fourth body, probably amido-diethoxy-methane, a brown residue is left behind. The separation of these bodies is accomplished as follows: The oil is heated on a metal bath in a distilling flask to 150°. At first alcohol distills over, as soon as the thermometer indicates the temperature reach to 100–110° an oil goes over, which solidifies, with formation of crystals in the condensing tube. The distillation is continued until the oil passing over (left about 135°) no longer solidifies. The crystals present in the condenser are dissolved in ether and worked up as directed below. On continuing the distillation still further an oil is obtained which boils between 170° and 172° and which yields when fractionalised repeatedly a little more of the solid substance just mentioned. By repeated fractional distillations it was possible to prove the presence of two substances; one of them boils at 145–146° and contains of not perfectly pure ortho-formic ether.

Theory for 
C 56.75
H 10.80

Found
C 55.38
H 10.76

Traces of a body containing nitrogen were present, which in spite of the greatest efforts could not be removed. The substance obtained accorded perfectly in its boiling and its properties with a specimen of ortho-formic ether prepared for the purpose of comparison. An interesting fact in the behavior of this ether should be emphasized: While it can be boiled for a long time with dilute caustic alkali till much changing it is split at once in the cold by very dilute hydrochloric acid as well as slowly by cold water into formic acid and alcohol.

The second substance, separated from ortho-formic ether by fractional distillation is a faintly aromatic smelling oil, only slightly soluble in water, which boils at 163.164°. It contains much nitrogen (at analysis gave 10%), but it is not quite free from ortho-formic ether. When heated with water or alkali it is split into ammonia, alcohol and formic acid; with quite-dilute hydrochloric acid their decomposition occurs at once in the cold. It seems to be, therefore, very probable that this substance is amido-diethoxy-methane

\[
\text{C}_2\text{H}_2\text{O}_2\text{C}^+\text{N}+\text{H}_2
\]

not, however, perfectly pure. Further experiments upon this interesting body will soon be undertaken.
A mixture of the two substances just described, but no imido-formyl-cyanide, is obtained when the above-mentioned ethereal filtrate (resulting from the preparation of Primrose salt at a low temperature) is treated with concentrated sulphuric acid. In these cases I observed sometimes the presence of a third substance, which boils at 169-170° and is not decomposed by dilute hydrochloric acid. According to its analysis it contains 8.67% nitrogen and may possibly be identical with dieethoxy-glyoxalyl cyanide, \( \text{C}_2\text{H}_4\text{O}_2\text{CHCOCN} \). The substance is extremely stable.

![Imido-formyl cyanide](image)

The substance mentioned above, boiling at 110-130° and solidifying in the condensing tube is isolated from the ethereal solution in the following manner. Dry air at reduced pressure is first passed slowly through the flask containing the solution until the ether is for the most part removed; the oil resulting from this process causes the imido-formyl cyanide to separate out as a crystalline powder in fine crystals. These are filtered off as quickly as possible at a low temperature, brought upon a clay plate, sublimed and then worked over more with cold (-5°) ether. For the purpose of analysis it is again recrystallized from pure ether and after drying five minutes on a clay plate is kept in a closed vessel. The yield is 2 to 3 grains from 30 grains primrose acid; it may, however, be much increased.

0.1805 gram.

0.1016 gram heated with 5 ccm concentrated hydrochloric acid for three hours in a sealed tube gave 0.8251 ammonium chlorofluorate.

<table>
<thead>
<tr>
<th></th>
<th>Theory for ( \text{C}_2\text{H}_4\text{N}_2 )</th>
<th>Formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>44.44</td>
<td>43.84</td>
</tr>
<tr>
<td>H</td>
<td>3.71</td>
<td>3.77</td>
</tr>
<tr>
<td>N</td>
<td>51.85</td>
<td>51.50</td>
</tr>
</tbody>
</table>

Imido-formyl cyanide melts at 87° and boils without decomposition between 120-125° (the boiling point has not yet exactly determined). It is readily
soluble in water and organic solvents; in alcohol and ether at -5° it is, however, slightly soluble. The substance is extraordinarily volatile: when an etherial solution is distilled it gives over in great quantities with the ether. In several decigrammes left standing in a desiccator or in the air at the room temperature (20° C.) disappear in a very short time. When kept in a loosely closed test tube "mild"-formyl cyanide sublimes in magnificient crystals clear as water, which often look particularly like dodecahedra.

Mr. T. F. Porter of the University of Chicago was so kind as to make an optical examination of these crystals. He describes them as follows: "Optically uniaxial crystals, negative, strongly double refractive (almost like D). Very flat rhombohedra with a short prism of the second order."

