لا يوجد نص يمكن قراءته بشكل طبيعي من الصورة المقدمة. قد تحتاج إلى تقديم الصورة بشكل أكبر أو في شكل يمكن قراءته بشكل طبيعي.
cyanurate 7). He used form-cyanogen instead of chlor-cyanogen in his experiments and found to his astonishment that the presence of such 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 form-cyanogen on sodium ethylate contains substances which are soluble in water, among which urethane can easily be detected.

2) The portion insoluble in water—clotric substance—contains at first C\textsubscript{4}H\textsubscript{4}OCN, C\textsubscript{4}H\textsubscript{4}OH, and gives only after long standing over sulphuric acid in the vacuum analytical figures C\textsubscript{4}H\textsubscript{4}OCN. The product contains much ethyl cyanurate, but also another body, perhaps ethyl cyanurate.

Ponomareff 73 undertook to study the action of form-cyanogen on sodium ethylate almost at the same time as Mulder. He found that form-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 (as 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 cyanurate. He was strengthened in this opinion by finding that the oil was in 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.

The subject was in this somewhat confused state when I undertook further experiments. It was first determined that pure form-cyanogen and sodium ethylate do not act still 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 form- or chlor-cyanogen 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 ether 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 water reduced then at ordinary pressure. It is a colorless, strongly basic smelling oil boiling at 138°-140°, identical in every respect with the imido-carbolic ether described above. The yield from 18 g of chloro-cyanogen is 26 g of pure imido-ether; from 41 g of bromo-cyanogen 30 g of imido-ether.

The same result is of course obtained by filtering the reaction product from the sodium salt and distilling directly; but which 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 Oldhausen, Mulder and Posmaroff 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 yet at a somewhat higher temperature there is formed besides imido-carbolic 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 in. mercury. The reaction when the alcohol used contains water.

Now since imido-carbolic ether forms a hydrate with water (see above) and ethyl cyanurate, as Mulder has shown, gives with water a hydrate of the formula \( [C_2H_5OCN]_3 + 12H_2O \) as well as with alcohol an alcoholate, \( [C_2H_5OCN]_3 + 3C_2H_5OH \); the earlier observations concerning this reaction are fully explained. In whatever way the experiment is carried out (addition of chloro-cyanogen to alcohol...
sodium ethylate or vice versa, with or without cooling) imido-carbamic ether is always formed as the chief product of the reaction; the substance was overlooked by all the earlier workers and only mentioned by Ponomareff as a nonlative 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

\[ \mathrm{N:CCL + NaOC2H5 = N:COC2H5 + NaCl} \]

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

\[ \mathrm{H\text{N:CCL}} \]

\[ \stackrel{\text{O}}{\text{C2H5}} \]

was never taken into consideration; regarded from the standpoint of the substitution theory such a reaction would be incomprehensible 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° to 10°) mixture of chlor-cyanogen (or brom-cyanogen), water (five parts) and alcohol (two 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 ethereal extract worked up precisely as in the above experiment with sodium ethylate. Imido-carbamic ether is obtained as the chief product and urethane as a by-product (about in the proportion of 5:1). The urethane obtained in this way boiled at 181° and melted at 52°.

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

Theoretical for \( \text{C}_3\text{H}_7\text{N}_2 \)

\[ C 15.73 \%

The yield of imido-carbamic 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
small or large, whether the reaction is carried out at low or at ordinary temperatures; at low temperatures, however, the formation of ethyl cyanurate is 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 bicarbonic 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

\[
\text{H:CN:Cl} \\
\text{\quad C}_2\text{H}_5\text{O}^+ \quad \text{CNO}^- \\
\text{C}_2\text{H}_5\text{N}^+ \quad \text{C}_2\text{H}_5\text{O}^+ \quad \text{CNO}^-
\]

is then simply converted by alcohol or water present into

\[
\text{C}_2\text{H}_5\text{O}^+ \quad \text{CNH}^+ \quad \text{and} \quad \text{C}_2\text{H}_5\text{O}^+ \quad \text{C} \quad \text{O}.
\]

