fourth body, probably amido-di-ethoxy-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 180°. At first alcohol distills over; as soon as the ~~thermometer indicates the~~ temperature rises 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 (b.pt. about 135°) no longer solidifies. The crystals present in the condenser are dissolved in ether and worked up as directed below. By continuing the distillation still further an oil is obtained which boils between 140° and 170°, and which yields when fractionated repeatedly a little more of the solid substance just mentioned. By repeated fractional distillations I succeeded in proving it was possible to prove the presence of two substances; one of them boils at 145–146° and consists of not perfectly pure ortho-formic ether.

	Theory for $C_7H_{16}O_3$	Found
C	56.75	55.38
H	10.80	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 behavior and its properties with a specimen of ortho-formic ether prepared for the purpose of comparison. An interesting fact in the behavior of ~~those~~ this ether should be emphasized: While it can be boiled for a long time with dilute caustic alkalies with much change, 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 (an analysis gave 10%), but it is not quite free from ortho-formic ether. When heated with water or alkalies it is split into ammonia, alcohol and formic acid; with quite dilute hydrochloric acid this decomposition occurs at once in the cold. It seems to me, therefore, very probable that this substance is amido-diethoxy-methane

$$(C_2H_5O)_2C<^{H}_{NH_2},$$

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 too when the above mentioned etherial filtrate (resulting from the preparation of Pinner's salt at a low temperature) is treated with powdered sodic hydrate. In these cases I observed sometimes the presence (in small quantities) of a third substance, which boils at 169-170° and is not decomposed by dilute hydrochloric acid. According to an analysis it contains 8.87% nitrogen and may possibly be identical with diethoxy-glyoxalyl cyanide, $(C_2H_5O)_2CH-CO-C:N$. The substance is extremely stable.

Imido-formyl Cyanide,

$$HN:CH$$
$$|$$
$$C:N.$$

The substance mentioned above boiling at 110-130° and solidifying in the condensing tube is isolated from the etherial 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 cold resulting from this process causes the imido-formyl cyanide to separate out as a crystalline powder fine crystals. These are filtered off as quickly as possible at a low temperature, brought upon a clay plate, pulverized and then washed once 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 grams from 30 grams prussic acid; it may, however, be much increased.

0.1808 grams

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

	Theory for $C_2H_2N_2$	Found
C	44.44	43.84
H	3.71	3.77
N	51.85	51.50

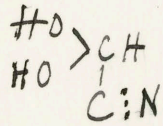
Imido-formyl cyanide melts at 87° and boils without decomposition between 120-125° (the boiling point has not yet been exactly determined). It is readily

soluble in water and organic solvents; in alcohol and ether at −5° it is, however, slightly soluble. The substance is extraordinarily volatile; when an ethereal solution is distilled it goes over in great quantities with the ether. Several decigrams left standing in a desiccator or in the air at the room temperature (+15°) disappear in a very short time. When kept in a loosely closed test tube imido-formyl cyanide sublimes in magnificent crystals clear as water, which often look precisely like dodecahedra. Mr. J. Iddings 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). Very flat rhombohedra with a short prism of the second order."

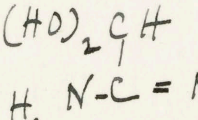
The molecular weight was determined by means of the lowering of the freezing point in benzene solution. Two observations gave the molecular weight—64 (theoretical 54). It is possible that the too high number found was the result of an impurity in the benzene; it happened accidentally that only American 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.

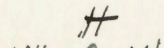
By sodic hydrate or dilute hydrochloric acid imido-formyl cyanide is split smoothly in the cold into ammonia and formic acid. An aqueous solution of the substance decomposes very slowly in the cold, rapidly when heated to 100° in a sealed tube, giving the formate of formamidine and ammonium formate.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



which then absorbs ammonia on the cyanogen group,



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



The University of Chicago

The presence of form-amidine may easily be proved, as I showed in the case of the hydrochloride of form-amidine, by shaking with cold sodic hydrate and benzoyl chloride. A precipitate is formed which consists of benzamide and dibenzoyl-form-amidine; these substances may easily be separated, since the latter is hardly ~~x~~ at all soluble in cold and very difficultly soluble in hot alcohol. Di-benzoyl-form-amidine separates out from hot alcohol in ~~white~~, voluminous white needles, which melt at 236°. The benzamide was obtained in colorless leaflets melting at 128°.