The molecular weight was determined by means of the lowering of the freezing point in benzene solution. Two observers gave the molecular weight 64 (theoretical 54). It is possible that the too high number found was the result of an impurity in the benzene; it happened accidentally that only American benzene was at the time accessible. The experiment will soon be repeated, and a determination of the vapor density according to Hofmann's method will be carried out.

Although the presence of two carbon atoms in the molecule is proved also by the physical properties of the substance, it gives in many chemical reactions only formic-acid derivatives.

By soaking hydrate or dilute hydrochloric acid mixture formyl cyanide is split into the cold into ammonia and formic acid. An aqueous solution of the substance decomposes very slowly in the cold, rapidly when heated to 100° in a sealed tube, giving the formate of formamide and ammonia formate. The "mild"-formyl cyanide must first split off ammonia giving over into cyan-form-aldehyde,

\[
\text{CHO} + \text{CH} = \overset{\text{C:N}}{\text{C:N}}
\]

which then absorbs ammonia in the cyanogen group,

\[
\text{(CHO)}_2 \overset{\text{C}}{\text{H}} + \text{H}_2 \overset{\text{N}}{\text{C}} = \overset{\text{N}}{\text{H}}
\]

This intermediate product then breaks down with water into ortho-formic acid and form-amidile,

\[
\overset{\text{H}}{\text{NH}_2} \overset{\text{C}}{\text{H:N}}
\]
The presence of some compound may easily be proved, as I showed in
the case of the hydrochloride of form-anilidine. By shaking with cold solvoly hydrate
and benzyl chloride, a precipitate is formed which consists of benzamide and
dibenzyloform-anilidine; these substances may easily be separated, since
the latter is hardly at all soluble in cold, but very difficultly soluble in hot
alcohol. Di-benzylform-anilidine separates at first hot alcohol in
aluminoate white needles, which melt at 236°. The benzamide was obtained in
colorless caplets melting at 128°.

A mixture of benzamide and di-benzylform-anilidine is obtained
on shaking a solution of imido-formyl cyanide in boric hydrate with benzyl
dichloride. The analysis of the substance obtained in this way gave the following
results:

I. 0.1224 grams, dried at 110°, gave 13.2 cc. of nitrogen at 26° and 746 mm. pressure.

Theory for
C_{6}H_{5}CO\(\text{N:C=N+}\)CO C_{6}H_{5}

\[\text{N} \quad 11.11\]

Found
\[\text{N} \quad 11.74\]

II. 0.2086 grams, recrystallized from benzene, gave 21 cc. of nitrogen at 21°
and 747 mm. pressure.

Theory for
C_{6}H_{5}CONH_{2}

\[\text{N} \quad 11.57\]

Found
\[\text{N} \quad 11.30\]

On adding a concentrated solution of silver nitrate (one molecule)
to an aqueous solution of imido-formyl cyanide, cooled to +5°, there is formed at once
a white crystalline precipitate, which is readily soluble in boric and somewhat
soluble in cold water. This precipitate was washed five times with very cold water,
dried first on a clay plate and then for 48 hours over sulphuric acid in
a vacuum. The analysis gave the following figures:

\[C = 12.42; \quad H = 1.62; \quad N = 16.46; \quad Ag = 54.50,\]
which correspond almost exactly to the atomic relation $C_2H_2N_2H_3$. It is therefore, very probable that a salt, like $\text{C}_2\text{H}_2\text{N}_2\text{H}_3\text{H}_2\text{O}$, is here in question, to which $\text{H}_2\text{O}$, nitric acid (formed in the reaction) still adheres. The salt can be recrystallized from water and volatile, but on prolonged heating it blackens.

Very interesting is the behavior of imido-formyl cyanide in absolute ethyl alcohol solution toward hydrochloric acid. A heavy, crystalline precipitate is formed, exactly with the salt obtained by Claisen and Matthias. The precipitate, obtained from prussic acid and hydrochloric acid, $\text{HNC}_3\text{H}_4\text{Cl}_2$. It is well known that Claisen and Matthias' product shows perfect conformity with a salt, isolated in HNC, HCl, isolated in a similar manner by Gautier. Furthermore, I succeeded, by means of quinoline, in splitting off hydrochloric acid from a salt, $2\text{HNC}_3\text{H}_4\text{Cl}_2$, prepared directly from prussic acid and hydrochloric acid, thus converting it into imido-formyl cyanide.