The formation of ethyl cyanurate at higher temperatures is then also easily explained:

a small portion of the intermediate product

\[
\text{C}_2\text{H}_5\text{O}^+ \quad \text{CNO}^- \quad \text{N}^+ \quad \text{C}
\]

before it can be acted upon by the alcohol present loses hydrochloric acid forming

\[
\text{C}_2\text{H}_5\text{O}^+ \quad \text{CNO}^- \quad \text{N}^- \quad \text{which in the vacuo state polymerizes to ethyl cyanurate.}
\]

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:

\[
X\cdot\text{CN} + 2\text{KOH} = X\cdot\text{C} \quad \text{NH}^- + \text{KCO}_3 + \text{HX} + \text{H}_2\text{O} \quad (X = \text{Cl or Br})
\]

It has long been known 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 cyanogen halides. 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
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 atomic weight \( w \) of the halogen present increases.

Special attention should be called 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 \( I - C : N H + \) breaks down spontaneously as shown above in the case of other analogous substances, into its components, prussic acid \( C : N H + \), and hypiodous acid, \( H O I \); the latter then gives at once iodine and hydroiodic acid.

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

\[
\begin{align*}
C_2H_5O & > C = N H + \\
& \text{Cl}
\end{align*}
\]

thus formed being an acid chloride is at once converted by the alcohol into the hydrochloride of methoxycarbonyl chloride.

\[
\begin{align*}
C_2H_5O & C - N H_2 \\
& \text{Cl}
\end{align*}
\]

This salt is very easily decomposed at ordinary temperatures giving methylene 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; the reaction takes place much less readily than

---

74 Compare Liebigs Annalen 276, 237.
75 Wiel, Liebigs Ann. 79, 281.
in the case of cyanogen chloride so that it is necessary to heat in a sealed tube. Ammonium bromide, carbon dioxide, mephine and ethyl bromide are formed as Mulder has shown. He also obtained in this reaction a substance having the formula
\[
C_8H_4Br_2N_2O_3
\]
which melts at 121° and is soluble in hot water. This product is in all probability identical with the substance which Bischoff obtained by the action of bromine on alcohol

\[
CH_3\overset{Br_2}{\rightarrow}CH<\overset{NH\cdot COOC_2H_5}{\rightarrow}N\cdot COOC_2H_5
\]

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

\[
\text{Br}_2, O\overset{CNH}{\rightarrow}
\]
into prussic acid and ethyl bromide, \( C_8H_5OBr \); the latter then decomposes with the formation of ethyl acetate, alcohol, which condenses with the mephine formed in the reaction. The processes which take place when chlorine or bromine is let into alcoholic prussic acid are also very easily intelligible. Chloro or bromo-cyanogen and halogen hydride are first formed; at the solution becomes richer in halogen hydride there is formed more and more of the imido derivative

\[
H\cdot N: C <\overset{X}{\rightarrow}
\]

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

\[
C_8H_5O\overset{CNH}{\rightarrow}
\]

The latter is known to decompose easily into mephine and halogen ethyl. If more chlorine or bromine continue to be let into the solution a part of the alcohol is nascently oxidized to halogen-substituted aldehydes which then simply condense with the mephine present. That this explanation of the reaction is correct follows from the following experiments: Chloro or bromo-cyanogen treated in alcoholic solution with dry hydrochloric or hydrobromic acid are all at once very energetically decomposed and mephine is formed in large quantities. It may incidentally be stated that when dry
Hydrobromic acid is added to an absolute ethereal solution of cyanogen bromide, a yellowish-white, very hygroscopic precipitate of imido-cyanogen bromide, $\text{H}N\text{C} < \text{Br}_2 < \text{C}_6\text{H}_5$, and the 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**