A mixture of benzamide and di-benzoyl-form-amidine is obtained on shaking a solution of imido-formyl cyanide in sodic hydrate with benzoyl chloride. The analyses of the substances obtained in this way gave the following results:

I. 0.1224 grams, dried at 110°, gave 13.2 ccm nitrogen at 26° and 746 m m pressure.

	Theory for $C_6H_5-CO\,N:C-NHCO\,C_6H_5$ (H)	Found
~~x~~ N	11.11	11.74

II. 0.2086 grams, recrystallized from benzene, gave 21 ccm nitrogen at 21° and 747 m m pressure.

	Theory for $C_6H_5-CONH_2$	Found
N	11.57	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 lukewarm, and somewhat soluble in cold water. This precipitate was washed five times with very cold water, dried first ~~x~~ on a clay plate and then for 48 hours over sulphuric acid in a vacuum. The analysis gave the following figures:

C = 12.42; H = 1.62; N = 16.46; Ag = 54.50,

which correspond almost exactly to the atomic relation Ag, C_2, N_2, H_3. It is, therefore, very probable that a silver salt of imido-formyl cyanide hydrate, ~~is here in~~ ~~question~~ AgC_2N_2H, H_2O, is here in question, to which 5% nitric acid (formed in the ~~reaction~~) still adheres. The salt can be recrystallized from lukewarm water, but on prolonged heating it blackens.

Very interesting is the behavior of imido-formyl cyanide in absolute ethereal solution toward dry hydrochloric acid. A heavy, crystalline precipitate is formed, which in behavior and properties accords ~~perfectly~~ exactly with the salt obtained by Claisen and Matthews[105] from prussic acid and hydrochloric acid, $2HNC, 3HCl$. It is well known that Claisen and Matthews' product shows perfect conformity with a salt, ~~isolated in~~ HNC, HCl, isolated in a similar manner by Gautier[106].

Furthermore I succeeded, by means of quinoline, in splitting off hydrochloric acid from a salt, $2HNC, 3HCl$, prepared directly from prussic acid and hydrogen chloride, thus converting it into imido-formyl cyanide.

On leading carefully dried hydrochloric acid for one and one half hours over a solution of 15 grams prussic acid in 60 grams absolute ether a separation of heavy crystals begins after the gas has been passed for ~~forty~~ 40 minutes; this separation requires 12 hours for completion. 13 grams of dry salt were obtained (theory for $2HNC, 3HCl$ 14.5 grams). This salt possesses all the properties of the salt described by Claisen and Matthews.

When ten grams of this salt are added to the theoretical quantity (three molecules) of quinoline there is a considerable evolution of heat; the mixture is heated for a short time on the 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, breaks down very easily into its components.

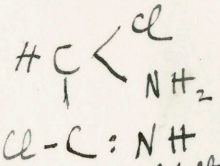
The results already given prove, however, completely that the so-called salts of prussic acid with the halogenhydrides are derivatives of imido-formyl cyanide.

---

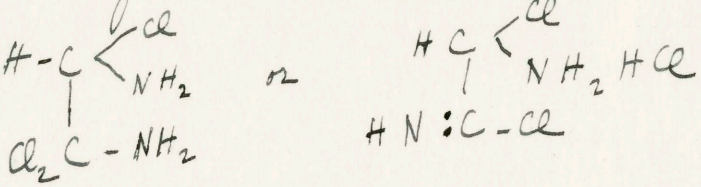
105) Ber. d. Chem. Ges. 16, 311.

106) Ann. de Chim. et de Phys. [4] 17, 129–140.

Gautier's salt, $C_2N_2H_2, 2HCl$, has the constitution



while to the salt obtained by Claisen and Matthews and by me the constitution



belongs.