Furthermore, when carefully dried hydrochloric acid for one and one-half hours over a solution of $7$ gr. of prussic acid in $60$ grams of absolute ether, a separation of heavy crystals begins after the gas has been passed for thirty minutes; this separation requires $1/2$ hours for completion, $3$ gr. of dry salt were obtained (theory for $2\text{HNC}_3\text{H}_4\text{Cl}_2$ $4/5$ gr. This salt possesses all the properties of the salt described by Claisen and Matthias.

When ten grams of this salt are added to the theoretical quantity (therein noted) of quinoline, there is a considerable evolution of heat; the mixture is heated for a short time on waterbath, during which process a few milligrams of imido-formyl cyanide separate out in the upper part of the flask and in the condenser. The experiment was repeated several times with the same result; in whatever way it was carried out, the yield was always very small. This is not surprising since Gautier observed that the salt, HNC, HCl, broke down very easily into its components.

The results already given prove, however, completely, that the so-called salts of prussic acid with the hydrocyanic hydrides are derivatives of imido-formyl cyanide.

Faujas's salt, $C_2N_2H_2$, is its constitution
\[ \text{Cl} - \text{C} \equiv \text{N} = \text{H} \]
while the salt obtained by Claisen and Matthaeus and by me is the constitution
\[ \text{H} - \text{C} < \text{Cl} \quad \text{or} \quad \text{H} - \text{C} < \text{Cl} \]
\[ \text{H} - \text{C} < \text{N} \equiv \text{H} \quad \text{or} \quad \text{H} - \text{C} < \text{N} \equiv \text{H} \]
belongs. If the reactions of imido-formyl cyanide itself are compared with those of its salts, a striking similarity of behavior is at once observed. They all break down on treatment with water, sodic hydrate or dilute acids giving formic acid and ammonia or form-amino. We are here dealing with substances which spontaneously on treatment with reagents break down into simpler molecules. Countless such examples have been observed by me during the course of my work on tri- and tetra-carbon. The decomposition observed by Fieser and Fieser of dihydroxycarboc acid into carbonic oxide and oxycarbolic ether, and the splitting off oxalic-acetic ether into carbonic oxide and malonic ether, mentioned by W. Wallach 107, are further instances of such decompositions.

109 The facts stated in this paper suffice perfectly to explain the synthesis of benzoin as well as the conversion of benzaldehyde into benzoic acid and alcohol. Benzaldehyde in the presence of alkali, at least, first gives the addition product
\[ C_6H_5\text{C} < \text{O} \]
which like acetaldehyde or the derivative of ortho-acetic acid ether
\[ \text{H}_3\text{C} < \text{O} \]
(0(C=C))

compare Claisen, Ber. d. Chem. Ges. 20, 636. It is converted by means of the alkali condensation into the intermediate product
\[ C_6H_5\text{C} \equiv \text{O} + \text{H} \]

in the presence of mild alkali (amide of phenyl
singly the alcohol forming benzoin. In the presence of a stronger alkali, for instance cactic
stale or sodium ethylate, splitting into benzene leid and ethyl alcohol takes place according to the equation:
\[ \text{H}_3\text{C} < \text{O} \quad \text{H}_2\text{O} = C_6\text{H}_5\text{C} + \text{H}_2\text{O} + \text{C}_2\text{H}_5\text{C} = \text{C}_2\text{H}_5\text{O} + + C_6\text{H}_5\text{O} + \text{H}_2\text{O} \]
The facts stated fully explain the processes which take place when hydrochloric acid acts upon formic acid with or without alcohol. Imido-formyl chloride,
\[ HN:CCl \]
is first formed. This reacts at once by absorption with a second molecule of formic acid, just as formyl chloride-oxime reacts with sodium fulminate,
\[ HN:C\overset{\text{Cl}}{-}C:NH = \overset{\text{Cl}}{H}\overset{\text{CN}}{N}:NH. \]
The imido chloride & arising in this way then simply absorbs one or two molecules of hydrochloric acid; it results, however, as an acid chloride with alcohol forming
\[ \overset{\text{Cl}}{C_2H_5O}C\overset{\text{Cl}}{-}C-N\overset{\text{Cl}}{N\overset{\text{H}}{H}}_2, \]
which substance, as was shown above, is present in great quantity in Pinner's salt mixture. Since the imido group existing in imido-formyl cyanide can easily be replaced by oxygen it follows further, especially in the presence of much alcohol, that the intermediate product
\[ HN:C\overset{\text{Cl}}{C}C=N\overset{\text{Cl}}{H} \]
may be converted, with formation of ammonium chloride into
\[ \overset{\text{Cl}}{(C_2H_5O)}_2C\overset{\text{Cl}}{C}C\overset{\text{Cl}}{N\overset{\text{H}}{H}}_2, \]
as well as also into
\[ \overset{\text{Cl}}{(C_2H_5O)}_2C\overset{\text{Cl}}{C}C\overset{\text{Cl}}{N\overset{\text{H}}{H}}_2, \overset{\text{Cl}}{J}\overset{\text{Cl}}{C_2H_5} \]
The presence of salt III in Pinner's mixture is made probable by the isolation of the free base diethoxy-ortho-succino- glyoxylic ester; this base breaks down on distillation at ordinary pressure into ortho-fumaric ether and amido-di-ethoxy-maltnone according to the following equation:
The hydrochloride of di-ethoxy-imido-glyoxylic ester II is easily decomposed by water giving ammonium chloride and di-ethoxy-glyoxylic ester,