$$\text{H}N\text{C} < \text{C}_6\text{H}_5$$

On boiling chlorocyanogen with an alcoholic solution of sodium phenolate and subsequently distilling the oily reaction product of phenyl and aluminum chloride, a yellowish oil with much phenyl, phenyl cyanurate ($\text{C}_8\text{H}_4\text{OCN}$), melting at 115°. They concluded that phenyl cyanurate is the first product of the reaction, and that on distilling it simply polymerizes. This assumption is incorrect: not a trace of phenyl cyanate or of its phenyl cyanurate is formed, as is shown by the following experiments.

If a solution of 53.3 grammes phenol (two molecules) and 48.6 grammes anhydrous potassium carbonate in 300 grammes water is added slowly with constant shaking to a cold solution (20°) of 46 grammes from-cyanogen in two and one-half liters of water, reaction sets in at once; the solution becomes turbid, giving an alkaline reaction and a yellowish oil separates out. As soon as the odor of from-cyanogen has disappeared, the oil solidifies. The precipitate is dissolved in ether, which, with dilute acetic acid and the solution evaporated after drying with solid calcium chloride, the solution is evaporated. The yield is about 67 grammes of almost perfectly pure imido-phenyl carbonate. For the purpose of analysis, a portion was recrystallized from lake warm ligroin (b.p. 76°-80°), in this way were obtained colorless needles, melting at 54° and possessing a faint odor similar to that of phenol.

0.3195 g dried in a vacuum over H₂SO₄ gave 17.6 cm nitrogen at 18° and 748 mm pressure.

0.1402 g, dried in the vacuum over H₂SO₄, gave 0.3747 CO₂ and 0.0674 H₂O.

**Theory for**

<table>
<thead>
<tr>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>73.24</td>
<td>5.16</td>
<td>6.57</td>
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</table>

Found:

<table>
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<tr>
<th>C</th>
<th>H</th>
<th>N</th>
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</thead>
<tbody>
<tr>
<td>72.89</td>
<td>5.33</td>
<td>6.76</td>
</tr>
</tbody>
</table>

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

\[
\text{BrC}_6\text{H}_4\text{N} + 2\text{NaOC}_6\text{H}_5 + \text{H}_2\text{O} = \text{BrC}_6\text{H}_4\text{NBr} + \text{NaOC}_6\text{H}_5 + \text{H}_2\text{O} = \\
\text{C}_6\text{H}_5\text{OC}_6\text{H}_5 + \text{NaNH} + \text{NaBr} + \text{NaOH}.
\]

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

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

In its chemical behavior, it resembles in every respect the corresponding indole-ethyl carbonate. Dilute hydrobromic acid converts it into the salt completely with phenyl carbonate (spt. 58° from alcohol) as ammonium chloride. While 10 grams of the substance are heated for 20 minutes with three molecules of alcoholic potash 1.7 grams almost perfectly pure potassium cyanate separates out as fine crystals. The salt gave on treatment with 2 grams ammonium sulfate 0.9 grams pure white melting at 152°. The following reaction therefore takes place:

\[
\text{HNC}<\text{OC}_6\text{H}_5> + 3\text{KOH} = 2\text{C}_6\text{H}_5\text{OK} + \text{KOC}_6\text{H}_4\text{N} + 2\text{H}_2\text{O}.
\]

On heating in a tube indole-phenyl carbonate is completely decomposed giving phenol and phenyl cyanurate according to the equation:

\[
3\text{C}_6\text{H}_5\text{OC}_6\text{H}_5\text{N} = 3\text{C}_6\text{H}_5\text{OH} + 3\text{C}_6\text{H}_5\text{OC}_6\text{H}_4\text{N}.
\]