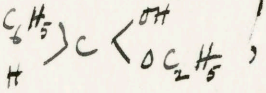
If the reactions of imido-formyl cyanide itself are compared with those of its salts a striking similarity of behavior is at once observed. All these substances They all break down on treatment with water, sodic hydrate or dilute acids giving formic acid and ammonia or form-amidine. We are here dealing with substances which spontaneously or on treatment with reagents break down into simpler molecules. Countless such examples have been observed by me during the course of my work on bivalent carbon. The decomposition, observed by Anschütz and Pauli, of dioxysuccinic ester into carbonic oxide and oxymalonic ether[107], and the splitting of oxalo-acetic ether into carbonic oxide and malonic ether, mentioned by W. Wislicenus[108], are further instances of such decompositions[109].

---

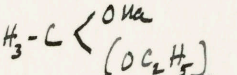
107) Ber. d. Chem. Ges. 27, 1304.

108) Ber. d. Chem. Ges. 27, 792.

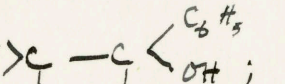
109) The facts stated in this paper suffice perfectly to explain the synthesis of benzoïn as well as the conversion of benzaldehyde into benzoic acid and benzyl alcohol. Benzaldehyde in the presence of alkali and alcohol first gives the addition product



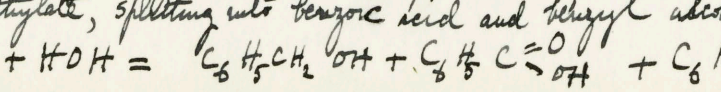
which like acetaldehyde or the derivative of ortho-acetic acid ether



(compare Claisen, Ber. d. Chem. Ges. 20, 636) is converted by means of the aldol condensation into the intermediate product



; in the presence of a mild alkali (cyanide of potassium) this simply loses alcohol forming benzoïn. In the presence of a stronger alkali, for instance caustic potash or sodium ethylate, splitting into benzoic acid and benzyl alcohol takes place according to the equation:



The facts stated fully explain the processes which take place when hydrochloric acid acts upon prussic acid with or without alcohol. Imido-formyl chloride,

$$HN:C<\begin{matrix}H\\Cl\end{matrix},$$

is first formed. This reacts at once by absorption with a second molecule of prussic acid, just as formyl-chloride-oxime reacts with sodium fulminate,

$$HN:C<\begin{matrix}Cl\\H\end{matrix} + C:NH = \begin{matrix}HN:C-C:NH,\\ H\quad\ Cl\end{matrix}$$

The imide chloride arising in this way then simply absorbs one or two molecules of hydrochloric acid; it reacts, however, as an acid chloride with alcohol forming

$$\text{I.}\quad \begin{matrix}C_2H_5O\\H_2N\end{matrix}>C-\overset{\overset{Cl}{|}}{\underset{\underset{OC_2H_5}{|}}{C}}-NH_2,$$
$$\quad\ H$$

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

$$HN:C-\overset{\overset{Cl}{|}}{C}=NH$$
$$\quad H$$

may be converted, with formation of ammonium chloride into

$$\text{II.}\quad (C_2H_5O)_2=C-\overset{\overset{Cl}{|}}{\underset{\underset{OC_2H_5}{|}}{C}}<NH_2,$$
$$\quad\ H$$

as well as also into

$$\text{III.}\quad (C_2H_5O)_2CH-\overset{\overset{OC_2H_5}{|}}{\underset{\underset{OC_2H_5}{|}}{C}}<NH_2,HCl$$

The presence of salt III in Pinner's mixture is made probable by the isolation of the free base diethoxy-ortho-amido-glyoxylic ester; this base breaks down on distillation at ordinary pressure into ortho-formic ether and amido-di-ethoxy-methane according to the following equation:

$$(C_2H_5O)_2CH-C\begin{matrix}NH_2\\(OC_2H_5)_2\end{matrix} + HOC_2H_5 = (C_2H_5O)_3CH + HC\begin{matrix}NH_2\\(OC_2H_5)\end{matrix}.$$

