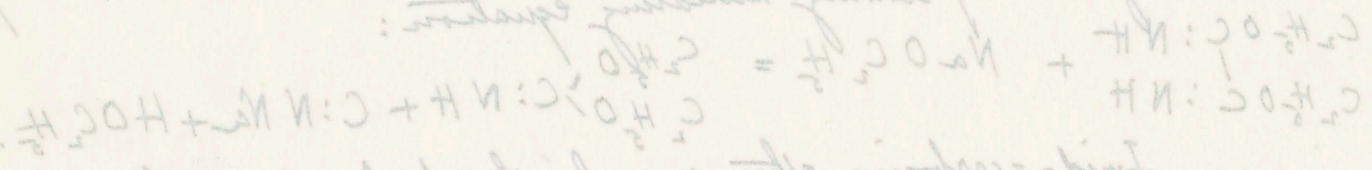


The University of Chicago

made strongly alkaline with caustic soda and extracted six times with ether. The ethereal solution was washed three times with dilute sulfuric acid, in order to remove any ether soluble, and then dried with solid caustic potash. After distilling off the ether the oily residue was dried again with caustic potash and the fractionated at reduced pressure. In this way was obtained 12 grams of perfectly pure mixed-carbonic ether; a basic smelling oil which boils at 62° at 28 mm., at 77° at 80 mm., at 138-140° at ordinary pressure; in the last case there is a very slight decomposition, which however cannot be detected by analysis. Specific gravity 0.948 at 23° (corrected).

Mixed-carbonic ether is also readily obtained on heating open-mixed-carbonic ether with alcoholic sodium ethylate; in this reaction di-mixed-carbonic ether is first formed by an absorption of alcohol (it may in fact be isolated as the chief product on allowing the solution to stand for a short time at 0°). An open-mixed with 10 grams open-mixed-carbonic ether, 5.4 grams sodium and alcohol yielded 4.6 grams sodium cyanide (theory 5.2 grams) and 7 grams mixed-carbonic ether, boiling point 138-140°. This substance is, therefore, formed according to the following interesting equation:



Mixed-carbonic ether may also be prepared in the following ways (in all I have probably manufactured about 350 grams of this ether): From chlor- or bromoacetylene by means of alcoholic sodium ethylate or dilute aqueous alcoholic sulfuric hydrate; from ethyl hypophosphite and aqueous potassium cyanide in the presence of alcohol; by decomposition of mixed (3) from potassium cyanide, sulfuric hydrate, alcohol and dilute (yield 30 grams from 50 grams potassium cyanide, best method).

At first the analysis of the substance always gave numbers which only approached the theoretical; this led to the suspicion that some impurity must be present. The substance was consequently converted in quantities of 20 grams each into chlor-mixed-carbonic ether and the product, after it had been thoroughly

several times from dilute alcohol (melting point $44-45^\circ$) reconverted into imido-carbonic ether. The substance thus recovered (30 grams) gave at first no better results on analysis, although its properties, boiling point etc. indicated a homogeneous body. Finally it was discovered that the substance during the process of combustion gives ethylene, which in part remained unburned. By conducting combustion very slowly and taking a layer of copper oxide as long as possible figures were obtained which accorded with those demanded by the theory. The analysis of all the other volatile compounds described in this paper was consequently carried out in a similar way.

0.1680 grams gave 0.3147 CO_2 and 0.1439 H_2O .

0.2211 grams " 23.8 ccm nitrogen at 20° and 754 mm pressure.

Theory for	Found
$\text{C}_5\text{H}_{11}\text{NO}_2$	
C 51.28	51.08
H 9.40	9.52
N 11.97	12.11

As was mentioned above, Sandmeyer has already obtained this substance in a slightly impure state; its constitution as imido-carbonic ether was rigidly determined by him by means of its decompositions. He dried the oil which is separated out by caustic soda with solid caustic potash, and as it does not boil without decomposition, he at once determined its nitrogen content. The oil which is precipitated by aqueous alkalis does not, however, consist of imido-carbonic ether but of a hydrate of the same (compare the behavior of di-imido-oxalic ether toward water), which contains much water. When the oil is subsequently dried with caustic potash this water separates out in considerable quantities, so that it is necessary at first to decant repeatedly and finally to allow long contact with caustic potash. The oil dried in this way gives without further treatment the correct amount of nitrogen on analysis; it also distills without decomposition. It is, therefore, probable that the oil obtained by Sandmeyer still contained small amounts of water. In other respects the statements of Sandmeyer concerning this substance were fully confirmed. The following facts in regard to its behavior must be added: It is impossible by treatment with caustic alkalis

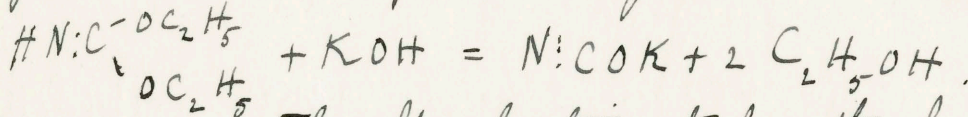
Several times from white (50 grams) preserved (50 grams) gave at first
 in better results on analysis, although its properties, boiling point etc.
 indicated a homogeneous body. Finally it was discovered that the substance
 during the process of combustion gave off a gas which in part remained unburned
 oil. By continuing combustion very slowly and taking a layer of copper oxide
 as long as possible figures were obtained which agreed with those demanded
 by the theory. The analysis of all the other white compounds described in this paper
 was consequently carried out in a similar way.

0.1680 grams gave 0.3141 CO₂ and 0.1489 H₂O.
 0.2211 grams " 0.3800 CO₂ and 0.1489 H₂O.
 0.2211 grams " 0.3800 CO₂ and 0.1489 H₂O.
 0.2211 grams " 0.3800 CO₂ and 0.1489 H₂O.

Found	Calculated for
51.08	C ₂ H ₂ O ₂
9.22	H
12.11	O

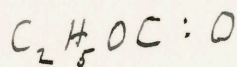
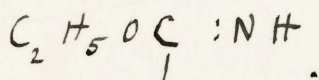
It was mentioned above, Sandmeyer has already obtained this
 substance in a slightly impure state; its constitution as mixed-carbonic
 ether was originally determined by him by means of the decomposition. He
 dried the oil which is separated out by caustic soda with solid caustic potash
 and at the same time without decomposition, he at once determined its nitrogen
 content. The oil which is precipitated by aqueous alcoholic base is, however,
 consist of mixed-carbonic ether but of a hydrate of the same (compare the sol-
 uis of bin-mixed-oxalic ether toward water), which contains much water. When
 the oil is subsequently dried with caustic potash the water separates out in con-
 siderable quantities, so that it is necessary at first to heat repeatedly and
 finally to allow long contact with caustic potash. The oil dried in this way give
 without further treatment the correct amount of nitrogen on analysis; it also yields
 without decomposition. It is, therefore, probable that the oil obtained by Sandmeyer
 still contained small amounts of water. In other respects the statements of
 Sandmeyer concerning the substance were fully confirmed. The following facts regarding
 its behavior must be added: It is insoluble in treatment with caustic alkalis

to split imido-carbonic ether into ammonia and carbonic acid. Prolonged heating on the water bath with alcoholic potash (or with alcoholic sodium ethylate) splits it into potassium cyanate and alcohol according to the equation:

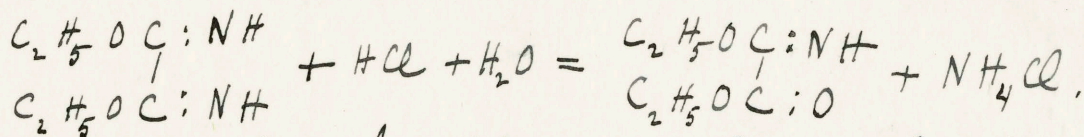


The salt separating out from the alcohol was pure cyanate, as was proved by its reactions and by its conversion into urea. 3.5 grams imido-ether, alcohol and 1.4 grams sodium boiled for several hours gave 0.5 grams sodium cyanate, which was converted into 0.2 grams urea. 2.8 grams imido-ether and alcoholic potash (3 grams KOH) heated an hour gave 0.8 grams potassium cyanate and 0.5 grams urea (melting point 132°).

Monimido-oxalic ether,

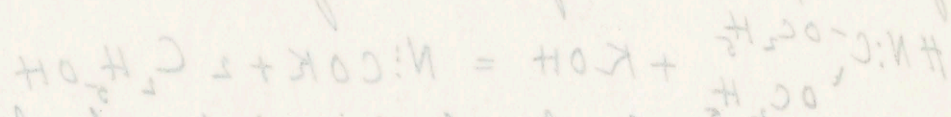


333 grams $\frac{1}{10}$ normal hydrochloric acid are added to 48 grams di-imido-oxalic ether dissolved in 240 grams of water; the acid must be added quickly and care be taken to shake continually. The resulting solution is at once perfectly neutral which shows that a complete reaction has taken place according to the equation:



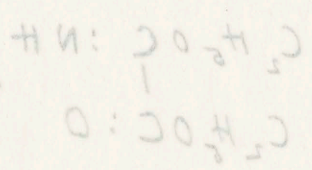
The solution is extracted four times with ether and the ether dried with calcium chloride. After removing the ether there remains an oil which boils at $69^\circ - 71^\circ$ at 18 mm pressure; it consists chiefly of monimido-oxalic ether, but contains small quantities of di-imido-oxalic ether and of oxalic ether from which it can easily be separated, since the former is much more soluble in water than the non-imido-oxalic ether, and the latter hardly at all soluble. The oil (30 cc) was treated four times with small quantities

to split - into - carbonic
larger boiling in the water bottle with alkali
effluents) split it into potassium carbonate and alcohol according to the equation

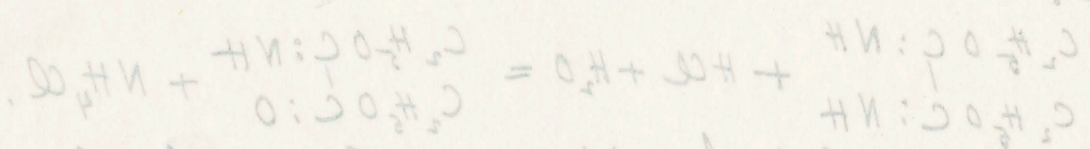


The salt separating out from the alcohol was pure carbonate, as
was proved by the reaction and by its conversion into urea. 3.2 grams
methyl-ether, alcohol and 1.4 grams sodium hydroxide for several hours gave
0.2 grams sodium carbonate, which was converted into 0.2 grams urea. 2.8 grams
methyl-ether and alcoholic potash (3 grams KOH) heated in turn gave 0.8
grams potassium carbonate and 0.5 grams urea (boiling point 132°).