\[(C_2H_5O)_2CH - C - NH_2\]
\[+ 2HCl \rightarrow (C_2H_5O)_2CH + H_2O + \text{NH}_4Cl\]

\[\text{The formation of the last substance when hydrochloric acid is added into fumic acid and an excess of alcohol, observed by Prinse and Klein, is thus explained in a very simple manner. In a corresponding experiment with isobutyl alcohol, fumic acid and hydrochloric acid Prinse and Klein obtained first a substance boiling at } 218^\circ, \text{ which by subsequent treatment with hydrochloric acid gas was converted into the isobutyl ester of di-isobutyl-oxy-glyoxylic acid.}\]

\[(C_4H_9O)\cdot C\cdot C\cdot C\cdot C\cdot O\]

boiling at 250°. This substance is very probably the corresponding imido-ester,

\[(C_4H_9O)\cdot C\cdot C\cdot C\cdot NH\]

whose formation in the above reaction would be readily comprehensible. The analytical figures found by Prinse and Klein 110 agree very closely with those demanded by this formula.

If this becomes evident that on heating hydrochloric acid into an ethereal solution of equivalent quantities of fumic acid and alcohol the following hydrochloric acid salts must be formed:

\[\text{H}_2\text{N}\cdot C\cdot H\cdot C\cdot (\text{OC}_2\text{H}_5)\cdot \text{NH}_2, \text{HCl; (C}_2\text{H}_5\text{O)\cdot C\cdot C\cdot C\cdot NH}_2, \text{HCl; H}_2\text{N}\cdot C\cdot C\cdot C\cdot (\text{OC}_2\text{H}_5)\cdot \text{HCl; H}_2\text{N}\cdot C\cdot C\cdot C\cdot \text{NH}_2, 3\text{HCl.}}\]

Prinse's substance is simply a crystalline mixture of these five hydrochloric acid salts.

Furthermore, the results obtained can be explained only by the isocyanogen hydride formula. Fuscle acid is, therefore, identical with isocyanogen.

The isomutarces react with hydrochloric acid forming entirely analogous salt-like compounds which have the general formula \( \text{RNCl}_3 \). In my first paper I regarded these bodies as hydrochlorides of alkyl-imido-formyl chloride,

\[ (\text{RN} : \text{C} < \text{Cl} ) \text{HCl}^+ \]

since they break down easily when treated with water, alkalies, etc., into the isomutarces or formic acid derivatives. This conclusion is no longer justifiable.

The salts of the isomutarces, \( \text{RNCl}_3 \cdot \text{HCl} \), are most probably salts of di-allyl di-imido-glyoxalyl chloride,

\[ \text{RN} : \text{C} < \text{H} - \text{C} : \text{N} \text{R} , \]

having the constitution

\[ \text{RN} + \xrightarrow{\text{HCl}} \text{C} - \text{N} \text{H} + \text{R} ; \]

careful work should convert them into derivatives of glyoxylic acid. Experiments in this direction will soon be taken up.

In a similar way the remarkable behavior of the isomutarces toward acetic acid may be explained. The products of this reaction are alkyl-form-amide and acetic anhydride. From the first-formed addition product,

\[ \text{RN} : \text{C} < \text{OCOC}_3 \text{H}_5 \]

arises either by direct addition of acetic acid or by the intermediate formation of a glyoxylic acid derivative. The product

\[ \text{RNH} + \xrightarrow{\text{OCOC}_3 \text{H}_5} \]

which breaks down on distillation into acetic anhydride and alkyl-form-amide.

11. Liebig Annalen 270, 303-305.
Jacquin found [13] that on heating the salt $\text{HNC}_2\text{H}_2\text{O}$, which as was known above,

for the constitution

$$\text{H}_2\text{N} > \text{C} \equiv \text{O},$$

with glacial acetic acid

the chief products were formamide, ammonium chloride and hydrochloric acid.

