. As soon as the evolution of oxygen ceased water is added and the solution extracted five times with ether; the ethereal solution is washed with water and dried with calcium chloride. 21 grams of the crude product were obtained. It consisted of much oxygen - which - carbonic ether and a little di-methyl oxalic ether. These substances may be easily separated by fractional distillation at reduced pressure.

A corresponding experiment was carried out in which oxygen gas (from 20 grams potassium superoxide) was led into a solution, cooled to 0°; of 5 grams sodium in 100 grams alcohol. A brown coloration appeared and potassium carbonate and potassium superoxide separated out of the solution. 18.5 grams of oil were obtained. It consisted when distilled at reduced pressure almost all of the product (10 grams) boiled between 88° - 91° and consisted of pure di-methyl - oxalic ether.

The action of pure Ethyl or Propyl on oxygen and the formation of

It is known that the pure ethyl reacts with
acid chlorides, $\text{R} \cdot \text{C} \cdot \text{O} \cdot \text{R}'$, and ether, $\text{R} \cdot \text{C} \cdot \text{O} \cdot \text{R}'$.

with aldehydes, $\text{R} \cdot \text{C} \cdot \text{O} \cdot \text{H}$, and ketones, $\text{R} \cdot \text{C} \cdot \text{O} \cdot \text{R}'$.

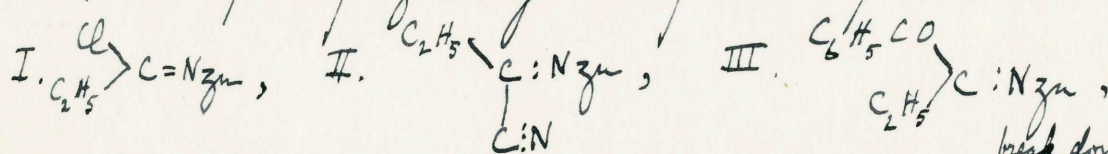
with forming addition products in which the zinc ethyl is simply absorbed by the carbonyl group existing in these substances.



It is, therefore, to be expected that the zinc alkyls will add themselves in a similar way to the very reactive triple bond existing in the cyanogen derivatives.

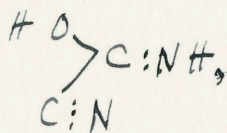
Gal found⁸²⁾ that chlor-cyanogen treated with zinc ethyl undergoes decomposition giving ethyl cyanide and zinc chloride; E. Frankland and Graham⁸³⁾ found that zinc ethyl and cyanogen interact with formation of zinc cyanide and ethyl cyanide; E. Frankland and Lewis⁸⁴⁾ obtained zinc cyanide and ethyl-phenyl ketone from benzoyl cyanide and zinc ethyl.

An absorption of zinc ethyl⁸⁵⁾ with formation of the intermediate products



easily explains these reactions. The intermediate products then ^{break down} at once, I giving ZnCl_2 and $\text{C}_2\text{H}_5\text{C}:\text{N}$; II $\text{C}:\text{Nzn}$ and $\text{C}_2\text{H}_5\text{C}:\text{N}$; and III $\text{C}:\text{Nzn}$ and $\text{C}_6\text{H}_5\text{COC}_2\text{H}_5$. The splitting of II and III is ~~entirely~~ perfectly analogous to that of imido-oxalic ether into prussic acid and ethyl carbonate.

The decomposition of cyanogen by water or alkalis may be explained in a perfectly analogous manner; an absorption of water gives first the intermediate product



which breaks down spontaneously into prussic acid (or azulmic acid) and cyanic acid $\text{HOC}:\text{N}$. The decomposition, first observed by Wöhler⁸⁶⁾, of an aqueous solution of cyanogen into urea, azulmic acid, prussic acid and ammonium oxalate and carbonate ~~is~~ therefore, readily comprehensible.

⁸²⁾ Compt. Rend. 66, 48.

⁸³⁾ Journ. Chem. Soc. 37, 740.

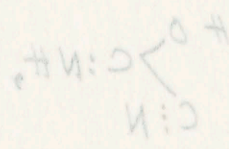
⁸⁴⁾ Journ. Chem. Soc. 37, 742.

⁸⁵⁾ The formula $\text{C}_2\text{H}_5\text{zn}$ is here given to zinc ethyl, zn indicating half an atom of zinc.

⁸⁶⁾ ~~Annales de Chim. et de Phys.~~ [47] 17, 114-122. Pogg. Ann. 15, 627.

It is therefore to be expected that the decomposition of cyanogen will proceed in a similar way to the decomposition of the cyanogen derivative. The decomposition of cyanogen is a process of great interest, and the formation of the intermediate products is a subject of great importance. The decomposition of cyanogen is a process of great interest, and the formation of the intermediate products is a subject of great importance.