The phenyl cyanurate formed being very difficultly soluble in alcohol was recrystallized from glacial acetic acid; it melts at 225° and in every respect identical with the product obtained by Hofmann and Bohnen and in treating from 4-nor-chlorocyanogen in alcoholic solution either with aqueous
or with alcoholic sodium phenylate, imido-phenyl carbonate is likewise formed as the chief product. In this case, however, imido-phenyl-ethyl carbonate,

\[ \text{N:C}<\text{OC}_2\text{H}_5 \]

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

\[ \text{C}_6\text{H}_5\text{OC}_2\text{H}_4\text{N}^+ \]

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

It is, therefore, established that Hofmann and Olahuang's phenyl cyanurate did not result from the polymerization of phenyl cyanurate but was formed from imido-phenyl carbonate during the process of distillation! The above mentioned imido-phenyl ethyl carbonate boils at about 120° at 15 mm pressure; it was, however, not obtained perfectly pure.
The Ester of Normal Cyanic Acid, RO-C\(_2\)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°, an exothermic reaction takes place; besides much ethyl alcohol, however, only cyanimidane-carbonic ether was obtained. This leads to the conclusion that ethyl cyanate, C\(_2\)H\(_4\)OC\(_2\)N, is at once decomposed by water. On treating silver cyanate, by C\(_2\)N, with ethyl iodide under mild ethyl iodogenate was obtained—

A most 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 masked or overlooked\(^\text{59}\). The experiment will soon be repeated with larger quantities of silver cyanate. The possibility still exists that bromo- or chloro-cyanogen may be converted into esters of normal cyanic acid by heating in a sealed tube with perfectly dry and sodium ethylate or sodinum 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 hydrobromic acid are accessible. Ethyl hypobromite for instance will react 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 alkali cyanogen, C\(_2\)N, easily may be made to absorb either one or two molecules of alcohol giving

\(^{59}\) Compare Ponomareff, J. Chem. Soc. 18, 3263.
or dimido-oxalic ether,
\[ \text{C}_2\text{H}_4\text{O.C:NH} \]
\[ \text{C}_2\text{H}_4\text{O.C:NH} \]

The cyanogen used was prepared according to the method of Jacquier, &v; the stater that 850 cc. of this gas are obtained from 100 grams of potassium cyanide. On adding cyanogen (from 100 grams potassium cyanide) pretty rapidly to a solution of 10 grams potassium cyanide, 50 grams water, and 70 grams alcohol, a dark red solution appears at once. As soon as the solution of cyanogen causes water to be 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 dimido-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\°C. 6 grams of potassium in 175 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\°C and consisted of pure dimido-oxalic ether.

The Action of Zinc Ethyl on Cyanogen and its Derivatives.

It is known that the zinc alkyls react with acid chlorides, \( R.C\text{O} \), acid esters, \( R.C\text{O}.R' \), with aldehydes, \( R.C\text{=O} \), and ketones, \( R.C=O \), with forming addition products in which the zinc alkyl is simply absorbed by the carbonyl group existing in these substances.

\[ R.C\text{O} + \text{ZnR}_2 \rightarrow R.C\text{O}_2\text{R}_2 \]

\[ \text{C}_2\text{H}_5\text{C} = \text{O} - \text{ZnC}_2\text{H}_5 \]

\[ \text{C}_2\text{H}_5\text{O} = \text{ZnC}_2\text{H}_5 \]

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

I find that chlor-cyanogen reacted with zinc ethyl undergo decomposition giving ethyl cyanide and zinc chloride; E. Frankland and Graham 53 found that zinc ethyl and cyanogen interact with formation of zinc cyanide and ethyl cyanide; E. Frankland and Levin 54 obtained zinc cyanide and ethyl phenyl ketone from phenyl cyanide and zinc ethyl.

The formation of zinc ethyl with formation of the intermediate products

\[
\begin{align*}
I. & : C_2H_5 \rightarrow C=N_{Zn}, \\
II. & : C_2H_5 \rightarrow C=N_{Zn}, \\
III. & : C_2H_5\text{CO} \rightarrow C=N_{Zn},
\end{align*}
\]

readily explain these reactions. The intermediate products then react, I giving zinc and \(C_2H_5C=N\); II \(C=N_{Zn}\) and \(C_2H_5C=N\); and III \(C=N_{Zn}\) and \(C_2H_5\text{CO}C=N\).