In this reaction the first step must be the separation of ammonium chloride with formation

of the ester derivative

$$\left(\text{CH}_3\text{COO}\right)_2 \text{C} \equiv \text{C} < \text{NH}_2 \quad \left(\text{OCOCH}_3\right)_2,$$

which on distillation, in a manner analogous is the di-ethoxy-orthoorneido-glyoxylic

ester, breaks down into formic acid, acetic anhydride, and formamide.

The formation, too, of acetonamide on heating prunic acid with glacial

acetic acid at 200°, pointed out by Jacquin [14], depends on an intermediate

formation of acetic anhydride and formamide, which interact at a high temperature

giving acetonamide and formic acid [15].

On Polymerized Prunolic Acid. It is shown by the experiments of

Lange [16], of Wimmerman [17] and of Lebeouf and Rigaud [18] that prunolic acid and

its salts, if in the presence of little water polymerize to a tri-molecular substance.

The constitution of this substance has been established by Wimmerman's experiments. It is

amido-malonamide,

$$\text{H}_2\text{N} > \text{C} \equiv \text{CN}.$$

boiling with alkali or with acids converts it smoothly into equivalent quantities of carbon

dioxide, ammonia and glycerol. The formation of this substance from prunolic

acid may be explained in the following simple manner:

I. $2\text{HNC}_2\text{H}_2\text{O} = \text{HN} \equiv \text{C} > \text{H} + \text{O} + \text{C} \equiv \text{N} + \text{H} + \text{O} = \text{H}_2\text{O} + \text{H}_2\text{O}.$

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[Chemical equations and diagrams]

[Handwritten notes and calculations]
Hydroxyl diguanide from Prussic Acid and Acetic Anhydride.

Prussic acid (10 grams) and acetic anhydride (37.4 grams) were heated for five hours to 190-200° in a sealed tube. The deep brown oil was carefully fractionated and much of the original material recovered unchanged. The flask was then heated in a metal bath 15-210° and as soon as nothing more passed over the residue was distilled with steam. The oil passing over was taken up with ether and dried with calcium chloride; freed from ether it crystallized on cooling when scratched with a glass rod. It was spread out on a clay plate, washed with a little cold ether, dried over sulphuric acid in a vacuum and analyzed.

0.1253 g gave 22.60 ccm nitrogen at 10° and 751 mm pressure.

Theoretical
C₂H₃N/O
N 20.09

Found
20.58

The direct acyl diguanide obtained crystallized in baffle melting at 70°; it was perfectly identical with a preparation made in comparison.

Prussic Acid and Brom-acetyl.

In the course of this work it has been shown that acid formides are much more readily absorbed by unsaturated bodies than acid chlorides. The behavior of prussic acid was therefore toward brom-acetyl and brom-benzoyl was therefore tried and it was found that in both cases there was interaction; in the case of brom-benzoyl gentle warming was necessary. Only the reaction product of prussic acid and brom-acetyl has as yet been thoroughly studied. 15 grams prussic acid and 75.5 grams (one mole) of pure brom-acetyl were allowed to stand for four weeks in a closed tube at the room temperature. A considerable quantity of a yellow powder separated out. The precipitate was washed from the tube with absolute ether, then washed as quickly as possible with ether and dried on a clay plate. The yield is 30-35 grams. The substance is very hygroscopic.

[Note: The text appears to be interrupted or cut off at this point, making it difficult to complete the sentence accurately.]
for the odor of hydrobromic acid and is at once decomposed by water giving prussic acid, acetic acid and hydrobromic acid. It probably consists of imido-acetyl bromide,

\[ \text{HN:C<Br}_2 \]

all efforts, however, to convert it into a known derivative of prussic acid have so far been fruitless. The imido-acyl bromide prepared directly from acetyl cyanide in absolute ethereal solution by means of dry hydrobromic acid showed an entirely similar behavior.

It is well known that acetyl cyanide itself is decomposed by cold water giving prussic acid and acetic acid. The intermediate product-

\[ \text{HN:C<OCCH}_3 \]

is first-formed, as is made evident shown by the above experiments with imido-oxalic ether; this then breaks down spontaneously, like many other isocyanogen addition products, into HNC and

\[ \text{CH}_3\text{C}=\text{C} \text{H}^+ \text{O}^- \text{H}^- \]

If the reaction is compared with the behavior of prussic acid amide,

\[ \text{CH}_3\text{C}^-\text{C}^-\text{C}^-\text{NH}_2 \]

discovered by Clinard and Shadwell 120, one becomes convinced that the acid amide, in a free state, have really the constitution expressed by the name. The behavior 120 of formoamide in a free state can only be explained by the formula

\[ \text{H}_2\text{N}=\text{C}::\text{O} \]

The Behavior of Prussic Acid toward Aldehydes and Ketones.