The decomposition of cyanogen is a process of great interest, and the formation of the intermediate products is a subject of great importance. The decomposition of cyanogen is a process of great interest, and the formation of the intermediate products is a subject of great importance. The decomposition of cyanogen is a process of great interest, and the formation of the intermediate products is a subject of great importance.



which breaks down spontaneously into formic acid (or cyanic acid) and cyanogen. The decomposition, first observed by Wöhler, of an aqueous solution of cyanogen into formic acid, cyanic acid, and ammonium carbonate is a process of great interest, and the formation of the intermediate products is a subject of great importance.

82) The formula $\text{C}_2\text{H}_2\text{N}_2$ is the same as the formula of cyanogen. 83) The formula $\text{C}_2\text{H}_2\text{N}_2$ is the same as the formula of cyanogen. 84) The formula $\text{C}_2\text{H}_2\text{N}_2$ is the same as the formula of cyanogen. 85) The formula $\text{C}_2\text{H}_2\text{N}_2$ is the same as the formula of cyanogen.

IV. Prussic Acid is identical with Isocyanogen Hydride, $\text{HN}\cdot\text{C}$.

Preparation of absolutely pure prussic acid. Gaudier was the first to obtain prussic acid free from water and capable of preservation for an indefinite period ⁸⁷). He showed that ~~that~~ by Gay-Lussac's method a prussic acid is obtained which contains traces of water and of ammonium cyanide, and that these substances cause it to go over into azulmic acid. From silver cyanide and dry hydrogen sulphide ^{on the contrary} as well as from yellow prussiate of potash and sulphuric acid Gaudier was able to prepare a pure prussic acid, which boils at 26° ; melts at -14° and which may be preserved unchanged. By fractional recrystallization of 600 grams of such a substance Gaudier proved that he was dealing perfectly homogeneous compound; furthermore he carried out a very careful study of its physical properties, specific gravity density, boiling point and melting point. The hydrate of this substance was also thoroughly studied. The analyses show, however, an inexplicable loss of $\frac{1}{200}$ substance; moreover the vapor-density determinations carried out at different temperatures by the methods of ~~the~~ Dumas and Gay-Lussac point to an abnormal behavior of the body. At 31° the density 0.936 was found; this diminishes constantly as the temperature rises and at 197° was 0.903. Gaudier explains these peculiar phenomena by the assumption that the coefficient of expansion of the gas is greater than that of the air. It is much more probable that ^{traces of} a foreign substance ~~were~~ ^{namely ammonium cyanide} present. An impurity of 2% of this substance in pure prussic acid would fully explain the losses in analysis as well as the abnormal densities observed: the theoretical ^{vapor} density ~~for~~ when the ammonium cyanide is undissociated is 0.947; when the salt is completely dissociated into ammonia and prussic acid it is 0.928; Gaudier found at 47° the density 0.953, at 158° 0.924.

The acid prepared according to the method of Gaudier was free from water, since it was passed through a long U-tube filled with calcium chloride. No precautions, however, were taken to remove the ammonium cyanide probably present. By a method of preparation which must remove also the last mentioned

Preparation of absolutely pure formic acid. Further was the first to obtain formic acid free from water and capable of polymerization for an indefinite period (87). He showed that the by-product obtained in formic acid is obtained which contains traces of water and of ammonium cyanide, and that these substances cause it to be not so pure as sulphuric acid. For other cyanide and this hydrogen sulphide the yield as from yellow formic acid of 100% and sulphuric acid further was able to prepare a pure formic acid, which boils at 25° and melts at -14°, and which may be preserved unchanged. By fractional rectification 100 grams of such a substance further found that he was dealing with a chemical compound; furthermore he carried out a very careful study of the physical properties, specific gravity, boiling point and melting point. The highest of the substance was also thoroughly studied. The analysis shows, however, an insignificant loss of 1/100 substance; however the vapor density determination carried out at different temperatures by the method of the Ramsay and Gay-Lussac found to be an abnormal behavior of the body. At 31° the density 0.938 was found; the densities constant as the temperature rises and at 117° was 0.908. Further explain these peculiar phenomena of the assumption that the coefficient of expansion of the gas is greater than that of the air. It is much more probable that a foreign substance was present. The impurity of 2% of the substance in pure formic acid would fully explain the fact in analysis as well as the abnormal density observed. The theoretical density of pure formic acid is 0.947; when the ammonium cyanide is undissociated is 0.947; when the salt is completely dissociated into ammonia and formic acid it is 0.928; further found at 147° the density 0.923, at 158° 0.924. The acid prepared according to the method of further was free from water, since it was passed through a long U-tube filled with calcium chloride. In preparation, however, were able to remove the ammonium cyanide probably present. By a method of preparation which must remove also the last mentioned

body - the use, namely, of phosphorous pentoxide - prussic acid is obtained perfectly pure and possessing physical properties which differ from those of Gantier's substance.