The hydrochloride of di-ethoxy-imido-glyoxylic ester II ~~is~~ maybe easily decomposed by water giving ammonium chloride and di-ethoxy-glyoxylic ester,

$$(C_2H_5O)_2CH-C\begin{matrix}=O\\OC_2H_5\end{matrix}.$$

The formation of the last substance when hydrochloric acid is led into prussic acid and an excess of alcohol, observed by Pinner and Klein, is thus explained in a very simple manner. In a corresponding experiment with isobutyl alcohol, prussic acid and hydrochloric acid Pinner and Klein obtained first a substance boiling at 218°, which by subsequent treatment with hydrochloric acid gas was converted into the isobutyl ester of di-isobutyl-oxy-glyoxylic acid.

$$(C_4H_9O)_2=C\begin{matrix}H\\|\\O-C:O\end{matrix}C_4H_9,$$

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

$$(C_4H_9O)_2C\begin{matrix}H\\|\\NH\end{matrix}:C-OC_4H_9,$$

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

It thus becomes evident that on leading hydrochloric acid into an ethereal solution of equivalent quantities of prussic acid and alcohol the following hydrochloric acid salts must be formed:

$$\begin{matrix}H_2N\\C_2H_5O\end{matrix}\!\!>CH-C\begin{matrix}OC_2H_5\\=NH\end{matrix},HCl;\quad (C_2H_5O)_2CH-C\begin{matrix}NH\\OC_2H_5\end{matrix},HCl;$$

$$(C_2H_5O)_2CH-C\begin{matrix}(OC_2H_5)_2\\NH_2\end{matrix},HCl;\quad \begin{matrix}H_2N\\Cl\end{matrix}\!\!>C-C\begin{matrix}OC_2H_5\\=NH\end{matrix},HCl;\quad HN:CH-C:N,3HCl.$$

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

---

110) Ber. d. Chem. Ges. 11, 1478.

Furthermore the results obtained can only be explained only by the isocyanogen hydride formula. Prussic acid is, therefore, identical with isocyanogen hydride. The isonitriles react with hydrochloric acid forming entirely analogous salt-like compounds which have the general formula $2\,RNC, 3\,HCl$ [111]. In my first paper I regarded these bodies as hydrochlorides of alkyl-imido-formyl chloride,

$$\left(RN:C\begin{matrix}H\\Cl\end{matrix}\right)HCl$$ [112],

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

The salts of the isonitriles, $2\,RNC, 3\,HCl$, are most probably salts of di-alkyl-di-imido-glyoxalyl chloride,

$$RN:CH-\underset{\displaystyle Cl}{\overset{\displaystyle |}{C}}:NR,$$

having the constitution

$$RNH\begin{matrix}Cl\\ \\ \end{matrix}\!\!>CH-\underset{\displaystyle Cl}{\overset{\displaystyle |}{C}}\!\!<\begin{matrix}NHR\\ \\Cl\end{matrix};$$

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 isonitriles toward acetic acid may be explained. The products of this reaction are alkyl-form-amide and acetic anhydride. From the first-formed addition product,

$$RN:C\begin{matrix}OCOCH_3\\H\end{matrix},$$

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

$$RNH\begin{matrix}H\\ \\ \end{matrix}\!\!>C\!\!<\begin{matrix}OCOCH_3\\OCOCH_3\end{matrix},$$

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

[111] Gautier, Annales de Chim. et de Phys. [4] 17, 223, 240.

[112] Liebig's Annalen 270, 303-305.

$$RNH\!>\!C:O.$$
$$H$$

Gautier found [113] that on heating the salt HNC_3HCl, which, as was shown above, has the constitution

$$\begin{matrix} Cl \\ H_2N \end{matrix}\!>\!CH\text{-}C\!\begin{matrix} =NH \\ -Cl \end{matrix},$$

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 ortho derivative

$$(CH_3COO)_2CH\text{-}C\!<\!\begin{matrix} NH_2 \\ (OCOCH_3)_2 \end{matrix},$$

which on distillation, in a manner analogous to the di-ethoxy-orthoamido-glyoxylic ester, breaks down into formic acid, acetic anhydride and formamide.

The formation, too, of acetamide on heating prussic-acid with glacial acetic acid to 200°, pointed out by Gautier [114], depends on an intermediate formation of acetic anhydride and formamide, which interact at a high temperature giving acetamide and formic acid [115].