It is a long familiar fact — first observed by Gautier — that prussic acid unite with substances which contain carbonyl to form cyanohydrins having the general formula

\[ \text{R}\text{C}<\text{OH} \]

or

\[ \text{R}\text{C}=\text{O} \]

It may easily be proved that in these reactions, prussic acid acts as an isocyanogen hydrate.
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[Date]
for first the aldehydes are known to react with extraordinary ease with water, alcohol, hydrochloric acid etc. forming addition products which have the formula

\[ R > C < ^{\text{O} +} \]

\[ + X \]

(where \( X = \text{C}_2 \text{H}_4 \) or \( \text{C}_2 \text{H}_5 \)), and secondly dry prussic acid does not react at all with aldehydes and ketones in the absence of water. Gautier remarks that freshly prepared, pure acetaldehyde and prussic acid may be mixed without change of temperature and that then heated in a tube to 100° or higher, no slightest interaction takes place. An excellent way in which to accomplish an addition of prussic acid proved to be to carry out the experiment in the presence of hydrochloric acid (powdered potassium cyanide, aldehyde or ketone and concentrated hydrochloric acid) or in the presence of much water. Since prussic acid is not act on by water \( \times \) or concentrated hydrochloric acid in the cold while aldehydes and ketones unite very energetically with these reagents the reaction must take place in the following manner:

\[ R > C < ^{\text{O} +} + C : \text{N} + = R > C < ^{\text{O} +} \]

\[ + X \]

\[ C : \text{N} + = C : \text{N} + + X ^{+} \]

The cyan-hydrine and azo compounds all show, as is well known, a peculiarity of behaviour. They always break down on distillation and on treatment with water or alkali into the components; in this respect, therefore, they resemble strikingly the acid cyanides. This splitting off may be explained by an absorption of water or the cyano group. From acetaldehyde-cyan-hydrine, for instance, is formed first the intermediate product

\[ \text{CH}_3 > C < ^{\text{O} +} \]

\[ + \]

\[ \text{C} = \text{N} + ^{+} \]

\[ \text{O} + \]

which can easily split giving

\[ \text{CH}_3 > C < ^{\text{O} +} \]

\[ + \]

\[ \text{O} + \]
and C: N: H. Furthermore, it is evident that a trace of water is sufficient to complete the splitting at higher temperatures. The cyan-hydrazines may therefore all be distilled without decomposition if they are first dehydrated with the most exoeutectic piano.

V. Concluding Remarks

1. The Tautomeric Hypothesis.

The experiments given prove so conclusively that prussic acid and its salts react exclusively as derivatives of isocyanogen that further doubt concerning the nature of these bodies is hardly admissible. In their reactions the point of attack is the -carbon atom present. In all cases the bivalent carbon atom is by far the most reactive of the substituents known which contain an unsaturated carbon atom. In their nitriles, however, the behavior of prussic acid is precisely analogous to that of its salts; the only difference is in the case of acetate, acetic ether, and its salts, in the case in which the reaction takes place.

Prussic acid is known to be a very weak acid; according to the measurements of Ostwald, it is extraordinarily weak—a fact which the investigator in favor of the isocyanogen hydride formula. The weakness of the acid explains furthermore the peculiar behavior of cyanide of mercury, which behaves like the other metal salts of prussic acid is soluble in water with a neutral solution. The salt is a nonelectrolyte and is therefore acted on readily by anhydride or dilute hydrochloric acid concentrated. This fact does render explicable the great evolution of heat when mercury oxide is added to dilute aqueous prussic acid; the addition of caustic alkali to an aqueous solution of prussic acid sets free on the contrary very little heat; because potassium and sodium cyanide in aqueous solution are very much hydrolytically dissociated.

Nevertheless, the soluble double salts of prussic acid may be explained in a similar way. It should not, for instance, be assumed because of the existence of

123) Lütig, Annalen 270, 268.
124) Lehman, 1st edition, Vol. 2, 449. The figures given are, however, rather high, as the prussic acid contains some ammonium gasible (see above).
ferricyanide of potassium. The iron and potassium cannot alike be forced to oxidize, rather only that the iron does not pass into the electrolytically dissociated condition. The perfectly analogous potassium ferrificnitrate yields no ferricyanide acid, so ferricyanide acid is a stronger acid than prussic acid. The salt itself is dissociated by losing its crystal water, and when it reacts with silver nitrate only silver fulminate is formed.