Monomethyl-oxalic ether



333 grams $\frac{1}{10}$ normal hydrochloric acid are added to 48 grams
di-methyl-oxalic ether dissolved in 240 grams of water; the acid must be
added quickly and care be taken to shake constantly. The resulting solution is at once
perfectly neutral which shows that a complete reaction has taken place according to
the equation:



The solution is extracted four times with ether and the ether dried with
calcium chloride. After removing the ether there remains an oil which boils at
69-71° at 18 mm pressure; it consists chiefly of monomethyl-oxalic ether,
but contains small quantities of di-methyl-oxalic ether and of oxalic ether
from which it can easily be separated, since the former is much more
soluble in water than the di-methyl-oxalic ether, and the latter hardly
at all soluble. The oil (80 cc) was treated four times with small quantities

(25)
of water and each time filtered after thorough shaking.

There remained undissolved after washing
with 60 ccm water / 24 ccm oil I
from I " 55 ccm " 19.5 ccm oil II
" II " 14.5 ccm " 8.5 ccm oil III
" III " 60 ccm " 4.5 ccm oil IV.

In the portion which finally remained undissolved (IV) the presence of oxalic ether could be detected after drying with calcium chloride. The aqueous solution of the third fraction, 14.5 ccm, cannot on the other hand contain di-imido-oxalic ether; it was extracted four times with ether and worked up as directed above. Eight grams of a colorless, odorless oil which boiled at 73° at 18 mm pressure were obtained.

0.1807 grams gave 14.6 ccm nitrogen at 12° and 751 mm pressure.

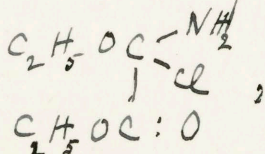
Theory for
 $C_6H_4NO_3$

Found

N 9.65

9.47

The substance cannot be kept without decomposition, but changes color turning first yellow then dark brown; at ordinary pressure it boils with considerable decomposition at 175° . It is readily soluble in water; in water at $15-20^\circ$, however, much less soluble than di-imido-oxalic ether. On cooling a concentrated aqueous solution no hydrate corresponding to the hydrate of di-imido-oxalic ether separates out; mercuric chloride, however, gives a white, insoluble precipitate. Mon-imido-oxalic ether is almost instantaneously converted into oxalic ether ^(Opt. 181°) on treatment even with very dilute hydrochloric acid. When dry hydrogen chloride is led into an absolute ethereal solution of the mon-imido ether the hydrochloric acid salt of ~~this~~ the ether,



separates in colorless needles. This same salt is also obtained from cyan-carbonic ether, $N:C-COOC_2H_5$, on passing dry hydrochloric acid over an ethereal solution (in the presence of alcohol). It is decomposed at once by water into ammonium chloride and

of water and each time the first 10 cc. of water was removed and the remaining water was added. The remaining water was removed after washing with 60 cc. water. I

from I	"	25 cc. m.	19.2 cc. m. oil. II
"	II	"	8.2 cc. m. oil. III
"	III	"	4.2 cc. m. oil. II

In the portion which finally remained undisturbed (II) the presence of oxalic ether could be detected after drying with calcium chloride. The aqueous solution of the thick fraction, 14.5 cc. m., poured on the other hand contained di-methyl-oxalic ether; it was extracted four times with ether and washed up as directed above. Eight grams of a colorless, odorless oil which boils at 78° at 18 mm. pressure was obtained.

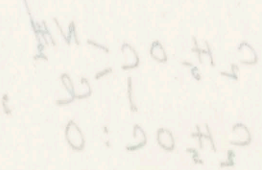
0.1807 grams gave 14.6 cc. m. nitrogen at 12° and 751 mm. pressure.

They for
 $C_4H_8O_3$
 " " 3
 N 1.62

found

9.47

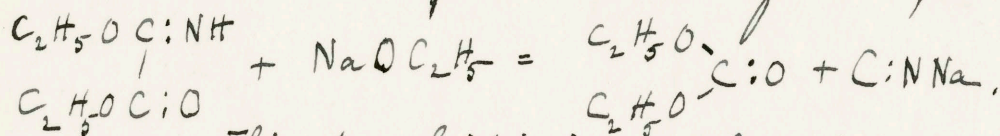
The substance cannot be left without decomposition, but changes color turning first yellow then dark brown; at ordinary pressure it boils with considerable decomposition at 175°. It is readily soluble in water; in water at 15-20° however, much less soluble than di-methyl-oxalic ether. On cooling a concentrated aqueous solution or liquid corresponding to the hydrate of di-methyl-oxalic ether separates out; numerous crystals, however, give a white, insoluble precipitate. (24.18-19) These -methyl-oxalic ether is almost instantaneously converted into oxalic ether on treatment even with very dilute hydrochloric acid. When dry hydrogen chloride is led into an absolute ethereal solution of the di-methyl ether the hydrochloric acid salt of the ether, $C_4H_8O_3 \cdot HCl$, is formed.



separated in colorless needles. The same salt is also obtained from cyan-carbonic ether $N:C-COOC_2H_5$, on passing dry hydrochloric acid over an ethereal solution (in the presence of alcohol). It is decomposed at once by water into ammonium chloride and

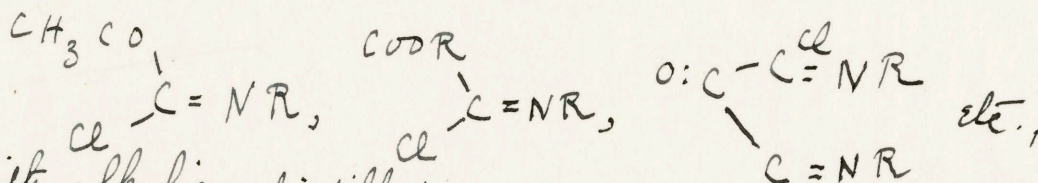
oxalic ether.

The behavior of non-imido-oxalic ether towards alcoholic sodium ethylate is especially noteworthy. It is split at once, even at -10° , into sodium cyanide and carbonic ether (bpt. 125°) according to the equation:



This decomposition is entirely analogous to that of di-imido-oxalic ether into sodium cyanide and imido-carbonic ether; it takes place, however, much more readily.

Moreover these reactions correspond perfectly to the decomposition which quite generally has been found to take place when isocyanogen addition products, such as



are treated with alkalis, distilled or even kept for a time ³⁶⁾.

These reactions, together with the observation that the cyanogen group adds alcohol in the presence of an alkali, are of fundamental importance in the Chemistry of cyanogen and of isocyanogen derivatives; they serve to explain all reactions which take place in the conversion of compounds containing cyanogen into those containing isocyanogen and vice versa.

Experiments with benzoyl cyanide and with cyan-carbonic ether.

If benzoyl cyanide (bpt. 208°) or cyan-carbonic ether is treated with one molecule of sodium ethylate or with aqueous-alcoholic potassium cyanide decomposition at once takes place, even at -10° , into sodium cyanide (or prussic acid) and benzoic or carbonic ether.

In these cases the products first formed by the addition of alcohol to the cyanogen group, $\text{C}_6\text{H}_5\text{CO} \text{C} \text{ : NH}$ and $\text{COOR} \text{C} \text{ : NH}$, are split at once, like many

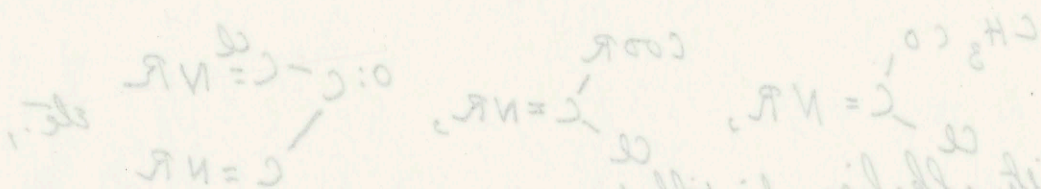
36) Liebig's Annalen 270, 297, 322; 280, 299.

over the ether. The behavior of the various ethers is rather peculiar. It is especially noteworthy that it is split at once, even at -10; into sodium cyanide and carbonic ether (H₂C=O) according to the equation:



The decomposition is entirely analogous to that of the mixed ethers with sodium cyanide and mixed carbonic ether; it takes place, however, much more readily.