The prussic acid used in my experiments was prepared by heating yellow prussiate of potash (500 grams) and sulphuric acid (350 grams conc. acid and 650 grams water); in this process the directions of Gantier and of Wöhler (88) were essentially followed. It ^{was} ~~has~~ been found very advantageous to connect a short condenser placed in a slanting position with the neck of the retort. The prussic acid vapor was then led through two large U-tubes filled with calcium chloride, which were placed in water kept at 35-40°; it afterward passed through a very long condenser and was received in a condensing tube fitted with ground glass stopcocks, which was packed in a freezing mixture of ice and salt. The mixture in the retort was ~~made~~ ^{caused} to boil violently toward the close of the reaction, which usually lasts an hour. The yield is almost 100 grams of prussic acid free from water. Several portions prepared in this way were brought into a flask and phosphorous pentoxide added. The flask was connected with a U-tube, which contained a mixture of glass beads and phosphorous pentoxide and which during the distillation was placed in water at 40-50°. The other end of the U-tube was connected with a long condenser and a receiver, as described above, the receiver being protected from moist ~~in~~ air by a long tube filled with calcium chloride and phosphorous pentoxide. The apparatus set up in this way was allowed to stand 12-20 hours and then the prussic acid was distilled. After repeated distillations a prussic acid is obtained which boils constant at 25° corr. ().

A short, so-called Roeschütz'sches thermometer divided into fifths of a degree was used. Its zero point stood at +0.2°. I formerly prepared prussic acid free from water in large quantities (500 grams) according to the method of Gantier and observed that when the same thermometer was used it boiled at 26.2° (corr. 26°).

The purest prussic acid free from ammonium chloride bds, therefore, an entire degree

body - the use, namely, of phosphoric acid - phosphoric acid is obtained perfectly pure and free from phosphoric acid which differs from that of phosphoric acid.

The phosphoric acid used in my experiments was prepared by heating yellow phosphorus of 100 grams (500 grains) and sulphuric acid (250 grains) and acid and 500 grains water; in the process the distillate of phosphoric acid and 80 (80) were essentially formed. It has been found very advantageous to connect a short condenser placed in a slanting position with the neck of the retort. The phosphoric acid vapor was then led through two large U-tubes filled with calcium chloride, which were placed in water kept at 32-40°; it afterwards passed through a very long condenser and was received in a condensing tube filled with ground glass stopcocks, which was placed in a freezing mixture of ice and salt. The mixture in the retort was ~~kept~~ ^{allowed to} boil vigorously toward the close of the reaction, which usually lasts an hour. The yield is about 100 grams of phosphoric acid free from water. Several portions prepared in this way were brought into a flask and phosphoric pentoxide added. The flask was connected with a U-tube, which contained a mixture of glass beads and phosphoric pentoxide and which during the distillation was placed in water at 40-50°. The other end of the U-tube was connected with a long condenser and a receiver as described above, the receiver being fitted from front and back with air for long tube filled with calcium chloride and phosphoric pentoxide. The apparatus set up in this way was allowed to stand 12-20 hours and the phosphoric acid was distilled. After repeated distillations a phosphoric acid is obtained which boils constant at 28°.

I shall, as called for, submit the results of a series of experiments. The first point about 40-50°. I formerly prepared phosphoric acid free from water in large quantities (500 grains) according to the method of Gaudin and observed that when the same thermometer was used it boiled at 26.5° (corr. 26°).

The purest phosphoric acid free from ammonium chloride, therefore, in entire purity

lower than Gautier's prussic acid. The melting point, too, of this substance lies higher than Gautier found it (-14°); it lies between -10° and -12° . The lack of a suitable thermometer unfortunately prevented me from carrying out an exact determination. Prussic acid prepared in this way may be kept for months in vessels furnished with stopcocks without the slightest change. It was used for all the experiments described in this paper. As is to be expected prussic acid compared with its salts and with the alkyl isocyanides is a very inactive body⁸⁹⁾. At low temperatures it does not combine with chlorine⁹⁰⁾ nor with hydrochloric acid⁹¹⁾. I have found that molecular quantities of prussic acid and ethyl hypochlorite can be mixed at -10° without the evolution of heat, and even when the mixture stands for a long time at that temperature no interaction takes place.