On Polymerized Prussic Acids. — It is shown by the experiments of Lange [116], of Wippermann [117] and of Lescoeur and Rigaut [118] that prussic acid and its salts in the presence of little water polymerize to a tri-molecular substance. The constitution of this substance has been established by Wippermann's experiments. It is

$$\begin{matrix} H_2N \\ H \end{matrix}\!>\!C\!<\!\begin{matrix} CN \\ CN \end{matrix};$$

boiling with alkalies or with acids splits it converts it smoothly into equivalent quantities of carbon dioxide, ammonia and glycocoll. The formation of this substance from prussic acid may be explained in the following simple manner:

I. $2HN{:}C + H_2O = HN{:}C\!<\!\begin{matrix} H \\ OH \end{matrix} + C{:}NH = \begin{matrix} HN{:}CH \\ | \\ HO\,C{:}NH \end{matrix} = \begin{matrix} HN{:}CH \\ | \\ C{:}N \end{matrix} + H_2O = \begin{matrix} H_2N \\ HO \end{matrix}\!>\!CH.$
$$\begin{matrix} | \\ C{:}N \end{matrix}$$

113) Annales de Chim. et de Phys. [4] 17, 147.
114) Annales de Chim. et de Phys. [4] 17, 146.
115) Compare Liebig's Annalen 270, 278.
116) Ber. d. Chem. Ges. 6, 99.
117) Ber. d. Chem. Ges. 7, 767.
118) Ber. d. Chem. Ges. 12, 2162.

II. $HN{:}C + \begin{matrix} HO \\ H_2N \end{matrix}\!>\!CH\text{-}C{:}N = HN{:}C\begin{matrix} OH \\ NH_2 \end{matrix}\!\text{-}CH\text{-}C{:}N = N{:}C\text{-}\underset{\displaystyle NH_2}{\underset{|}{C}}H\text{-}CN + H_2O.$

Diacetyl Di-cyanide 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 to 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 grams gave 22.6 c.c.m. nitrogen at 18° and 751 m.m. pressure.

	Theory for C_5H_3NO	Found
N	20.29	20.58

The di-acetyl di-cyanide obtained crystallized in leaflets melting at 70°; it was perfectly identical with a preparation made for comparison.

Prussic Acid and Brom-acetyl.

In the course of this work it has been shown that acid bromides 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 45.5 grams (one molecule) of pure brom-acetyl were allowed to stand for four weeks in a closed tube at the room temperature.[119] 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

[119] Gal mentions, Liebig's Annalen 138, 40, that prussic acid unites with brom-acetyl to form a yellowish white compound which is decomposed at 100°.

has 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-pyruryl bromide,

$$HN{:}C\langle \begin{matrix} Br \\ COCH_3 \end{matrix};$$

all efforts, however, to convert it into a known derivative of pyruvic acid have so far (C. 04 I. 934) been fruitless. The imido-pyruryl 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 too that acetyl cyanide itself is decomposed by cold water giving prussic acid and acetic acid. The intermediate product

$$HN{:}C\langle \begin{matrix} OH \\ COCH_3 \end{matrix}$$

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

$$CH_3C{=}O \\ \quad\quad\; \backslash OH .$$

If this reaction is compared with the behavior of pyruvic acid amide,

$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 ,$$

discovered by Claisen and Shadwell [120] one becomes convinced that the acid amides, in a free state, have really the constitution expressed by this name. The behavior too of formamide in a free state can only be explained by the formula

$$H_2N \\ \quad\; H \rangle C{:}O .$$

The Behavior of Prussic Acid toward Aldehydes and Ketones.

It is a long familiar fact – first observed by Gautier – that prussic acid unites with substances which contain carbonyl to form cyan-hydrins having the general formula

$$R \\ H \rangle C\langle \begin{matrix} OH \\ C{:}N \end{matrix} \quad \text{or} \quad R \\ R \rangle C\langle \begin{matrix} OH \\ C{:}N \end{matrix} .$$

It may easily be proved that in these reactions prussic acid acts as isocyanogen hydride.