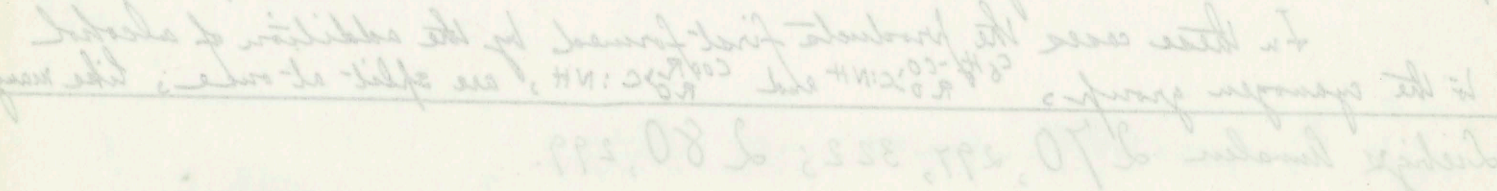
However these reactions correspond perfectly to the decomposition which quite generally has been found to take place when isocyanogen addition products, such as



are treated with alkalis, distilled or even left for a time (36). These reactions, together with the formation of the isocyanogen group, are of fundamental importance in the chemistry of isocyanogen and of isocyanogen derivatives; they serve to explain all reactions which take place in the conversion of compounds containing isocyanogen into those containing isocyanogen and vice versa.

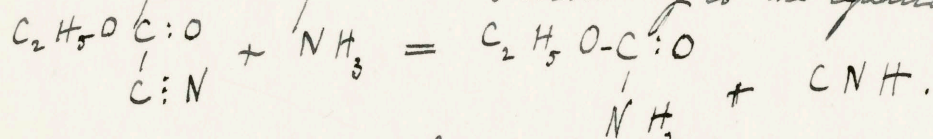
Experiments with isocyanogen cyanide and with cyan-carbonic ether. If isocyanogen cyanide (H₂C=O) or cyan-carbonic ether is treated with an excess of sodium cyanide or with cyanogen chloride potassium cyanide decomposes at once into place, even at -10; into sodium cyanide (or potassium acid) and isocyanogen or carbonic ether.

In these cases the products first formed by the addition of alkali to the isocyanogen group are



other isocyanogen addition products they are not capable of existence in the presence of an alkali. Monimido-oxalic ether, which, as was shown above, has been isolated by another method, does actually break down in this way, even at -10° , when treated with alcoholic sodium ethylate. If, however, an addition of alcohol to cyan-carbonic ether is brought about in acid solution, using the method of Pinner for the formation of hydrochloric acid salts of the imido esters, there is formed, as was described above, the hydrochloride of monimido-oxalic ether. In a similar way, as Claissen has shown ³⁷⁾, benzoyl-formic ether is formed from benzoyl cyanide and alcoholic hydrochloric acid; a reaction which is to be explained on the basis of an intermediate formation of benzoyl-imido-formic ether.

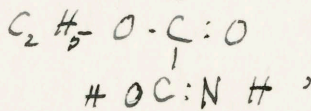
The observations just described enable us to interpret the processes which take place when ammonia and its substitution products, the primary amines, hydroxylamine and phenylhydrazine, act on cyan-carbonic ether (or on benzoyl cyanide) ³⁸⁾. There are formed in these reactions, as Weddige ³⁹⁾ has shown, prussic acid and urethane, or a substitution product of urethane, according to the equation:



It is evident that at first the cyanogen group absorbs the reagent forming the addition product $\begin{array}{c} \text{C}_2\text{H}_5\text{O}-\text{C}:\text{O} \\ | \\ \text{H}_2\text{N}-\text{C}=\text{NH} \end{array}$; this, however, like other isocyanogen addition products breaks down spontaneously.

As shown above such an intermediate product, cyan-aniline, has actually been isolated by the action of aniline on cyan-imido-carbonic ether.

The decomposition of cyan-carbonic ether by water or alkalis ⁴⁰⁾ is to be explained in an analogous manner: there is formed, through an absorption of water by the cyanogen group, the acid imide



which ^{breaks down} spontaneously into prussic acid, $\text{C}:\text{NH}$, and primary carbonic ether, $\begin{array}{c} \text{C}_2\text{H}_5\text{O} \\ | \\ \text{H O}-\text{C}:\text{O} \end{array}$.

37) Ber. der Chem. Ges. 12, 629.

38) E. Frankland and Lewis. Journ. chem. Soc. 37, 242.

39) Journ. f. pract. Chem. [2] 10, 204-208.

40) Weddige, Journ. f. pract. Chem. [2] 10, 197.

the presence of an alkali. The reaction is very slow, and has been isolated by another method, the actual mechanism in the way, even at -10°, when treated with alkali sodium hydroxide. If, however, an addition of alcohol to open-carbonic ether is brought about in acid solution, raising the yield of Turner for the formation of hydrochloric acid salt of the acid ester, there is formed, as was described above, the hydrochloride of mannitol-ester. In a similar way, as observed for 37) benzyl-formic ester is formed from benzyl cyanide and alkali hydrochloric acid; a reaction which is to be explained on the basis of an intermediate formation of benzyl-amine which is to be The observation just described enables us to interpret the process which takes place when mannitol and its substitution products, the primary amine, hydroxylamine and phenylhydrazine, act on open-carbonic ether (or on benzyl cyanide) (38). There are formed in these reactions, as Weidig (39) has shown, formic acid and water, as a substitution product of water, according to the equation:

$$\begin{array}{c} \text{C}_2\text{H}_5\text{O}-\text{C}-\text{O} \\ | \\ \text{O} \end{array} + \text{NH}_3 = \begin{array}{c} \text{C}_2\text{H}_5\text{O}-\text{C}-\text{O} \\ | \\ \text{O} \end{array} + \text{NH}_4^+ + \text{CNH}_2$$

It is evident that at first the oxygen group attacks the reagent forming the addition product $\begin{array}{c} \text{C}_2\text{H}_5\text{O}-\text{C}-\text{O} \\ | \\ \text{O} \end{array}$; this, however, like other oxygenous addition products breaks down spontaneously. As shown above such an intermediate product, open-amine, has actually been isolated by the action of amine on open-carbonic ether. The decomposition of open-carbonic ether by water or alcohol is to be explained in an analogous manner: there is formed, through an absorption of water by the oxygen group, the acid amide

$$\begin{array}{c} \text{C}_2\text{H}_5\text{O}-\text{C}-\text{O} \\ | \\ \text{O} \end{array} + \text{H}_2\text{O} = \begin{array}{c} \text{C}_2\text{H}_5\text{O}-\text{C}-\text{O} \\ | \\ \text{O} \end{array} + \text{H}_2\text{O}$$

which spontaneously splits into formic acid, $\text{C}_2\text{H}_5\text{O}-\text{C}-\text{O}-\text{H}$, and formyl carbonic ether, $\begin{array}{c} \text{C}_2\text{H}_5\text{O}-\text{C}-\text{O} \\ | \\ \text{O} \end{array}$.

37) Ber. der Chem. Ges. 12, 629.
 38) E. Frankland and Lewis, Journ. Chem. Soc. 3, 242.
 39) Journ. f. prakt. Chem., [2] 10, 204-208.
 40) Weidig, Journ. f. prakt. Chem., [2] 10, 197.

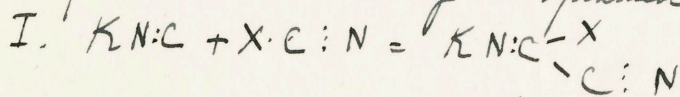
— a decomposition which corresponds exactly to that of monimido-oxalic ether 41). Since oxamethane, $C_2H_2O-C\equiv O$, is a very stable body, it is evident that the acid amides in a free $H_2N-C\equiv O$ state have really the constitution indicated by their name. Many other observations testify to this as will be shown below.

The action of chlor-cyanogen or of brom-cyanogen on potassium cyanide in aqueous-alcoholic solution.

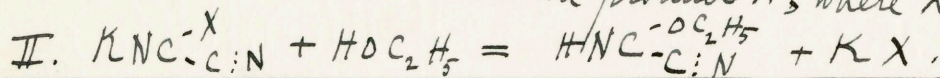
To a solution of 20 grams brom-cyanogen 42) in 30 grams alcohol and 30 grams water is added a solution of 13 grams potassium cyanide in 35 grams water. Reaction sets in at once accompanied by a brown coloration and a rise in temperature from 15° to 30° . After standing for an hour the odor of brom-cyanogen has disappeared and the solution gives a neutral reaction. Much water is then added and the solution extracted five times with ether; the ethereal solution is washed with water and dried with calcium chloride. 12 grams of an oil boiling at $35-40^\circ$ at 16 mm pressure are obtained (theory 18 grams); this oil consists chiefly of cyan-imido-carbonic ether, with which is mixed a small quantity of di-imido-oxalic ether. On fractionating once more at reduced pressure 8 grams of perfectly pure cyan-imido-carbonic ether were obtained; this was converted quantitatively into di-imido-oxalic ether according to the method given above.

A corresponding experiment with chlor-cyanogen carried out in an analogous manner, with the exception that the temperature was kept at 0° gave the following result. 10 grams chlor-cyanogen 43), 10.5 grams potassium cyanide, 28 grams alcohol and 50 grams water gave 10 grams perfectly pure cyan-imido-carbonic ether (theory 15.9 grams) besides a small amount of di-imido-oxalic ether.

The formation of cyan-imido-carbonic ether in these two cases can, after careful consideration only be explained on the basis of the following equations:



addition product-A, where $X = Cl$ or Br .



41) The formation of the salts of fulminic acid from alcohol, nitric acid and silver or mercury depends most probably upon the intermediate formation of mon-oximido-oxalic acid, $HO-C \begin{smallmatrix} \vdots \\ \vdots \\ \vdots \end{smallmatrix} NOH$, which breaks down in a perfectly analogous manner into fulminic acid, $C \equiv NOH$, and carbonic acid, $HO-C \begin{smallmatrix} \vdots \\ \vdots \\ \vdots \end{smallmatrix} O$.

42) Scholl, Beilstein, Handbuch, 3, 1st edition. 1434.