The splitting of II and III is almost perfectly analogous to that of mido-oxalic ether into prussic acid and ethyl carbonate.

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

\[
\begin{align*}
&: C=N\,+
\end{align*}
\]

which breaks down spontaneously into prussic acid (or azulenic acid) and cyanic acid \(HOC=N\). The decomposition, first observed by Köhler 56, of an aqueous solution of cyanogen into urea, azulenic acid, prussic acid and ammonium oxalate and carbonate. Therefore, readily comprehensible.

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52 Craft. Read. 66, 48.  
54 Journ. Chem. Soc. 87, 744.  
55 The formula \(C_2H_5\,\text{Fe} \cdot \text{CN}\) is here given to zinc ethyl, \(\text{Zn}\) indicating half an atom of zinc.  
56 De Chimie. de la France 17, 114, 1827. Pp. 91/3, 1827.
IV. Prussic Acid is identical with Iso-ammonium Hydride, \( \text{HNO}_3 \).

Preparation of absolutely pure prussic acid. Gaujard was the first to obtain prussic acid free from water and capable of preservation for an indefinite period. He showed that by Gay-Lussac's method the prussic acid is obtained which contains traces of water and of ammonium cyanide, and that these substances cause it to go over into acylphoric acid. From silver cyanide and dry hydrogen sulphide, he found as from yellow prussiate of potash and sulphuric acid Gaujard was able to prepare a pure prussic acid, which boils at 20\(^\circ\)C., melts at -19\(^\circ\)C. and which may be preserved unchanged. By fractional precipitation, from 600 grams of such a substance Gaujard proved that he was dealing with a single 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 70% substance: whereas the vapour density determinations carried out at different temperatures by the methods of

Dumas and Gay-Lussac point to an abnormal behavior of the body. At 3\(^\circ\)C. the density 0.9838 was found; this diminishes constantly as the temperature rises, and at 197\(^\circ\)C. was 0.903. Gaujard explains these peculiar phenomena by the assumption that the coefficient of expansion of the gas is greater than that of air. It is much more probable that a foreign substance were present.

The mixing of 20% of this substance in pure prussic acid would fully explain the losses in analysis as well as the abnormal densities observed. The theoretical density formula when the ammonium cyanide is undissociated is 0.947, when the salt is completely dissociated into ammonia and prussic acid it is 0.928. Gaujard found at 47\(^\circ\)C. the density 0.953, at 158\(^\circ\)C. 0.924.

The acid prepared according to the method of Gaujard was free from water, since it was passed through a long tube filled with calcium chloride. No precursory, however, were taken to remove the ammonium cyanide probably present. By a method of preparation which must remove also the last mentioned...
لا أستطيع متابعة ما يجري في هذه المكتبة، حيث أن هناك عنصرًان يمنعونني من التركيز على ما يتم مناقشته.

من ناحية الأدب، فإن الكلمات تلعب دورًا مهمًا في استخدام اللغة العربية. تساهم في التعبير عن الأفكار والأفكار من خلال تأويلها.

من ناحية الاجتماع، فإن الكلام يفتتح دائرة تفاعلية بين الأشخاص، حيث يتم مشاركة الأفكار والمشاعر.

فيما يتعلق بالأعمال، فإن الكلام هو الريه في التوازن بين الحضور والانسحاب.

من ناحية الفنون، فإن الكلمات ت konkالون الريش والمصورات لتصبح تعبيرًا فنيًا.

فيما يتعلق بالأدب، فإن الحوار هو الريه في تشعير الأفكار والمشاعر بين الأشخاص.