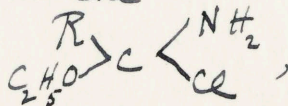
The hydrochloride of form-imido-ether does not exist; the so called salts of prussic acid with halogen hydrides are derivatives of imido-formylcyanide,

$$\text{H} \cdot \text{N} : \text{C} \begin{matrix} \text{H} \\ \diagup \\ \text{C} : \text{N} \end{matrix}$$

About twelve years ago Pinier⁹²⁾ on leading hydrochloric acid into an absolute ethereal solution of prussic acid and alcohol obtained a substance crystallizing in magnificent needles, ~~the~~ which he, ~~regarded~~, by reason of its numerous reactions, regarded as the hydrochloride of form-imido-ether,

$$\text{H} \cdot \text{N} : \text{C} \begin{matrix} \text{OC}_2\text{H}_5 \\ \diagup \\ \text{H} \end{matrix}, \text{HCl}.$$

This substance shows in comparison with all other known imido-ethers a very striking behavior as well toward alcohol, which converts it into ammonium chloride and ortho-formic ester, as toward heat, which decomposes it with formation of ethyl chloride, formic ester and the hydrochloride of form-amidine. The imido-ethers which according to the experiments of Lengfeld and Stieglitz⁹³⁾ are not salts but addition products having the constitution



89) Compare Liebig's Annalen 270, 267-270.

90) Gay-Lussac Annales de Chim. et de Phys. 95, 212.

91) Gautier, loc. cit. [4] 17, 129.

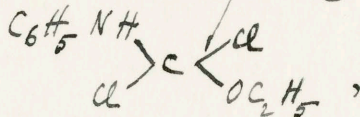
92) Ber. d. Chem. Ges. 16, 354, 1643.

93) Amer. Chem. Journ. 17, 98-112.

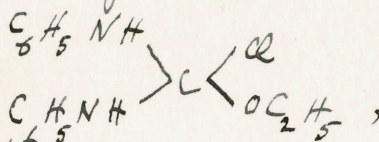
(60)

are, as we know, decomposed according to Pinner ^{by heat} as well ~~on heating~~ as by treatment with alcohol giving ethyl chloride and an acid amide

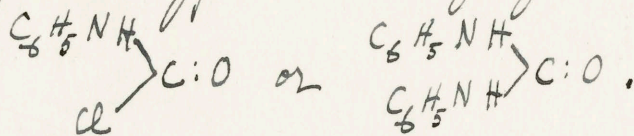
Derivatives, too, of the hypothetical hydrochloride of form-imido-ether, such as the hydrochloride of phenyl-imido-chlor-formic ether,



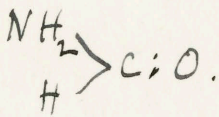
and the hydrochloride of phenyl-imido-amido-formic ether,



are split normally, as ^{shown by} Kungfeld and Stieglitz ⁹⁴ ~~have~~ ^{discovered} observed, into ethyl chloride and



It ^{is} ~~is~~ therefore, to be expected that the hydrochloride of form-imido-ether ~~will~~ ^{will} break down on heating or even at a very low temperature into ethyl chloride and form amide,



These considerations, as well as the fact that prussic acid is converted by alcoholic hydrochloric acid into diethoxy-glyoxylic ester ⁹⁵ caused me to doubt whether Pinner's substance was ^{really} identical with the hydrochloride of form-imido-ether. A new study of the subject was therefore taken up and it was found that no homogeneous body ^{is} ^{is} in question, but a ^{crystal} ^{crystal} mixture this mixture consists of the hydrochloride of imido-phenyl-cyanide - ^{of crystals}

⁹⁴ Pinner. Chem. Journ. 17, 102-104; Ber. d. Chem. Ges. 27, 926.

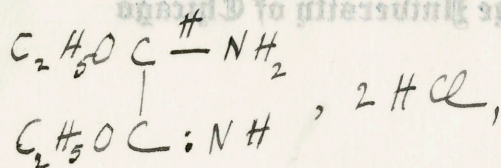
⁹⁵ Pinner and Klein, Ber. d. Chem. Ges. 11, 1473.