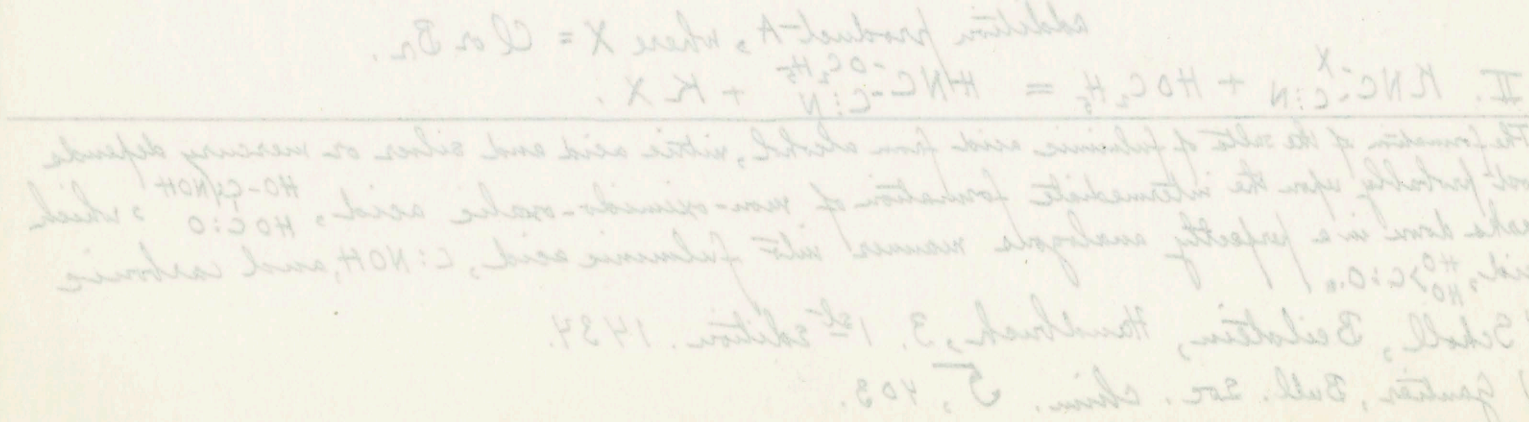
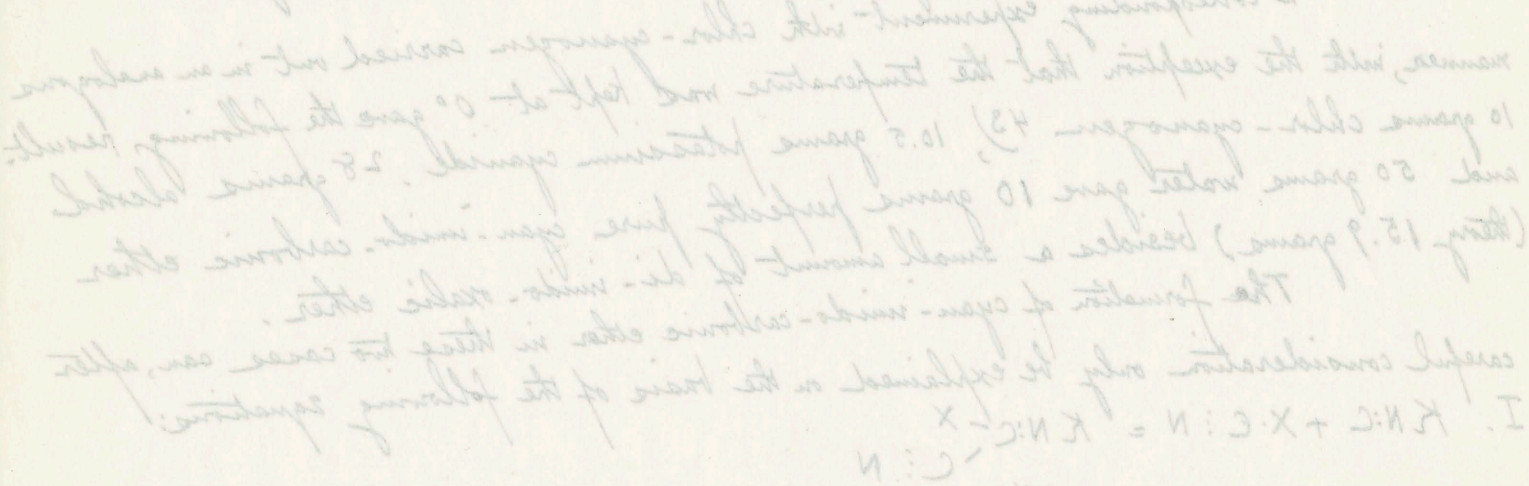
43) Gantier, Bull. Soc. chim. 5, 403.

...a description which...
 other 1) 2.5 g. substance...
 that the acid number is a few...
 by this name. Many other...
 The action of chloroform...
 in aqueous solution.

To a solution of 20 grams...
 20 grams water is added...
 water. Reaction sets in...
 in temperature from 15° to 30°. After standing...
 has disappeared and the solution...
 and the solution extracted five times...
 water and dried with calcium chloride. 12 grams...
 at 16 mm pressure are obtained (yield 18 grams); the oil consists chiefly of...
 organo-mineral-carbonic ether, with which is mixed a small quantity of di-mineral-carbonic...
 ether. In fractionating one more at reduced pressure 8 grams of perfectly pure...
 organo-mineral-carbonic ether were obtained; the two converted quantitatively into di-mineral-carbonic...
 ether according to the method given above.

A corresponding experiment with chloroform...
 manner, with the exception that the temperature was kept at 0° and the following results:
 10 grams chloroform, 10.5 grams potassium cyanide, 20 grams alcohol...
 and 20 grams water gave 10 grams perfectly pure organo-mineral-carbonic ether...
 (yield 12.9 grams) besides a small amount of di-mineral-carbonic ether.

The formation of organo-mineral-carbonic ether in these two cases can, after...
 careful consideration only be explained on the basis of the following equations:



An addition of alcohol to chlor-cyanogen with formation of the intermediate product $\text{Cl}-\overset{\text{C}_2\text{H}_5\text{O}}{\underset{|}{\text{C}}}\text{:N H}$, might be considered possible by reason of facts mentioned above; it cannot, however, have taken place in this case, since this intermediate product, as will be shown below, is converted by alcohol, even in the presence of much potassium cyanide, into imido-carbonic ether.

Furthermore the primary formation of cyanogen in this reaction is excluded on the following grounds: chlor- as well as brom-cyanogen acts, even at 0° , very energetically on a concentrated aqueous solution of potassium cyanide. One obtains, in whatever way the experiment is carried out — slow addition of potassium cyanide to finely powdered brom-cyanogen under water at 40° or addition of solid brom-cyanogen to potassium cyanide solution at a higher or lower temperature — not a trace of cyanogen gas. A strong brown coloration always appears at once and azulmic acid separates out in great quantity as a viscous, almost-black resin (44). Since much cyanogen is formed when copper sulphate is added to a concentrated potassium cyanide solution, it follows with absolute certainty that when brom-cyanogen acts on potassium cyanide cyanogen is not at first formed and afterward decomposed by the water or potassium cyanide present. Here, rather, is formed first the addition product $\text{K N}:\overset{\text{Br}}{\underset{|}{\text{C}}}-\overset{\text{C}}{\text{N}}$, which, like many other isocyanogen absorption products, breaks down with formation of resin, into its components. If, however, alcohol is present the addition product reacts as an acid bromide with formation of cyan-imido-carbonic ether.

The experiments just described furnish, therefore, a ^{second} very exact proof that potassium cyanide is identical with potassium isocyanide.

The Action of Chlorine on Potassium Cyanide in the Presence of Water and Alcohol.

Experiments in this direction were at first undertaken in the hope that it would

44) Langlois, Ann. de Chim. et de Phys., [3] 61, 481, states that much chlor- or brom-cyanogen is formed when chlorine or bromine is led into a concentrated solution of potassium cyanide. This statement does not accord with the facts given above; on repeating his experiments I obtained no appreciable quantities of chlor- or brom-cyanogen, but only much resin.

in addition of which with formation of the intermediate product $Cl-C:NH$, which is considered possible by reason of facts mentioned above; it cannot, however, have taken place in the case since the intermediate product, as will be shown below, is converted by itself, even in the presence of much potassium cyanide, into nitrile-carbonic ester.

Furthermore the primary formation of cyanogen in the reaction is excluded on the following grounds: 1st. as well as born-cyanogen acid, even at 0° very energetically on a concentrated aqueous solution of potassium cyanide. 2nd. whatever way the experiment is carried out - the addition of potassium cyanide to finely powdered born-cyanogen under water at 40° or addition of solid born-cyanogen to potassium cyanide solution at a higher or lower temperature - at a trace of cyanogen gas. A strong brown coloration always appears at once and cyanide acid separates out in great quantity as a viscous, almost black resin (44). Since much cyanogen is formed when cyan sulphate is added to a concentrated potassium cyanide solution, it follows with absolute certainty that when born-cyanogen acts on potassium cyanide cyanogen is not at first formed and afterwards decomposed by the water or potassium cyanide present. Now, further, is furnished the addition product $KN:C-NH$, which, like many other isocyanogen absorption products, breaks down with formation of nitrile into the components. If, however, nitrile is present the addition product breaks down as an acid bromide with formation of cyan-nitrile-carbonic ester. The experiment just described furnished, therefore, a very exact proof that potassium cyanide is identical with potassium isocyanide. The best of chlorine or Potassium cyanide in the presence of water and alcohol.