The assumption of tautomericism in the case of prussic acid and its salts is absolutely excluded by reason of the facts stated in this paper, an exhaustive discussion of the hypothesis, which has recently been applied by several chemists to this as well as to other fields of organic chemistry, is therefore entirely unnecessary. One formula is perfectly sufficient to explain the behavior of an organic compound; and there is not a single fact which proves that a substance does not possess a definite constitution.

Knorr has recently advanced the opinion that in the case of phenyl-methyl-pyrazolone, a double tautomeric exists, i.e. that the chemical behavior of the substance can only be explained by the assumption of three formulas. In a similar manner, he formerly assumed it to be necessary in order to explain the behavior of the pyrazole ring, it set down five formulas as equally justifiable; these he represented by the

\[
\begin{align*}
N - N \\
\text{CH} & \text{H} \\
\text{CH} & \text{H} \\
& \text{CH} \\
\end{align*}
\]

According to Knorr intramolecular motions or oscillations take place. He expresses the completion of the view of "doppelbindung" 127 and an hypothesis concerning what he calls the oscillations concerning tautomericism are supported by the non-existence of isomers, which from the standpoint of the structure theory ought to exist. Knorr found that 3-methyl and 5-methyl-pyrazole were identical.

124 Diez's handbuch 279, 280, 336.
126 Diez's handbuch 279, 186-216.
In a similar manner, the chemistry of structure leads us to expect in each case two substances having the formulas \( \text{HNC} \) and \( \text{HClN} \); \( \text{HOClN} \) and 
\[
\begin{align*}
\text{CH}_3\text{C} - \text{CH}_2\text{COOH} & \quad \text{and} \\
\text{CH}_3\text{C} - \text{CH} - \text{COOH}
\end{align*}
\]
e tc. The spectra in the ultraviolel light for these formulas is that it demands to the existence of two phthalic acetic,
\[
\begin{align*}
\text{CH} = \text{CH} - \text{COOH} & \quad \text{and} \\
\text{CH} = \text{CH} - \text{COOH}
\end{align*}
\]
but it is possible to show why these isomers have not yet been discovered. This would no longer be any ground for speculation on this subject. This may be done very simply as follows:

Why has cyanogen hydride, \( \text{HNC} \), not been discovered? Under what condition might this substance be prepared?

We have as yet no methods of building up organic substances in the absence of water, either in solid or liquid. Cyanogen hydride must, by reason of facts stated in this paper, be very easily, or spontaneously, converted by water into cyanogen hydride:

\[
\text{HNC} + \text{H}_2\text{O} = \text{HNCN} + \text{H}_2\text{O}
\]
a trace of water is sufficient eventually to accomplish this reaction.

It is easily conceivable that not all substances whose existence is known chemistry allows us to expect can be realized.

The molecules are indeed set in a rigid condition, a fact which Knorr emphasizes, but we have as yet no reason whatever to assume that the atoms or the valencies in the molecule change their places; in that case isomerism would be possible. Mechanics treats not only of motion but also of equilibrium relations, and the latter explain the existing facts in a very simple manner. Many delicately constructed molecules on the are known, like silver fluorinate, nitro-glyceride, etc., which break down at once on the slightest shock caused; they are in a condition of very unstable equilibrium.

In the case under discussion, equilibrium relations play a similar role; nitracyclic acid, \( \text{HNC} \), \( \beta \)-Keto-butyric acid, the \( \text{CH}_3\text{COCH}_2\text{COOH} \), cyanogen hydride, \( \text{HNC} \), are in a condition of unstable equilibrium; in the presence of water, acids, or alkali.
They must be converted, spontaneously or with extraordinary ease, into \( \text{HOCON}, \text{CH}_3 = \text{C} = \text{N}, \text{H} \text{NiCl} \). The same holds true for the pyrazol and benzol rings.

The second substance, isomer with 3- or 5- methyl pyrazol, as well as the second phthalic acid has not been discovered because its synthetic could only be possible accomplished in the absence of water, alkali, and acid. It is evident that in order to build up molecules whose equilibrium conditions are so exceedingly unstable much more delicate synthetic methods must be used than those which we now possess.

Since I have already isolated several such substances in the course of the work recorded in this paper, I do not regard this problem as insoluble; it is possible that resorine acid and true formonitrile will yet be discovered.