120/ Ber. d. Chem. Ges. 11, 1566.

for first the aldehydes are known to react with extraordinary ease with water, alcohol, hydrochloric acid etc. forming addition products which have the formula

$$\begin{matrix} R \\ H \end{matrix} > C < \begin{matrix} OH \\ X \end{matrix}$$

(where X = Cl, OH or OC_2H_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 when heated in a tube to 100° or higher not the slightest interaction takes place [121]. 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 acted on by water 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:

$$\begin{matrix} R \\ H \end{matrix} > C < \begin{matrix} OH \\ X \end{matrix} + C{:}NH = \begin{matrix} R \\ H \end{matrix} > C < \begin{matrix} OH \\ C{:}NH \\ X \end{matrix} = \begin{matrix} R \\ H \end{matrix} > C < \begin{matrix} OH \\ C{:}N \end{matrix} + XH.$$

The cyan-hydrins all show, as is well known, a peculiar behavior. They always break down on distillation and on treatment with water or alkalies into the components; in this respect, therefore, they resemble strikingly the acid cyanides. This splitting too may be explained by an absorption of water on the cyanogen group. From acetaldehyde-cyan-hydrin, for instance, is formed first the intermediate product

$$\begin{matrix} CH_3 \\ H \end{matrix} > C < \begin{matrix} OH \\ C=NH \\ | \\ OH \end{matrix},$$

which can easily split giving $\begin{matrix} CH_3 \\ H \end{matrix} > C < \begin{matrix} OH \\ OH \end{matrix}$

121/ Annales de Chim. et de Phys. [4] 17, 148.

and C:NH. Furthermore it is evident that a trace of water is sufficient to complete this splitting at higher temperatures. The cyan-hydrins may, therefore, all be distilled without decomposition if they are first dehydrated with the most excruciating pains.

V. Concluding Remarks.

1. The Tautomeric Hypothesis.

The experiments given prove so ~~exactly~~ rigidly that prussic acid and its salts react exclusively as derivatives of isocyanogen that any further doubt concerning the nature of these bodies is hardly admissible. In their reactions the point of attack is in most cases the bivalent carbon atom present. As was to be expected [122] prussic acid is less reactive than cyanide of mercury; on the other hand cyanide of potassium is by far the most reactive of the substances now known which contain an unsaturated carbon atom. In other respects, however, the behavior of prussic acid is precisely analogous to that of its salts; the only difference, just as in the case of aceto-acetic ether and its salts, is in the ease with which the reactions take place.

Prussic acid is known to be a very weak acid; according to the measurements of Ostwald [123] extraordinarily weak — a fact which ~~he interprets~~ in favor of the isocyanogen hydride formula. The weakness of the acid explains furthermore the peculiar behavior of cyanide of mercury, which alone of the heavy metal salts of prussic acid is soluble in water giving with a neutral reaction. The salt is a non-electrolyte and is therefore acted on neither by sodic hydrate nor dilute hydrochloric nor concentrated nitric acid. This fact too renders 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. ~~The behavior of the~~ In a similar way 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

---

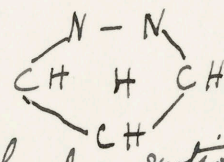
122) Liebig's Annalen 270, 268.

123) Lehrbuch, 1st edition, Bd 2, 849. The figures given are, however, rather high, as the prussic acid contains some ammonium cyanide (see above).

ferro-hydrocyanic acid, $(HN:C)_4Fe(NC)_2$, that in ferrocyanide of potassium the iron and potassium cannot alike be bound to nitrogen; rather only that the iron does not pass into the electrolytically dissociated condition. The perfectly analogous sodium ferro-fulminate[124] yields no ferro-fulminic acid, for fulminic acid is a stronger acid than prussic acid. The salt itself is dissociated on losing its crystal water, and when it reacts with silver nitrate only silver fulminate is formed.