Experiments in this direction were at first undertaken in the hope that it would be found, as the Chinese chemist, [3] 61, 481, states that much born-cyanogen is formed when chlorine or bromine is led into a concentrated solution of potassium cyanide. This statement does not accord with the facts given above; on repeating his experiments I obtained in appreciable quantities of brown born-cyanogen, but only much resin.

be possible, at a very low temperature, to prove experimentally the original formation of imido-phosgene, $\text{HN}:\text{C} \begin{smallmatrix} \text{Cl} \\ \text{Cl} \end{smallmatrix}$. That substance might as an acid chloride be converted in the presence of alcohol into imido-ethyl carbonate, since Sandmeyer showed that on leading chlorine into an aqueous solution of potassium cyanide, sodic hydrate and alcohol chlor-imido-carbonic ether is formed ⁴⁵. Sandmeyer explains this reaction in the following way: There is formed at first ethyl hypochlorite, which in a nascent condition acts upon potassium cyanide with formation of cyan-etholin. The cyan-etholin is then by the absorption of alcohol converted into imido-carbonic ether. This explanation of the process is incorrect, as will be shown below.

A stream of chlorine is led into a solution (cooled to 5°) of 40 grams potassium cyanide in 300 grams water and 50 grams alcohol, until the solution gives a faintly alkaline or a neutral reaction; thereupon are added directly 150 c.c.m. of a concentrated solution of caustic potash (1:2), cooling carefully. One obtains, after extracting three times with ether, drying the ethereal solution with solid caustic potash and distilling off the ether, an oily mixture, which at ordinary pressure boils between $135-180^\circ$ (25-30 grams). By means of fractional distillation it is easy to isolate 6-7 grams of imido-carbonic ether (bpt. 130° to 140°). In the higher boiling part the presence of a little wrethane (bpt. 182° , mpt. 54°) could be detected. The largest fraction, which boiled between 160° and 170° , was at first erroneously regarded as a mixture of imido-ethyl carbonate and wrethane; it was afterwards shown to consist of di-imido-oxalic ether.

The formation of imido-carbonic ether in the above reaction was for some time believed to be due to the action of alcohol upon the imido-phosgene first formed. But after it was found that chlor-cyanogen is converted into imido-carbonic ether and wrethane by means of dilute aqueous caustic alkalis in the presence of alcohol the reaction in question could be explained in another way.

Finally the observation was made that on leading chlorine into a solution of potassium cyanide in water and alcohol ~~not a trace of imido-carbonic ether is formed.~~

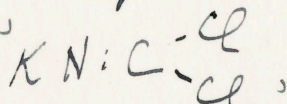
is possible, at a very low temperature, to convert the original form of the substance into a more stable form. The substance is a white solid, which is soluble in water and alcohol. It is a very stable compound, and its decomposition is very slow. The substance is a white solid, which is soluble in water and alcohol. It is a very stable compound, and its decomposition is very slow. The substance is a white solid, which is soluble in water and alcohol. It is a very stable compound, and its decomposition is very slow.

A stream of chlorine is led into a solution (containing 5%) of 440 grams potassium cyanide in 200 grams water and 50 grams alcohol, until the solution gives a faintly alkaline or a neutral reaction; therefore one added about 150 c.c. of a concentrated solution of caustic potash. B: 2) cooling carefully. One obtains, after extracting three times with ether, drying the ethereal solution with solid caustic potash and distilling off the ether, an oily mixture, which at ordinary pressure boils between 135-180° (1.2-20 grams). By means of fractional distillation it is easy to isolate 6-7 grams of imide-carbonic ether (b.p. 130°-140°). In the higher boiling part the presence of a little water (b.p. 182°; w.t. 24%) could be detected. The largest fraction, which boiled between 160° and 170°, was at first removed, regarded as a mixture of imide-ethyl carbonate and water; it was afterwards shown to consist of di-imide-ethyl ether. The formation of imide-carbonic ether in the above reaction was for some time believed to be due to the action of alcohol upon the imide-phosphoric acid formed. But after it was found that ether-cyanogen is converted into imide-carbonic ether and water by means of dilute aqueous caustic alkalis in the presence of alcohol the reaction in question could be explained in another way. Finally the decomposition was made that of heating ethanol into a solution of potassium cyanide in water and alcohol and a trace of imide-carbonic ether is formed. 45) Ber. d. Chem. Ges. 19, 222.

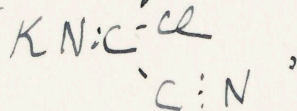
Three products result: chlor-cyanogen, cyan-imido-carbonic ether and di-imido-oxalic ether. The formation of imido-ethyl carbonate mentioned above takes place secondarily when the solution is treated with caustic alkali.

On passing a pretty rapid stream of chlorine into a solution of 50 grams potassium cyanide in 300 grams water and 100 grams alcohol, cooled to -5° or -10° , absorption occurs without a noticeable evolution of heat. The solution becomes yellow and toward the end turbid and brown. As soon as the solution, which smells strongly of chlor-cyanogen, gives only a faintly alkaline or a neutral reaction, — this is usually the case in 40–60 minutes — it is extracted five times with ether; the ethereal solution is washed three times with water in order to remove the alcohol and then dried with calcium chloride. After distilling off the chlor-cyanogen and ether there is obtained 30–35 grams of a brown oil. This oil consists of a mixture of about six parts cyan-imido-carbonic ether and one part di-imido-oxalic ether; since there is a difference of 30° in their boiling points these substances may be easily separated by fractional distillation under reduced pressure. By this method cyan-imido-carbonic ether was prepared in large quantities (300 grams). It is entirely free from imido-carbonic ether.

The following chemical changes must take place in the reaction just-described: The product first resulting from the action of chlorine on cyanide of potassium,



is not capable of existence, even at -10° , and splits at once into chlor-cyanogen, $Cl : C : N$ and potassium chloride. The chlor-cyanogen formed then acts at once, as has already been established, upon the potassium cyanide present forming



which is then converted by the alcohol into cyan-imido-carbonic ether.

The formation of di-imido-oxalic ether in this reaction is easily understood, since it has been shown above that it arises from cyan-imido-carbonic ether in

The University of Chicago

These products result: The formation of di- α -methyl carbonic ester and di- α -methyl ether. The formation of di- α -methyl carbonic ester and di- α -methyl ether is observed when the solution is treated with caustic alkali.

A passing a fairly rapid stream of chlorine into a solution of 50 grams of potassium cyanide in 200 grams water and 100 grams alcohol, cooled to -20°C . - 10°C ; absorption occurs without a noticeable evolution of heat. The solution becomes yellow and toward the end turbid and brown. As soon as the solution, which smells strongly of chloro-cyanogen, gives only a faintly alkaline or neutral reaction, this is usually the case in 40-50 minutes - it is extracted five times with ether; the ethereal solution is washed three times with water in order to remove the alcohol and the dried with calcium chloride.

After distilling off the chloro-cyanogen and ether there is obtained 30-35 grams of a brown oil. The oil consists of a mixture of about six parts cyan-methyl carbonic ester and one part di- α -methyl-oxalic ester; since there is a difference of 30° in their boiling points these substances may be easily separated by fractional distillation under reduced pressure. Of the methyl cyan-methyl carbonic ester was prepared in large quantities (300 grams). It is entirely free from methyl carbonic ester.

The following chemical changes must take place in the reaction just described: The product first resulting from the action of chlorine on cyanide of potassium.

KHCN
 $\text{KHCN} \cdot \text{CN}$
 $\text{KHCN} \cdot \text{CN} \cdot \text{CN}$

is not capable of existence, even at -10° and splits at once into chloro-cyanogen, CCl_2N and potassium chloride. The chloro-cyanogen forms then sets at once, as has already been established, upon the potassium cyanide present forming

$\text{KHCN} \cdot \text{CN}$
 C_2N_2

which is then converted by the alcohol into cyan-methyl carbonic ester.

The formation of di- α -methyl-oxalic ester in this reaction is easily understood, since it has been shown above that it arises from cyan-methyl carbonic ester in

the presence of potassium cyanide, water and alcohol.

The formation of imido-carbonic ether and of urethane when the reaction-product is subsequently treated with caustic alkali depends, as is now evident upon the fact that chlor-cyanogen under the existing conditions is converted into these two bodies (see below). The treatment with caustic alkali must, however, also convert all cyan-imido-carbonic ether into di-imido-oxalic ether. It is, therefore, to be expected that when chlorine is led into a solution of cyanide of potassium in water and alcohol and the reaction-product subsequently treated with caustic alkali imido-carbonic ether and di-imido-oxalic ether will be formed as chief products and urethane as a by-product; and this was verified by direct experiment. The separation of the two chief products is easily accomplished by fractional distillation under reduced pressure, there being a difference of 22° in the boiling points ⁴⁶⁾.

After all this it becomes evident that in Sandmeyer's experiments, when chlorine is led into a solution of potassium cyanide and sodic hydrate in alcohol and water, the following chemical changes take place. There is first formed from the potassium cyanide chlor-cyanogen; this in part then reacts with potassium cyanide and alcohol to form cyan-imido-carbonic ether, as well as in part with the alcohol and caustic soda to form imido-carbonic ether. The resulting cyan-imido-carbonic ether must, however, immediately be converted, because of the alkali and alcohol present, into di-imido-oxalic ether. Sandmeyer obtained in this reaction from 40 grams potassium cyanide 50 grams of chlor-imido-carbonic ether (in one experiment I obtained 55 grams); the simultaneous formation of di-imido-oxalic ester in the reaction was not observed by Sandmeyer. Its presence may easily be established by extracting the solution with ether; this, however, must be done before the solution has become neutral, since the di-imido body is ultimately decomposed by chlorine in the presence of an alkali.

⁴⁶⁾ If in the above reactions chlorine is replaced by bromine entirely analogous results are obtained; the reactions, however, take place more slowly and at a somewhat higher temperature.