من ناحية الاجتماع، فإن الحوار يفتح دائرة تفاعلية بين الأشخاص، حيث يتم مشاركة الأفكار والمشاعر.

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من ناحية الفنون، فإن الحوار ي konkالون الريش والمصورات لتصبح تعبيرًا فنيًا.
body—the one, namely, of phosphorus pentoxide—prussic acid is obtained perfectly pure and possessing physical properties which differ from those of Gauthier's substance.

The prussic acid used in my experiments was prepared by heating yellow prussiate of potash (500 grams) and sulphuric acid (350 grams of concentrated acid and 650 grams of water); in this process the directions of Gauthier and of Wöhler were essentially followed. It 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 stop-cocks, which was packed in a freezing mixture of ice and salt. The mixture in the retort was heated to 60-70° and immediately 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 phosphorus pentoxide added. The flask was connected with a U-tube, which contained a mixture of glass beads and phosphorus 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 moisture by a long tube filled with calcium chloride and phosphorus pentoxide. The apparatus set up in this way was allowed to stand 12-20 hours and then the prussic acid was distilled. After repeated distillation a prussic acid is obtained which boils constant at 15° Corr. (1)

A short, so-called Anschiwill-Schott thermometer divided into fifty parts 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 Gauthier, and observed that when the same thermometer was used it boiled at 26.2° (corr. 26°); the purest prussic acid free from ammonium chloride bore, therefore, an entire degree
lower than Galetier's prussic acid. The melting point, 150, of this substance
lies higher than Galetier found it (−14°); it lies between 110° and 120°. 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 stoppers without the slightest change. It was used for
all the experiments described in this paper. It is to be expected prussic acid
compared with its salts and with the alkyl isoanisides is a very inactive tool.79
At low temperatures it does not combine with chlorine,79 but with hydrochloric acid.79
I have found that molecular quantities of prussic acid and ethyl hydrochloride 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 hemogen hydrochloric are derivatives of imido-formylcyanide,

\[
\begin{align*}
\text{H} & \text{N} : \text{C} < \text{H} \\
\text{H} & \text{N} : \text{C} < \text{N} ,
\end{align*}
\]

About twelve years ago Prince 92) on boiling hydrochloric acid into an
absolute ethereal solution of prussic acid and alcohol obtained a substance crystallizing
in magnificent needles, which he regarded, in view of its numerous reactions,
regarded as the hydrochloride of form-imido-ether,

\[
\begin{align*}
\text{H} & \text{N} : \text{C} < \text{O} \mathcal{H} , \text{H} \text{Cl}.
\end{align*}
\]

This substance shows in comparison with all other known imidoethers a very
striking behavior as well toward alcohol, which converts it into ammonium chloride
and ethyl formic esters, as toward heat, which decomposes it with formation of
ethyl chloride, formic esters and the hydrochloride of form-anisidine! The imido-ether
which according to the experiments of Leibigfeld and Steglich 93) are not salts but
addition products having the constitution

\[
\begin{align*}
\text{R} & \text{C} < \text{N} \mathcal{H} , \\
\text{C} & \mathcal{H} 0 \text{C} < \text{C} \text{Cl}.
\end{align*}
\]

87) Compare Leibig Annalen 270, 267—270.
89) Guy-Lussac Annales de Chemie et de Physique 95, 212.
91) Stieglitz, loc. cit. 147, 17, 129.
92) Guy-Lussac Annales de Chemie et de Physique 95, 212.
93) Leibig, loc. cit. 17, 19, 112.
by heat

are, as we know, decomposed according to Pinner, as well as heating as by
treatment with alcohol, giving ethyl chloride and an acid amide

\[ R\overset{\text{C-NH}}{\rightarrow} \]

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

\[ \overset{\text{C}}{\text{C}}_{6}\overset{\text{H}_{5}}{\text{N}^{+}}\overset{\text{Cl}}{\rightarrow}\text{C}<\overset{\text{O}}{\text{C}_2\overset{\text{H}_5}} \]