These considerations, as well as the fact that fusinic acid is con-
 verted by alkaline hydrochloride into diethyl-*phosphoric ester* cannot
 be to doubt whether fusinic substance was identical with the hydrochloride of
 form-methyl-ether. A new study of the subject was therefore taken up and it
 was found that in benzene solution it is in equilibrium with a *phosphoric ester*
 the mixture consists of the hydrochloride of methyl-formyl-*phosphoric ester*
 and the hydrochloride of methyl-methyl-*phosphoric ester*, such as the
 formation, too, of the hydrochloride of form-methyl-*phosphoric ester*, such as the
 treatment with alcohol giving ethyl chloride and in acid mixture
 and, as we know, decomposition of the ester as well as heating as by

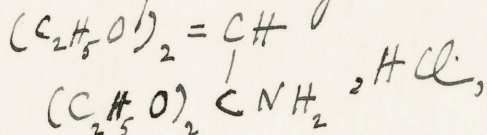
It is therefore, to be expected that the hydrochloride of form-methyl-*phosphoric ester*
 will break down on heating or even at a very low temperature into ethyl
 chloride and form-methyl-*phosphoric ester*.

Chem. Jour. 17, 102-104; Ber. d. Chem. Ges. 27, 928.
 1879. Pinner and Klein, Ber. d. Chem. Ges. 11, 1473.

dialcoholate,

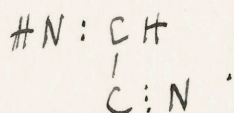


and of the hydrochloride of diethoxy-ortho-amido-glyoxylic ~~ether~~ ether,

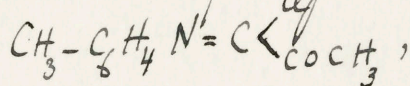


along with other salts.

In a perfectly analogous manner it was found that the salts which prussic acid forms with halogen haloids discovered by Gautier are not salts of imido-formyl haloid as Claisen and Matthes⁹⁶ assume and as I myself formerly supposed⁹⁷ but addition products or salts of imido-formyl cyanide,



The fact that all these substances break down on heating or on treatment with water or alcohol into derivatives of formic acid cannot by reason of former observations be accepted as a certain proof that in them we possess true formic acid derivatives. It was even found that the phenyl-imido-pyruvyl chloride⁹⁸ is split by treatment with alcohol into acetic ether and the hydrochloride of form-amidine⁹⁹. Ortho-tolyl-imido-pyruvyl chloride, ~~breaks down completely into~~



breaks down completely when it is poured into seven parts of cold water giving acetic acid and form-ortho-toluidine⁹⁹. The numerous ^{instances} ~~cases~~ already mentioned in this paper in which molecules rich in carbon break down into molecules of a simpler

⁹⁶) Ber. d. Chem. Ges. 16, 311.

⁹⁷) Liebig's Annalen 270, 307.

⁹⁸) Liebig's Annalen 270, 297.

⁹⁹) Liebig's Annalen 270, 316.

diabazite.

and of the hydrochloride of dihydroxy-*isobutyric* acid.

$$C_2H_3O_2 \cdot H_2O = C_2H_4O_3$$

$$C_2H_3O_2 \cdot H_2O = C_2H_4O_3$$

I am a perfectly analogous manner it was found that the salts which formic acid forms with hydrogen chloride dissolved by fumes are not salts of imide-formyl but of imide as Claisen and Hantzsch assume and as I myself formerly supposed but addition products or salts of imide-formyl compounds.

$$H_2N : CH$$

$$H_2N :$$

The fact that all these substances break down on heating or on treatment with water or alcohol into derivatives of formic acid cannot by reason of former observations be accepted as a certain proof that in them we possess the formic acid derivative. It was even found that the formyl-imide-formyl chloride is split by treatment with alcohol into acetic ether and the hydrochloride of form-imide. Other-*isobutyric*-formyl chloride, ~~breaks down completely~~

$$CH_3-C(=O)-NH-C(=O)-CH_3$$

breaks down completely when it is passed into some parts of cold water giving acetic acid and form-imide. The numerous ~~formic~~ *isobutyric* already mentioned in the paper in which molecules break down into molecules of a simple

10/300. d. Chem. Soc. 10, 311.
11/300. d. Chem. Soc. 10, 311.
12/300. d. Chem. Soc. 10, 311.
13/300. d. Chem. Soc. 10, 311.
14/300. d. Chem. Soc. 10, 311.

characters further confirm the view that it is not always possible to ~~draw~~ draw a certain inference from the decomposition products of a substance in regard to the number of carbon atoms in its molecule.

The Action of Hydrochloric Acid upon Prussic Acid and Alcohol in Ethereal Solution.