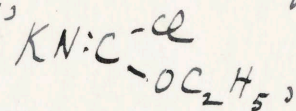
the presence of potassium cyanide, water and alcohol. The formation of a white precipitate was observed when the reaction product is subsequently treated with caustic alkali. It is, therefore, to be expected that when chlorine is fed into a solution of potassium cyanide in water and alcohol and the reaction product subsequently treated with caustic alkali, methyl-carbonic ether and di-methyl-ether will be formed as chief products and methane as a by-product; and this was verified by direct experiment. The separation of the two chief products is easily accomplished by fractional distillation under reduced pressure. After all this it became evident that in subsequent experiments when chlorine is fed into a solution of potassium cyanide and alcohol, the product in alcohol and water, the following chemical changes take place. The first formed from the potassium cyanide chloro-cyanogen; this in part then reacts with potassium cyanide and alcohol to form cyan-carbonic ether, as well as in part with the alcohol and caustic soda to form methyl-carbonic ether. The resulting cyan-carbonic ether must, however, immediately be converted, because of the alkali and alcohol present, into di-methyl-ether. Cyanogen obtained in the reaction from 40 grams potassium cyanide 50 grams of chloro-methyl-carbonic ether (in one experiment - I obtained 25 grams) the simultaneous formation of di-methyl-ether in the reaction was not observed by Sandmeyer. The presence may easily be established by extracting the solution with ether; this, however, must be done before the solution has become neutral, since the di-methyl-ether is ultimately decomposed by chlorine in the presence of alkali.

16) If in the above reaction chlorine is replaced by bromine entirely and - some results are obtained; the reaction, however, takes place more slowly and at a somewhat higher temperature.

The Action of Ethyl Hypochlorite on Potassium Cyanide in the Presence of Water and Alcohol.

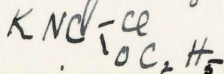
36 grams of ethyl hypochlorite are brought into a solution of 60 grams potassium cyanide in 300 grams water and 60 grams alcohol, cooled to -7° ; the temperature must never be allowed to rise above 0° . The solution remains perfectly clear and only towards the end of the reaction is there a separation of the hydrate of di-imido-oxalic ester. After extracting with ether (five times), drying with calcium chloride etc, 45 grams of an oil which boils between $60-90^{\circ}$ at 36 mm pressure are obtained; this oil is readily soluble in cold water and calc, therefore, contain only traces of cyan-imido-carbonic ester. It consists of about one part di-imido-ethyl oxalate and two parts imido-carbonic ether. By means of fractional distillation 15 grams of imido-carbonic ether boiling at $52-54^{\circ}$ at 18 mm pressure were obtained; the substance is, however, not yet pure enough for analysis, since it contains traces of cyan-imido-carbonic ether which can however be removed by gentle warming with alcoholic sodium ethylate. 8 grams of perfectly pure di-imido-oxalic ester were obtained.

These experiments show that the intermediate product arising first from the action of ethyl hypochlorite on potassium cyanide,



reacts in part and by preference with the alcohol present to form imido-carbonic ether as well as in part with a second molecule of potassium cyanide to form cyan-imido-carbonic ether. The cyan-imido-carbonic ether is then, because of the presence of alcohol and potassium cyanide converted for the most part into di-imido-oxalic ether.

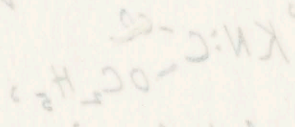
The results obtained prove decisively that when chlor-cyanogen acts upon a solution of potassium cyanide in alcohol and water, or when chlorine is led into a similar mixture of potassium cyanide, water and alcohol the intermediate product have cannot possibly be formed, since in both these reactions not a trace of imido-ethyl carbonate



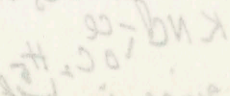
The Reaction of Ethyl Hypochlorite on Potassium Cyanide in the Presence of Water and Alcohol

30 grams of ethyl hypochlorite are brought into a solution of 60 grams potassium cyanide in 300 grams water and 60 grams alcohol cooled to -7° ; the temperature must never be allowed to rise above 0° . The solution remains perfectly clear and only towards the end of the reaction is there a separation of the hydrate of di-methyl-carbic ester. After extracting with ether (five times), shaking with calcium chloride etc, 45 grams of an oil which boils between $60-70^{\circ}$ at 30 mm pressure are obtained; this oil is readily soluble in cold water and etc, therefore, contains only traces of open-methyl-carbonic ester. It consists of about one part di-methyl-ethyl carbonate and two parts methyl-carbonic ester. By means of fractional distillation 12 grams of methyl-carbonic ester boiling at $51-54^{\circ}$ at 18 mm pressure were obtained; the substance is, however, not yet pure enough for analysis, since it contains traces of open-methyl-carbonic ester which can be removed by gentle warming with alcoholic sodium hydroxide. 8 grams of perfectly pure di-methyl-carbic ester were obtained.

These experiments show that the intermediate product arising first from the action of ethyl hypochlorite on potassium cyanide,



resides in part and by preference with the alcohol present to form methyl-carbonic ester as well as in part with a second molecule of potassium cyanide to form open-methyl-carbonic ester. The open-methyl-carbonic ester is then, because of the presence of alcohol and potassium cyanide converted for the most part into di-methyl-carbic ester. The results obtained have decisively that open ether-cyanogen acts upon a solution of potassium cyanide in alcohol and water, so when chlorine is led into a similar mixture of potassium cyanide, water and alcohol the intermediate product cannot possibly be formed, since in both these reactions not a trace of methyl-ethyl carbonate

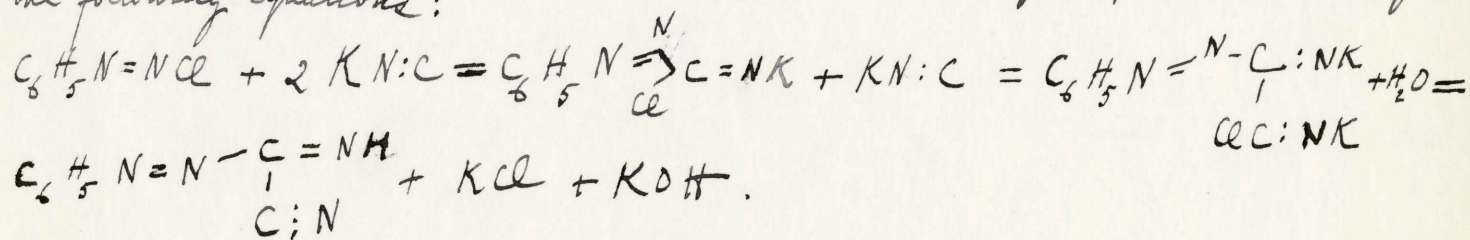


pure

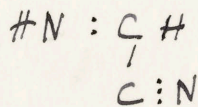
appears.

The Action of Diazo benzol Chloride on Cyanide of Potassium.

Some time ago Gabriel 47, by the addition of a diazobenzol chloride solution to an aqueous solution of potassium cyanide, obtained a solid, yellow substance, to which he gave the formula $C_6H_5N:N-C:N + HCN$, because it is easily decomposed with formation of prussic acid. From the results obtained in this paper it is clear that this body is formed according to the following equations:

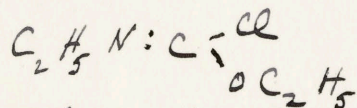


It should, therefore, be called benzol-azoinido-formyl cyanide; its formation is perfectly analogous to that of cyan-imido-carbonic ester from potassium cyanide, water and ethyl hypochlorite. A decomposition of this substance, noticed by Gabriel, into prussic acid and an oily compound, probably diazobenzol cyanide 48, $C_6H_5N=N-C:N$, is to be expected by reason of the many other analogous reactions mentioned in this paper. The constitution suggested for Gabriel's compound is also made probable when one considers the properties of the mother substance, imido-formyl cyanide,



[see below] 49).

Ethyl-imido-chlor-carbonic Ester,



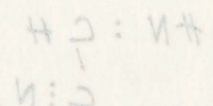
In order to establish that ethyl hypochlorite and chlor-cyanogen are also absorbed in a normal fashion by other unsaturated bodies their behavior toward ethyl isocyanide was first carefully studied

47) Ber. d. Chem. Ges. 12, 1637.

48) Hantzsch has recently obtained this substance in two modifications, Ber. d. Chem. Ges. 28, 671.

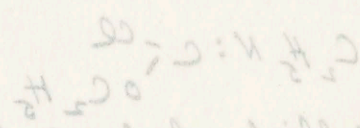
49) A further study of benzol-azoinido-formyl cyanide to confirm the standpoint reached here, (over)

has finally been rendered unnecessary as Hantzsch has since established the constitution of the compound by reduction into cyan-phenyl hydrazine, Ber. 28, 2074



(see below) 49)

ethyl-amine-ether-carbonate ester,



In order to establish that ethyl isopropylate and ethyl-amine-ether-carbonate ester are also absorbed in a normal fashion by the untreated bodies their behavior toward ethyl isopropylate was first carefully studied.

47) Ber. d. Chem. Ges. 102, 1637.
48) Hantzsch has recently obtained the substance in two modifications. Ber. d. Chem. Ges. 28, 2074.
49) A further study of methyl-amine-ether-carbonate ester to confirm the result first reached here (over)

toward ethyl isocyanide was first carefully studied ⁵⁰⁾

If to ethyl isocyanide (cooled to -10° or -15°) ^{is added slowly} one molecule of ethyl hypochlorite, ~~is added slowly~~ dried with calcium chloride and cooled to -5° ; absorption takes place instantaneously with marked heat evolution. The temperature must never rise above 0° ; and as soon as the theoretical quantity of hypochlorite has been added an excess of a few drops causes a yellow coloration and an odor of hypochlorite to appear.