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

\[ \overset{\text{C}}{\text{C}}_{6}\overset{\text{H}_{5}}{\text{N}^+}\overset{\text{C}}{\text{H}}_{\text{NH}}\overset{\text{Cl}}{\rightarrow}\text{C}<\overset{\text{O}}{\text{C}_2\overset{\text{H}_5}} \]

are split normally, as Hugfeld and Stieglitz have observed, into ethyl chloride and

\[ \overset{\text{N}^+}{\text{H}}_{2}\overset{\text{C}}{\rightarrow}\text{C}<\overset{\text{O}}{\text{C}_2\overset{\text{H}_5}} \]

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

\[ \overset{\text{N}^+}{\text{H}}_{2}\overset{\text{C}}{\rightarrow}\text{C}<\overset{\text{O}}{\text{C}_2\overset{\text{H}_5}} \]

These considerations, as well as the fact that formic acid is con-
verted by alcoholic hydrochloric acid into diethyglyoxalic ester, cannot

\[ \overset{\text{C}}{\text{C}}_{6}\overset{\text{H}_{5}}{\text{N}^+}\overset{\text{C}}{\text{H}}_{\text{NH}}\overset{\text{Cl}}{\rightarrow}\text{C}<\overset{\text{O}}{\text{C}_2\overset{\text{H}_5}} \]


95/ Pinner and Klein, Ber. d. Chem. Ges. 11, 1473.
diethylamino-
\[ C_2H_5OC\rightleftharpoons NH_2, 2 \text{ HCL}, \]
\[ C_2H_5OC\rightleftharpoons NH \]

and of the hydrochloride of diethyl-carb-imidoyl-glyoxylic ester,
\[ (C_2H_5O)_2 CH\ rightleftharpoons C\rightleftharpoons NH_2, \text{ HCL}, \]
along with other salts.

In a perfectly analogous manner it was found that the salts which prussic acid forms with hydrogen halides discovered by Guenter are not salts of imido-formyl halide as Claisen and Matthias assume and as I myself formerly supposed, but addition products or salts of imido-formyl cyanide,

\[ \text{H} : \text{C} \rightleftharpoons \text{N} \]

The fact that all these substances break down on heating 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 have true formic acid derivatives. It was even found that phenyl-imido-formyl chloride is split by treatment with alcohol into acetic ether and the hydrochloride of form-amidine.\footnote{Liebigs. Annalen 270, 297.}

Chloroformamide
\[ \text{CH}_3\rightleftharpoons \text{C} \rightleftharpoons \text{N} = \text{C} \rightleftharpoons \text{COCH}_3, \]
breaks down completely when it is poured into seven parts of cold water giving acetic acid and form-amidine.\footnote{Liebigs. Annalen 270, 309.} The numerous p. 7 cases already mentioned in the papers in which molecular rich in carbon break down into molecules of a simpler
character further confirm the view that it is not always possible to 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.

Pruner and Klein[105] and Pruner[106], as well as Claude and Matthew[107], state that on adding dry hydrogen chloride into prussic acid diluted with alcohol, alcohol and ether or with water ether interaction begins at once. In the two first cases and especially when alcohol alone is the solvent the reaction according to Pruner 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 ethers only very slowly and quietly. Indeed no reaction is noticeable until the solution had 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 phosphorus pentoxide and the greatest care taken to prevent the access of water during the course of the experiment. The precautions employed were also performed with especial care and the care was not at all to make them chalybditic[108]. The final result is, however, the same, as after wards became evident. If the dried hydrochloric acid dried by means of phosphorus pentoxide and calcium chloride and phosphorus pentoxide is placed for one hour into a mixture of 15 grams prussic acid, 25.6 grams alcohol (one mole) and 60 grams absolute ether a separation is first noticed after 8 to 10 hours. The solution then becomes turbid and ammonium chloride first separates out as a white powder, after that a separation of Prussic acid, long, flat, transparent needles begins; 12 hours are necessary for the completion of