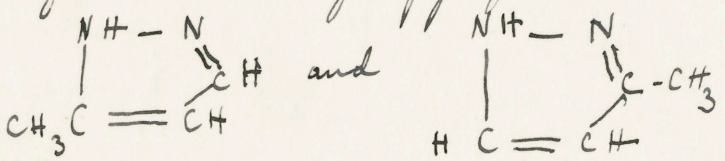
The assumption of tautomerism in the case of prussic acid and its salts is absolutely excluded by reason of the facts stated in this paper; an exhaustive discussion of this hypothesis, which has recently been applied by several chemists to this as well as to other fields of organic Chemistry, is, therefore, 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-pyrazolon a double tautomerism exists, i.e. that the chemical behavior of this substance can only be explained by the assumption of three formulas[125]. In a similar manner he formerly assumed it to be necessary[126], in order to explain the behavior of the pyrazol ring, to set down five formulas as equally justifyable; these he represent by the



According to Knorr intramolecular motions or oscillations take place. He expresses this conception by the words „fliessende Doppelbindung"[127] and by an hypothesis concerning „valence bodies".

The speculations concerning tautomerism 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-pyrazol, ~~were identical~~.



were identical.

124/ Liebig's Annalen 280, 336.
125/ Ber. d. Chem. Ges. 28, 706.
126/ Liebig's Annalen 279, 186-216.
127/

In a similar manner the Chemistry of structure leads us to expect in each case two substances having the formulas $H{-}N{:}C$ and $H{-}C{:}N$; $HO{-}C{:}N$ and $H{-}N{:}C{:}O$;

$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}COOR \quad \text{and} \quad CH_3{-}\overset{OH}{\overset{|}{C}}{=}CH{-}COOR$$

etc. The objection to Kekulé's benzol formula is that it demands the existence of two phthalic acids,

$$\begin{matrix} CH=CH-C\,COOH \\ | \qquad\quad \| \\ CH=CH-C\,COOH \end{matrix} \quad \text{and} \quad \begin{matrix} CH-CH=C-COOH \\ \| \qquad\quad | \\ CH-CH=C-COOH \end{matrix}$$

In all these cases only one substance has as yet been obtained. Because of the non-existence of the other it has been assumed that the substance actually obtained must be expressed by all possible formulas.

The entire discussion of the last twenty-five years concerning the constitution of the ring compounds as well as concerning tautomerism results, therefore, from the attempt to draw from negative experimental results (the non-existence of isomers) positive conclusions. If it were possible to show why these isomers have not yet been discovered there would no longer be any ground for speculation on this subject. This may be done very simply as follows:

Why has cyanogen hydride, $H{-}C{:}N$, not been discovered? Under what conditions might this substance be prepared?

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

$$H{-}C{:}N + H_2O = \overset{H}{\underset{HO}{}}\!\!>C{:}NH = H_2O + H{-}N{:}C;$$

a trace of water is sufficient eventually to accomplish this reaction.

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

The molecules are indeed not in a rigid condition, a fact which Knorr emphasizes, but we have as yet no reason whatever to assume that the atoms or the valences in the molecule change their places; in that case no 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 are known, like silver fulminate, nitroglycerine etc., which break down at once on the slightest shock concussion; they are in a condition of very unstable equilibrium.

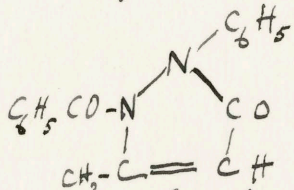
In the cases under discussion equilibrium relations play a similar role; isocyanic acid, $H{-}N{:}C{:}O$, β-Keto-butyric acid ether, $CH_3{-}CO{-}CH_2{-}COOR$, and Cyanogen hydride, $H{-}C{:}N$ are in a condition of unstable equilibrium; in the presence of water, acids or alkalies

they must be converted, spontaneously or with extraordinary ease, into $HOC{:}N$, $CH_3-C(OH)=CH-COOR$, $HN{:}C$. The same holds true for the pyrazol- and benzol-ring.

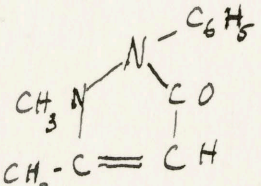
The second substance, isomeric with 3- or 5-methyl pyrazol, as well as the second phthalic acid has not been discovered because its synthesis could only be accomplished in the absence of water, alkalies and acids. It is evident that in order to build up molecules whose equilibrium conditions are so exceedingly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

Since I have already isolated[1] several such substances[2] in the course[3] of the work recorded in this paper, I do not regard this problem as insoluble; it is possible that isocyanic acid and true formonitrile will yet be discovered.