The oil obtained (80-90 grams were prepared) boils perfectly constant at 63° at 88 mm pressure, 68° at 100 mm, 126° at ordinary pressure. It is colorless, has a very pungent odor (like the alkyl isocyanates) and attacks the eyes; it is slowly decomposed by moist air. Its analysis offered a good deal of difficulty, since the substance decomposes at higher temperatures giving ethyl chloride and ethyl cyanate ⁵¹⁾. This explains why analytical figures varying somewhat from those demanded by the theory were obtained.

0.1434 grams gave 15 c c m nitrogen at 18° and 749 mm pressure.
 0.1749 grams " 18 c c m " " 14° " 747 mm "
 0.2076 grams " 0.2305 silver chloride by the method of Carus (heated eight hours to 220°)

Theory for	Found
$C_5H_{10}NClO$	
C 44.28	42.85
H 7.38	7.23
N 10.33	11.90
Cl 26.20	27.47

Ethyl-imido-chlor-carbonic ether is slowly decomposed with heat evolution on treatment with dilute hydrochloric acid or water: the products formed are carbonic acid, ethyl chloride, ethyl urethane (bpt. 175° ; chief product) and diethyl urea (mpt. 108°).

⁵⁰⁾ Corresponding experiments with ethylene derivatives are also soon to be undertaken.

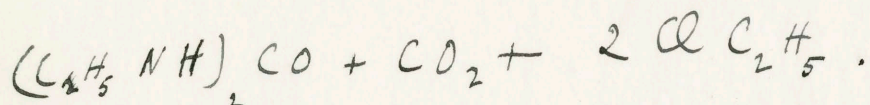
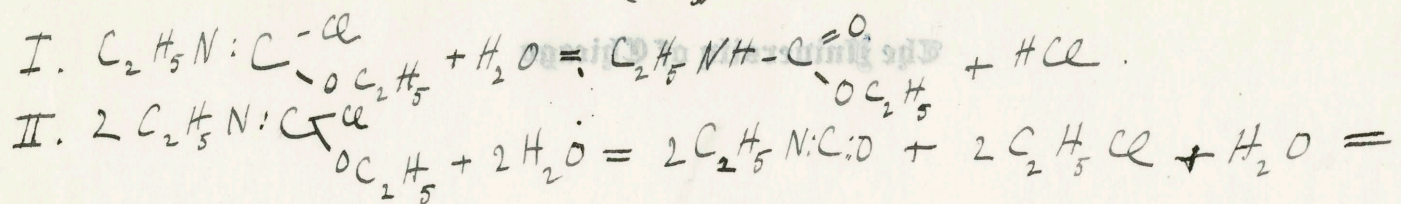
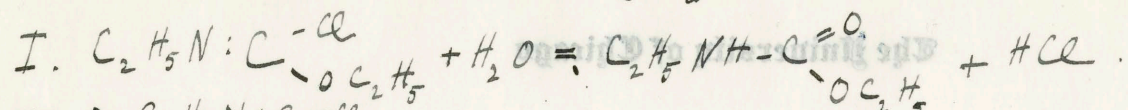
⁵¹⁾ W. R. Smith, Amer. Chem. Jour. 16, 389.

It is a very pungent odor (like the ethyl isocyanate) and attacks the eyes; it is slowly decomposed by moist air. The analysis offered a good deal of difficulty, since the substance decomposes at higher temperatures giving ethyl chloride and ethyl cyanate. This explains why analytical figures varying somewhat from the calculated by the theory were obtained.

The oil obtained (80-90 grams were prepared) has perfectly constant b.p. 68° at 15 cm pressure. It is colorless, has a very pungent odor (like the ethyl isocyanate) and attacks the eyes; it is slowly decomposed by moist air. The analysis offered a good deal of difficulty, since the substance decomposes at higher temperatures giving ethyl chloride and ethyl cyanate. This explains why analytical figures varying somewhat from the calculated by the theory were obtained.

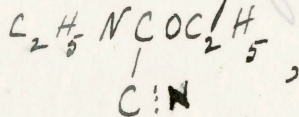
Found	Calcd for
42.8%	C ₄ H ₁₀ ClO
7.2%	H 7.88
11.9%	N 10.23
27.4%	Cl 22.20

3) Ethyl-oxal-chlor-carbonate ester is slowly decomposed with heat and on treatment with dilute hydrochloric acid in water; the products formed are carbonic acid, ethyl chloride, ethyl oxalate (b.p. 175°; chief product) and diethyl oxalate (b.p. 108°).

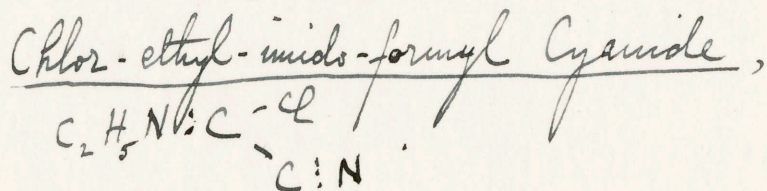


Treated with alcoholic sodium ethylate (one molecule) ethyl-imido-chlor-carbonic ether is converted into a colorless, strongly basic smelling oil having a specific gravity less than 1.00, and which is insoluble in water; it boils without decomposition at 147° . This oil is very probably ethyl-imido-carbonic ester, $\text{C}_2\text{H}_5\text{N}:\text{C}(\text{OC}_2\text{H}_5)_2$, for it is completely converted into ethyl carbonate by dilute hydrochloric acid; it was not analyzed.

On the addition of 10 grams of ethyl-imido-chlor-carbonic ether to a solution of 10 grams potassium cyanide in 35 grams water and 30 grams alcohol, cooled to -5° , an energetic reaction takes place and the temperature rises to $+10^\circ$. After standing 20 minutes water was added and the solution extracted with ether. A sweet and at the same time pungent smelling oil boiling at 78° at 82 mm pressure was obtained. This oil is probably ethyl-imido-cyan-carbonic ether,



for when treated with dilute hydrochloric acid it is completely converted into cyan-carbonic ether.



Chlor-cyanogen (10 grams) and ethyl isocyanide (one molecule) at ordinary temperatures ⁵²act upon each other only very slowly. After standing two days the mixture was heated for 15 minutes to 70° ; during which process it began to turn dark with formation of resin. Much unchanged chlor-cyanogen and isonitrile were recovered during distillation; one fraction, however (5 grams) boiled between 120° and 130° . This was shaken with 20 cc. very dilute hydrochloric acid until the odor of isocyanide disappeared; the oil, which is heavier than water, was then

$(C_4H_5NH)CO + CO_2 + 2C_2H_5$
 Treated with alcoholic sodium ethoxide (one molecule) ethyl-iodide-chlor-
 carbonic ether is converted into a viscous, strongly basic smelling oil having
 a specific gravity less than 1.0, which is insoluble in water; it has a boiling
 temperature of 147°. This oil is very probably ethyl-iodide-chlor-
 $C_4H_5NH:C(OC_2H_5)_2$, for it is completely converted into ethyl carbonate by dilute
 hydrochloric acid; it was not analyzed.
 On the addition of 10 grams of ethyl-iodide-chlor-
 solution of 10 grams potassium cyanide in 32 grams water and 80 grams alcohol,
 cooled to -5°, an energetic reaction takes place and the temperature rises
 to +15°.

52) Brom-cyanogen reacts much more easily with ethyl isocyanide; heat is
 evolved, but the mass is almost entirely converted into a viscous resin.

Chlor-ethyl-iodide-formyl cyanide
 $C_4H_5NH:C(OC_2H_5)_2$
 $C_4H_5NH:C(OC_2H_5)_2$
 Chlor-cyanogen (10 grams) and ethyl isocyanide (one molecule) at ordinary
 temperatures but from each other only very slowly. After standing for days the
 mixture was heated for 15 minutes to 70° during which process it began to
 turn black with formation of resin. Much unchanged chlor-cyanogen and isocyanide
 were recovered during distillation; one fraction, however (3 grams) boiled between
 150° and 180°. This was shaken with 20 cc. very dilute hydrochloric acid until the
 color of isocyanide disappeared; the oil, which is heavier than water, was then

separated off, washed with water, dried with calcium chloride and directly distilled. A pungent smelling, colorless oil, boiling at 126° , was obtained.

0.1354 grams gave 28.8 ccm nitrogen at -16° and 749 mm pressure.

0.2103 grams " 0.2586 grams silver chloride (method of Carius).

Theory for
 $C_6H_5N_3Cl$

N 24.03

Cl 30.47

Found

24.43

30.42

II Behavior of Acid Haloids and of Acid Anhydrides toward Some of the Salts of Prussic Acid.

Tri-molecular Benzoyl Cyanide, $[C_6H_5COCN]_3$. The ordinary, mono-molecular benzoyl cyanide is formed, as is well known, by heating dry cyanide of mercury with benzoyl chloride. This compound is also obtained when cyanide of silver is heated with benzoyl chloride; from 30 grams $AgCN$ and 31.5 grams C_6H_5COCl 23.5 grams of perfectly pure benzoyl cyanide boiling at $208-210^{\circ}$ were obtained after 20 minutes heating at 220° .