Pinner and Klein ¹⁰⁰⁾, and Pinner ¹⁰¹⁾, as well as Claisen and Mattheus ¹⁰²⁾ state that on leading dry hydrogen chloride into prussic acid diluted with alcohol, alcohol and ether or with acetic ether interaction begins at once. In the two first cases and especially when alcohol alone is the solvent the reaction, according to Pinner and Klein, often begins with explosive violence. I found, in accordance with Gautier, that at a low temperature dry hydrogen chloride acts upon prussic acid alone or in the presence of alcohol or of alcohol and ether only very slowly and quietly. Indeed no reaction is noticeable until the solution has stood for some time. These contradictions depend upon the presence or absence of water. In my experiments, as well as in those of Gautier, the hydrochloric acid was dried with phosphorous pentoxide and the greatest ~~care~~ ^{precautions were} taken to prevent the access of water during the course of the experiment. The reagents employed were also ^{especially} prepared, with especial care ^{being taken} ~~in each case~~ ^{to make them perfectly} anhydrous ¹⁰³⁾. The final result is, however, the same, as afterwards became evident. If ~~HCl~~ dried hydrochloric acid dried by means of sulphuric acid and calcium chloride and phosphorous pentoxide is led for one hour into a mixture ^(cooled with ice and salt) of 15 grams prussic acid, 25.6 grams alcohol (one molecule) and 60 grams absolute ether a separation is first noticed after 3 to 4 hours. The solution then becomes turbid and ammonium chloride first separates out as a white powder, after that a separation of ~~transparent~~ long, flat, transparent needles begins; 12 hours are necessary for the completion of

¹⁰⁰⁾ Ber. d. Chem. Ges. 11, 1473.

¹⁰¹⁾ Ber. d. Chem. Ges. 16, 354.

¹⁰²⁾ Ber. d. Chem. Ges. 16, 311.

¹⁰³⁾ Ether dried by means of sodium is not absolutely anhydrous; it is certainly to be expected that a more complete ^{dehydration} may be attained by carrying out the distillation over phosphorous pentoxide; compare Liebig's Annalen 276, 244.

character further confirmed by the fact that it is not always possible to show a certain inference from the decomposition products of a substance in regard to the number of carbon atoms in its molecule.

The Action of Hydrochloric Acid upon Phosphorus Pentoxide and Chloride in Ethereal Solution.

Turner and Klein (100) and Turner (101), as well as Chinn and Mather (102) state that on heating dry hydrogen chloride with phosphorus pentoxide and chloride, alcohol, aldehyde and other volatile products are obtained. In the first case and especially when alcohol is the solvent the reaction, according to Turner and Klein, often begins with explosive violence. I found, in accordance with Turner, that at a low temperature dry hydrogen chloride acts upon phosphorus acid above or in the presence of alcohol, and other only very slowly and quietly. Indeed no reaction is noticeable until the solution has stood for some time. These contradictions depend upon the presence or absence of water. In my experiments, as well as in those of Turner, the hydrochloric acid was dried with phosphorus pentoxide and the greatest care taken to prevent the escape of water during the course of the experiment. The reagents employed were also purified, with especial care to remove any traces of water. To make these points clear (103) the final result is, however, the same, or after weeks become identical. If the dried hydrochloric acid is dried by means of sulphuric acid and phosphorus pentoxide it is not so good as one dried by means of phosphorus pentoxide and phosphorus pentoxide. The solution then becomes turbid and a separation is first noticed after 5 to 8 hours. The solution then becomes turbid and ammonium chloride first separates out as a white powder, after that a separation of phosphorus pentoxide, transparent needles begin; 12 hours are necessary for the completion of the reaction. The reaction is not absolutely anhydrous; it is certainly to be expected that a more complete study be attained by carrying out the distillation over phosphorus pentoxide; compare also the results of Turner (101) and Chinn and Mather (102).

- 100) Ber. d. Chem. Ges. 11, 1473.
- 101) Ber. d. Chem. Ges. 16, 374.
- 102) Ber. d. Chem. Ges. 16, 311.

103) It is dried by means of sulphuric acid and phosphorus pentoxide; it is certainly to be expected that a more complete study be attained by carrying out the distillation over phosphorus pentoxide; compare also the results of Turner (101) and Chinn and Mather (102).

the reaction. If on the other hand the solution saturated with hydrochloric acid is warmed to 15° or 20° a very energetic reaction sets in, and the separation of crystals is complete in an hour. The violence of the reaction may easily be controlled by shaking and cooling with running water. In this case 60-66 grams of crystals are always obtained and the ethereal filtrate leaves no residue after treatment with caustic soda in ethereal suspension and distilling off the ether. In the first case on the contrary only 24-42 grams of crystals are obtained and the ethereal filtrate, treated in the same way, yields an oily mixture, which boils between 140° and 170° and consists in part of ortho-formic ether. (~~bpt. $144-145^{\circ}$~~) The crystals obtained show all the properties of Pinner's substance; an experiment with alcohol gave from 42 grams original substance 32 grams ortho-formic ether (bpt. $144-145^{\circ}$) and 26 grams ammonium chloride. On treatment with alcoholic ammonia and also on heating the hydrochloride of form-simidine is formed.