Finally, only one more remark in regard to the double tautomorism assumed by Knorr in the case of phenyl- methyl pyrazol. Knorr found that the substance treated with sodium ethylate and methyl iodide gave six methyl derivatives, which were derived respectively from the indol, methyl and pheno-form of pyrazol. He therefore assumes that these formule should be ascribed to the sodium salt of this substance. Now I have shown that from the sodium-phenyl-methyl-pyrazol and benzyl chloride exclusively the benzyl derivative having the constitution

\[
\text{CH}_3\text{CO-}\text{N} = \text{CO} \\
\text{CH}_3\text{C} = \text{C} \\
\text{H} \]

is formed. In a similar manner the silver salt and methyl iodide give only antipyrine.

The constitution of the same salt must, therefore, differ according to the reagent employed—which is manifestly an absurdity.

The results obtained by Knorr may be explained in a very simple manner.

I have already proved that

\[
\text{CH}_3\text{N} = \text{CO} \\
\text{CH}_3\text{C} = \text{C} \\
\text{H} \\
\]

that substitution and addition processes may be placed side by side. The carbonyl group present in sodium ethylate phenyl-methyl pyrazol can, moreover, add sodium ethylate.

129 Liebigs Annalen 266, 133.
and from this product, in the presence of methyl iodide, the formation of 5-methoxyphenyl-methyl-phenyl-pyrazole is self-evident.

2. The Polymerization of Unsaturated Bodies

I have already repeatedly emphasized the fact that the isocyanogen derivatives form in case addition products, which then break down again with surprising readiness into the components. The unsaturated carbon atom behaves therefore in a manner entirely analogous to the ethylene bond present in acetic acid, acetic ester, and similar compounds. These substances, as I have very distinctly proved, readily absorb halogen, acid chlorides, etc.; the addition products thus formed break down again easily, often spontaneously, splitting off halogen hydride and regenerating the double bond. This remarkable property seems indeed to belong generally to unsaturated bodies. The isocyanogen derivatives too, are known to react with halogen hydride forming addition products of the formula

\[
\text{R} - \text{C} = \text{N} \quad \text{or} \quad \text{R} - \text{C} - \text{N}_2 \text{H}_2,
\]

which again break down very readily, often spontaneously, into nitride and halogen hydride.

In those reactions the existing unsaturated groupings are converted to a certain extent into the resonance state

\[
\text{R} = \text{C} = \text{C} = \text{O} \text{R}, \quad \text{R} = \text{C} : \text{N},
\]

that is shown at the moment of splitting the valences exist free and in this condition polymerization can occur with especial ease. It seems to me that in general all the polymerizations of unsaturated substances depend on the remarkable property under discussion. A trace of water, alkali or halogen hydride is sufficient to bring continually absorbed and split off, in sufficient to bring an unsaturated substance into the resonant state; condensation & or polymerization then take place. The polymerization of peroxyc acid and of the alkyl isocyanide or their addition products on standing then takes place simply explained. In the case of cyanogen and acetylene derivatives polymerization takes place in a similar manner. Chlorauric brom cyanogen when perfectly dry and dry, may be kept
unchanged for months; in the presence, however, of a trace of water or more especially of hydrochloric or hydrobromic acid they are converted into halogen cyanamidates.ertiary cyanide, benzyl cyanide and cyan carbonate ethers are known to be converted in a perfectly analogous manner into the di- or tri-molecular condition in the presence of solid carbonate of potash, metallic sodium (which with water present forms cyanic soda) or traces of bromine (which form hydrobromic acid—the active agent); this depends on a continual absorption and splitting off of water with hydrobromic acid.

In the above work on cyanogen and isocyano-ger. I have been assisted in the most devoted and admirable manner by Mr. W. E. Whelan, to whom I wish here to express my warmest thanks.

It may perhaps not be superfluous to describe a method by which one can protect oneself perfectly against poisonous substances and those which attack the eyes.

By means of elastic and shower a protection for the eyes which is perfectly impermeable to air may be made from a pair of clear glass goggles. Mr. C. H. Stoeletting made according to my direction a convenient inhalation apparatus fitted with valves and rubber tubes. It is fastened around the head and by means of a girdle around the body in such a way as not to impede the movements of the wearer. Provided with this apparatus one can go without danger into a room where sealed flasks containing prussic acid may suddenly explode. In working with bromine, chloroform, ethyl cyanogen and other substances which attack the lungs the apparatus is to be recommended.

Chronic physiological effects of prussic acid, such as Gauthier mentions in his interesting paper, were, therefore, observed neither by me nor Mr. Whelan.

I do not propose to prepare ketylcyano-ger or derivatives of that substance which are free from nitrogen; many observations made in the course of this year testify to the existence of such substances.

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