Finally only one more remark in regard to the double tautomerism assumed by Knorr in the case of phenyl-methyl-pyrazol. Knorr found that this substance treated with sodium ethylate and methyl iodide gave six methyl derivatives, which are derived respectively from the imid- methylene- and phenol-form of pyrazol[128]. He therefore assumes that three formulas should be ascribed to the sodium salt of this substance. Now I have shown[129] that from the sodium-phenyl-methyl-pyrazol and benzoyl chloride exclusively the benzoyl derivative having the constitution



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



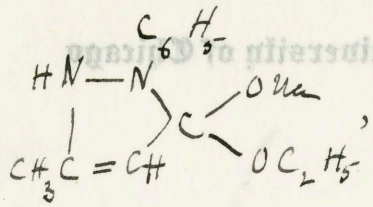
The constitution of the same salt must, therefore, differ according to the reagent employed — which is manifestly an absurdity.

The results obtained by Knorr may be explained in a very simple manner. I have already proved that substitution and addition processes take place side by side. The carbonyl group present in ~~sodium ethylate~~ phenyl-methyl pyrazolon can, moreover, add sodium ethylate,

---

128) Ber. d. Chem. Ges. 28, 707.

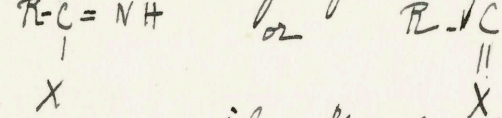
129) Liebig's Annalen 266, 133.



and from this product — the in the presence of methyl iodide, the formation of 5-methoxyphenyl-methyl-pyrazolon is self evident.

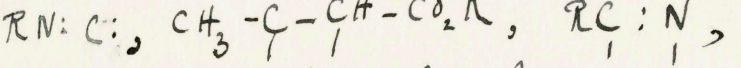
2. The Polymerization of Unsaturated Bodies.

I have already repeatedly emphasized the fact that the isocyanogen derivatives form with ease 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 existing in aceto-acetic ether and similar compounds. These substances, as I have very rapidly proved[130], readily absorb halogens, 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 cyanogen derivatives, too, are known to react with halogen hydride forming addition products of the formula



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

In these reactions the existing unsaturated groupings are converted to a certain extent into the nascent condition state



that is during 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, is sufficient to bring an unsaturated substance into the nascent state; condensation or polymerization then take place. The polymerization of prussic acid and of the alkyl isocyanides or their addition products on standing may thus be simply explained. In the case of cyanogen and acetylene derivatives polymerization takes place in a similar manner. Chlor- and brom-cyanogen, when perfectly pure and dry, may be kept

130) Liebig's Annalen 276, 235; 277, 76-78.

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 cyanurates. Acetyl cyanide, benzoyl cyanide and cyan-carbonic ether are known to be converted in a perfectly analogous manner into the di- or tri-molecular condition in the presence of solid caustic potash, metallic sodium (which with water present forms caustic soda) or traces of bromine (which form hydrobromic acid – the active reagent); this depends on a continual absorption and splitting off of water or of hydrobromic acid.

In the above work on cyanogen and isocyanogen I have been assisted in the most devoted and admirable manner by Dr. M. Ikuta, 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 himself perfectly against poisonous substances and those which attack the eyes.

By means of elastic and shellac a protection for the eyes which is perfectly imperious to air may be made from a pair of clear glass goggles. Mr. C. H. Stoelting made according to my directions a convenient inhalation apparatus fitted with valves and long 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 motions of the wearer. Provided with this apparatus one can go without danger into a room where sealed tubes containing prussic acid may suddenly explode. In working with bromine, phosgene, chlor-cyanogen and other substances which attack the lungs the apparatus is to be recommended 131).

Chronic physiological effects of prussic acid, such as Gautier mentions in his interesting paper 132) were, therefore, observed neither by me nor by Dr. Ikuta.

I soon propose to prepare methylene 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.

---

131) Mr. C. H. Stoelting's address is: 128–130 S. Clinton Street, Chicago, Ill.

132) Annales de Chim. et de Phys. [4] 17, 169.

The University of Chicago