Quite the same result was obtained by leading dry hydrochloric acid for an hour into 60 grams of ether and afterward adding first slowly 15 grams prussic acid and then 25.6 grams alcohol. In this experiment the separation of crystals began only after eight hours standing at -5° . The yield was 45 grams of magnificent needles, to all appearances perfectly homogeneous.

A substance crystallizing in long, transparent needles is likewise obtained when hydrochloric acid is led for an hour through a solution of 15 grams prussic acid (two molecules), in 12.5 grams alcohol (one molecule) and 60 grams absolute ether. In this instance no separation of ammonium chloride was noticed at the beginning. This substance gives all the reactions of Pinner's body; indeed the preparations obtained by these different methods can be distinguished from one another neither by their appearance nor by their behavior towards water, alcohol and heat; they all make the impression of a perfectly homogeneous body. The analyses, however, showed at once that mixtures must be in question. For the purpose of analysis only the most perfect crystals were taken, washed with absolute ether, pulverized and again washed with ether, then dried first on a clay plate and finally over sulphuric acid in a vacuum. Pinner gives no nitrogen determination of his substance.

The analytical figures cited by him depart noticeably from those demanded by theory. The analysis of a preparation made from the same relative quantities that Pinner mentions, and which ~~of~~ ^{directly} separated out at a low temperature, gave

the reaction. If on the other hand the reaction is carried to 150° or 200° a very energetic reaction sets in and the separation of crystals is complete in an hour. The violence of the reaction may easily be controlled by shaking and cooling with running water. In the case of 50-60 grams of crystals are always obtained and the residual filtrate leaves no residue after treatment with water. In the first run the crystals are obtained in a very fine state of division and the residual filtrate, treated in the same way, yields only a very small amount, which boils between 140° and 170° and consists in part of water-soluble ether (b.p. 144-145°). The crystals obtained are all the product of the reaction; an experiment with alcohol gave from 4.5 grams original substance 3.2 grams of the same ether (b.p. 144-145°) and 1.5 grams of anhydrous alcohol. The treatment with alcoholic ammonia and then heating the hydrochloride of am. ammonia is formed.

Since the same result was obtained by heating dry hydrochloric acid for an hour into 50 grams of ether and afterwards adding first 15 grams of anhydrous alcohol and then 1.5 grams of ether. In this experiment the separation of crystals began only after eight hours standing at -5°. The yield was 4.5 grams of insignificant needles. To all appearances perfectly homogeneous.

A substance crystallizing in long transparent needles is likewise obtained when hydrochloric acid is added for an hour through a solution of 15 grams of anhydrous alcohol (one washed) and 50 grams of absolute ether. In this instance no separation of ammonium chloride was noticed at the beginning. The substance gives all the reactions of Tinner body, which the fraction obtained by these different methods can be distinguished from one another by their appearance as by their behavior towards water, alcohol and ketone; they all make the appearance of a perfectly homogeneous body. The analysis, however, showed at once that mixtures must be in question. For the purpose of analysis only the most perfect crystals were taken, washed with absolute ether, purified and again washed with ether, then dried first on a clay plate and finally over sulphuric acid in a vacuum. Tinner gives no nitrogen determination of his substance.

The analytical figures cited by him depart entirely from the demands of theory. The analysis of a pure substance made from the same relative quantities of Tinner substance and which is separated out of a low temperature, gave

the following figures results:

Theory for	Found	Primer found
$C_2H_5N_2OCl$		
C 32.87	—	30.76
H 7.31	—	7.10
N 11.78	15.46	—
Cl 32.40	35.37	33.75

The analyses were made with the greatest care, for on heating the substance ethyl chloride is split off. The nitrogen and the chlorine determinations are about 3.5% too high!

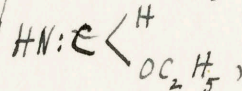
The analysis of a preparation in whose manufacture two molecules of prussic acid to one of alcohol were used gave the following result:

Found
Cl 40.40
N 15.23

The analysis of a preparation obtained by adding prussic acid and alcohol to hydrochloric acid in ethereal solution gave the following figures:

Found
Cl 34.20
N 13.82

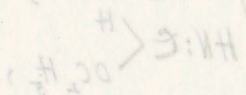
Primer states ¹⁰⁴ that on adding his substance to a very concentrated solution of caustic potash the free base, imido-formic ether,



separates out only with very great loss. He describes it as a very unstable oil of a peculiar basic smell which boils at 80°. The experiment was repeated several times and it became evident that the oil consisted only of ethyl alcohol mixed with some ammonia. The substance when poured into caustic alkalis is at once decomposed giving ammonia, alcohol and formic acid. Neither the concentration of the alkali nor the temperature at which the experiment is carried out makes any difference in the result.