108 Ether dried by means of sodium is not absolutely anhydrous; it is certainly to be expected that a more complete solution may be attained by carrying out the distillation over phosphorus pentoxide; compare Liebig's handbuch 27, 244.
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 the case 60-66 grams of crystals are almost 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 (Bp. 144-145°). The crystals obtained show all the properties of Riviere's substance; an experiment with alcohol gave from 12 grams of the substance 32 grams of ortho-formic ether (Bp. 144-145°) and 26 grams ammonium chloride. On treatment with alcoholic ammonia and also on heating the hydrochloride of form-ammonium is formed.

Quite the same result was obtained by leading dry hydrochloric acid for an hour into 50 grams of ether and afterward adding first slowly 15 grams of formic acid and then 25.6 grams alcohol. In this experiment the separation of crystals begins only after eight hours standing at -5°. The yield was 45 grams of magnificent needles, all appearance perfectly homogeneous.

The substance crystallizing in long, transparent needles is likewise obtained when hydrochloric acid is led for an hour through a solution of 15 grams of formic 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 Riviere'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 mixture 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. Riviere gave 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 Riviere mentions and which was separated out at a low temperature, gave
the following figures results:

<table>
<thead>
<tr>
<th>Theor.</th>
<th>Found</th>
<th>Prim. found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 32.57</td>
<td>—</td>
<td>30.76</td>
</tr>
<tr>
<td>H 7.51</td>
<td></td>
<td>7.10</td>
</tr>
<tr>
<td>N 11.78</td>
<td>15.46</td>
<td></td>
</tr>
<tr>
<td>Cl 32.40</td>
<td>35.37</td>
<td>33.75</td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>Theor.</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl 40.40</td>
<td>34.20</td>
</tr>
<tr>
<td>N 15.23</td>
<td>13.82</td>
</tr>
</tbody>
</table>

Primary states that on adding this substance to a very concentrated solution of
acetic potash, the free base, uric-formic ether,

\[ \text{HN:C} \left( \text{OC}_{2}\text{H}_{5} \right) \]

separates out only with very great loss. He describes it as a very volatile oil of a peculiar
basis 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 sub-
stance when poured into caustic alkali was 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 soda hydrate is suspended. 50 grams of salt to 45 grams of solid caustic
soda were used. The salt in 3 or 4 grams portion is brought into the mixture as rapidly
as possible, are being taken to shaker actively and to cool with running water. The off-

\[ 104/\text{Ber. d. Chem. Ges. 16, 885.} \]
of ammonium is noticed at once, and at a length becomes very strong. The masses which form under the other 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 amido-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 amido-formyl-cyanide diethololate,

\[
\text{C}_2\text{H}_4\text{O} < - \text{C} - \text{N} \text{H}^+ \\
\text{O} - \text{C}_2\text{H}_5^-
\]

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

\[
\text{C}_2\text{H}_4\text{O} < - \text{C} - \text{O} - \text{C}_2\text{H}_5
\]

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:

<table>
<thead>
<tr>
<th></th>
<th>Theory for</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{C}_2\text{N}_2\text{H}_3), (\text{C}_2\text{H}_5\text{OH})</td>
<td>(\text{C}_2\text{N}_2\text{H}_3), (\text{C}_2\text{H}_5\text{OH})</td>
</tr>
<tr>
<td>N</td>
<td>19.18</td>
<td>14.27</td>
</tr>
<tr>
<td></td>
<td>6.36</td>
<td></td>
</tr>
</tbody>
</table>

From 30 grams of formic 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 formic acid is used. Apparently somewhat more greater quantity of oil is formed when one half molecule of alcohol to each molecule of formic acid is taken. When distilled at ordinary pressure the 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, ortho-formyl-cyanide, ortho-formic ether and a