Quite another result is obtained when the salt is added to ordinary ether in which powdered sodic hydrate is suspended. 50 grams of salt to 45 grams of solid caustic soda were used. The salt in ~~for~~ 8 gram portions is brought into the mixture as rapidly as possible, care being taken to shake ^{vigilantly} actively and to cool with running water. The odor

as far as possible, care being taken to shake thoroughly and to cool with running water. The whole sides were washed. The salt in the 8 gram portion is brought into the mixture as rapidly as possible. 20 grams of salt to 45 grams of oil counts in which prepared acid hydrate is suspended. Quite another result is obtained when the salt is added to ordinary ether experiment is carried out under any difference in the results. Under the concentration of the alkali or the temperature at which the ester when fused into caustic alkali is at once decomposed giving ammonia, alcohol without that the oil consisted only of ethyl alcohol mixed with some ammonia. The salt basic small which boils at 80°. The experiment was repeated several times and it became separated out only with very great loss. He described it as a very volatile oil of a peculiar



caustic fused the free base, mixed-formic ester, Turner states 104 that on adding his substance to a very concentrated solution of

Found
Cl 34.20
N 18.82

hydrochloric acid in ethereal solution gave the following figures:

Found
Cl 40.40
N 17.23

The analysis of a preparation obtained by adding formic acid and alcohol to

formic acid to one of alcohol were used gave the following results:

Found
Cl 32.40
N 11.78

The analysis of a preparation in whose manufacture the substance of

minerals are about 3.2 to 4.1. The substance itself chloride is split off. The nitrogen and the chlorine later

33.75

710

3076

Turner found

C₂H₅NO₂Cl

Cl 32.40
N 11.78
H 7.81
C 32.87

Found

15.46

32.37

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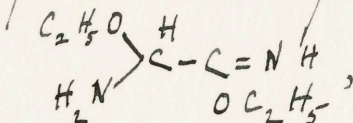
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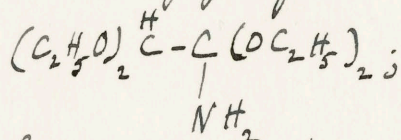
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of ammonia is noticed at once, and at ~~last~~ ^{length} becomes very strong. The ^{solid} masses which form under the ether are pulverized with a glass rod, cooling carefully during the process, and then the mixture, placed in cold water, is allowed to stand for one or two hours and filtered off. The precipitate contains much sodium formate and little sodium cyanide. The ethereal filtrate is carefully dried with calcium chloride and after distilling off the ether the residue, dried once more with calcium chloride, is distilled under reduced pressure. At first alcohol goes over (in varying quantities, often very little) and then a little imido-formyl-cyanide (see below), which solidifies in the condensing tube; the substance present in greatest quantity is a colorless, faint-smelling oil, which boils between 110° and 115° at 20 mm pressure. This consists, as will be shown below, of a mixture of much imido-formyl-cyanide diethylate,



and of di-ethoxy-ortho-amido-glyoxylic ether,



it may be repeatedly distilled at reduced pressure without decomposition. A nitrogen determination of an oil which had been three times distilled and which boiled at 104° at 15 mm pressure gave:

Theory for
 $\text{C}_2\text{N}_2\text{H}_2, 2 \text{C}_2\text{H}_5\text{OH}$

Theory for
 $(\text{C}_2\text{H}_5\text{O})_2 \text{C} \text{H}$
 $(\text{C}_2\text{H}_5\text{O})_2 \text{C} \text{NH}_2$

Found

N 19.18

6.36

14.27

From 30 grams of prussic acid, worked up in two portions, 10 to 20 grams of this high-boiling oil is always obtained. The result is the same whether much or little salt (25 to 66 grams) is formed during the treatment with alcohol, ether and hydrochloric acid, or whether one or one half molecule of alcohol to one molecule of prussic acid ^{in the experiment} is used. Apparently ~~some~~ ^{a somewhat} greater quantity of oil is formed when one half molecule of alcohol to each molecule of prussic acid is taken.

When distilled at ordinary pressure this high-boiling oil shows a remarkable behavior. Distilled rapidly, it boils for the most part between 190 and 220° ; distilled slowly, it is completely decomposed giving alcohol, imido-formyl-cyanide, ortho-formic ether and a