When cyanide of silver is treated with benzoyl Bromide the result is quite different: these bodies react so energetically when ^{mixed} treated that charring takes place. It was, therefore, necessary to proceed in the following way: 21 grams of benzoyl Bromide, bpt. $216-218^{\circ}$; 150 cc absolute ether and 20 grams of silver cyanide were heated for ten hours on a water bath warmed to 60° ; a condenser was used and precautions were taken to prevent the access of moist air. As the ethereal filtrate contained nothing the residue, 35.7 grams, was treated first with aqueous potassium cyanide in order to remove silver bromide, and thereupon dissolved in chloroform and the solution allowed to evaporate spontaneously. The yellowish mass remaining was twice recrystallized from hot benzene and 7 grams of pale yellowish,

Found
24.43
30.42

Thick for
 $C_4H_2N_2O_2$
N 24.02
O 30.47

II Behavior of Acid Halides and of Acid Anhydrides toward Some of the Salts of Organic Acids

Tri-molecular Benzoyl Cyanide, $[C_6H_5COCN]_3$. The compound is known as a well known, by heating dry cyanide of benzoyl with benzoyl chloride. This compound is also obtained when cyanide of silver is heated with benzoyl chloride; from 30 grams of $AgCN$ and 31.2 grams of C_6H_5COCl 2.5 grams of perfectly pure benzoyl cyanide boiling at 108-110° were obtained after 20 minutes heating at 120°.

When cyanide of silver is treated with benzoyl chloride the results are quite different: the bodies react so energetically when ^{mixed} that cleaning takes place. It was, therefore, necessary to proceed in the following way:

2.1 grams of benzoyl bromide, b.p. 116-118°/150°C absolute then and 20 grams of silver cyanide were heated for ten hours in a water bath warmed to 60°; a condenser was used and pressure was later to prevent the escape of moist air. As the ethereal filtrate contained nothing the residue, 2.7 grams, was treated first with aqueous potassium cyanide in water to remove silver bromide, and then with dilute hydrochloric acid and the solution allowed to evaporate spontaneously. The yellowish mass remaining was twice recrystallized from 100 cc benzene and 7 grams of pale yellow crystals.

needle-like crystals melting at 175° were obtained.

0.1907 grams substance, dried at 110° , gave 19.2 ccm nitrogen at 19° and 740 mm pressure.

0.1510 grams substance, dried at -110° ; gave 0.4074 CO_2 and 0.0541 H_2O .

Theory for C_8H_5NO

Found

C 73. 28

73.56

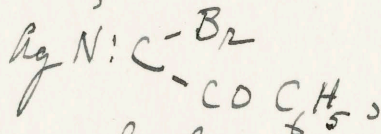
H 3.82

3.98

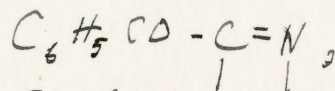
N 10.69

11. 26

The substance is insoluble in water and ether; boiling alcohol dissolves a trace, which separates out on cooling in voluminous, almost colorless needles. ~~In chloroform and hot benzene it is readily soluble~~ It is readily soluble in chloroform and hot benzene, but only moderately so in cold benzene. Heated to 300° the substance decomposes (this was carried out with 6 grams) with the formation of much benzo-nitrile. The product obtained here is probably a tri-molecular benzoyl cyanide which possesses a constitution analogous to cyanuric chloride. Its formation can be readily understood, for when silver bromide is split off from the intermediate product first formed,



the nascent benzoyl cyanide molecules,



can very easily polymerize. Furthermore it is also possible to convert ordinary benzoyl cyanide into this polymer by treating it in ethereal solution with dry hydrobromic acid. The solution becomes yellow and after a short time a white precipitate separates out, which, treated with water, leaves behind a small quantity of terbenzoyl cyanide. The chief product of the reaction is the imid bromide $C_6H_5C(O)C \equiv N^+H$, which gives with water benzoyl-formic acid amide

0.1907 grams substance, dried at 110°; gave 17.2 ccn nitrogen at 17° and 740 mm pressure.
 0.1210 grams substance, dried at 110°; gave 0.4074 CO₂ and 0.0341 H₂O.

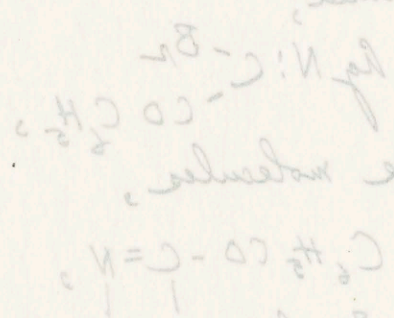
Found

73.2
 3.98
 11.26

Calcd for
 C₂H₂N₂O

C 73.28
 H 3.82
 N 10.69

The substance is water-soluble in water and ether; boiling alcohol dissolves a trace, which separates out on cooling in voluminous almost colorless needles. ~~In chloroform and hot benzene it is readily soluble. It is readily soluble in chloroform and hot benzene, but only slightly so in cold benzene.~~ Heated to 300° the substance decomposes (this was carried out with 6 grams) with the formation of much benzene-volatile. The product obtained here is probably a bit molecular weight of organic which possesses a constitutional analogue to oxymure chloride. The formation can be readily understood, for when silver bromide is split off from the intermediate product first formed.



can very easily polymerize. Furthermore it is also possible to convert ordinary benzyl cyanide into this polymer by treating it in ethereal solution with anhydrous acid. The solution turned yellow and after a short time a white precipitate separated out, which, treated with water, leaves behind a small quantity of benzyl cyanide. The chief product of the reaction is the insoluble C₂H₂CO-C=N, which gives with water benzyl-formic acid emulsion.

(soluble in water) and hydrobromic acid,

Di-molecular Benzoyl Cyanide, $(C_6H_5CO-CN)_2$. Wache⁵³⁾
 obtained bisbenzoyl cyanide by boiling an ethereal solution of benzoyl² cyanide with metallic sodium. This substance is also formed directly from aqueous cyanide of potassium on shaking with benzoyl chloride. A solution of 10 grams potassium cyanide in 30 grams water and 7.1 grams alcohol is cooled to -5° and 21.6 grams of benzoyl chloride added; a yellow coloration appears at once; the solution smells strongly of prussic acid and ethyl benzoate. After standing with occasional shaking for 40 minutes at -5° the mixture is extracted with ether. The ethereal solution, dried with calcium chloride, gives after the evaporation of the ether an oily residue, from which on adding a little alcohol and scratching with a glass rod crystals separate out (2 grams). A second experiment, in which the same quantities of acid chloride, water and potassium cyanide, but no alcohol, were used, yielded 2.3 grams of pure bisbenzoyl cyanide. The substance, recrystallized twice from alcohol, was obtained in colorless needles melting at $99-100^\circ$ (Wache states that the melting point is 95°). It was also observed that the compound boils without decomposition at 220° at 15 mm pressure.

0.1476 grams substance, burned with lead chromate, gave 0.3970 CO_2 and 0.0547 H_2O .
 0.2031 grams substance, dried over H_2SO_4 in vacuum, gave 19.4 cc nitrogen at 19° and 751 mm pressure.

Theory for
 $C_{16}H_{10}N_2O_2$

C	73.28
H	3.82
N	10.69

Found

73.35
4.12
10.85

Benzoyl Cyanide from Potassium Cyanide and Benzoin nitrile.

Kleemann⁵⁴⁾ has shown that acetic anhydride acts very energetically on solid potassium cyanide with formation of bisacetyl cyanide; — a substance which

⁵³⁾ Journ. f. israel. Chem. [2] 39, 260.

⁵⁴⁾ Ber. d. Chem. Ges. 18, 256.

Potassium benzoate (C_6H_5COOK) . (Wohl) obtained benzoic acid by boiling an ethereal solution of benzoic acid with metallic sodium. The substance is also formed directly from aqueous solutions of potassium on shaking with benzoic chloride. A solution of 10 grams potassium benzoate in 30 grams water and 7.1 grams alcohol is added to 5% and 2.6 grams of benzoic chloride added; a yellow coloration appears at once; the solution smells strongly of benzoic acid and ethyl benzoate. After standing with occasional shaking for 40 minutes at -2°, the mixture is extracted with ether. The ethereal solution, dried with calcium chloride, gives after the evaporation of the ether an oil residue, from which on adding a little alcohol and evaporating with a glass rod crystals separate out (2 grams). A second experiment, in which the same quantities of acid chloride, water and potassium benzoate, but in alcohol, were used, yielded 2.3 grams of pure benzoic acid. The substance, recrystallized twice from alcohol, was obtained in colorless needles melting at 99-100°. (Wohl states that the melting point is 95°). It was also observed that the compound boils without decomposition at 220° at 15 mm pressure.

0.1476 grams substance, burned with lead chromate, gave 0.3970 CO_2 and 0.0247 H_2O .
 0.2081 grams substance, dried over H_2SO_4 in vacuum, gave 19.4 cc in nitrogen at 19° and 751 mm pressure.

Found		Theory for	
C	H	C	H
73.82	7.12	73.82	7.12
10.78		10.69	

Benzoyl benzoate from Potassium benzoate and Benzoic anhydride.
 Klemm (24) has shown that acetic anhydride acts very energetically on acid potassium benzoate with formation of benzoyl benzoate; a substance which

24) Journ. f. prakt. Chem. [2] 39, 220.
 25) Journ. f. prakt. Chem. [2] 18, 228.

can also be obtained directly from acetyl cyanide by means of caustic potash or sodium.⁵⁵ This reaction is in all probability⁵⁶ to be explained on the basis of an addition of the acid anhydride to the bivalent-carbon atom present in cyanide of potassium. The intermediate product thus formed, $KN:C-OCOCH_3$, decomposes in great part, just as it is the case with the majority of the isocyanogen addition products, with much resin formation (azulmic acid) into its components. A small portion, however, splits into potassium acetate and acetyl cyanide, $CH_3-CO-C\equiv N$, which in the nascent state condenses to bisacetyl cyanide.

Benzoyl anhydride and potassium cyanide heated in equivalent quantities react at 190° . A yellow coloration is noticed at first and in a short time the whole mass becomes resinous and dark brown. Ether extracts from it small quantities (10%) of benzoyl cyanide. The benzoyl cyanide obtained boiled at $207-210^\circ$ and was converted into benzoyl-formic acid amide and benzoyl-formic acid. An analysis was, therefore, considered unnecessary.

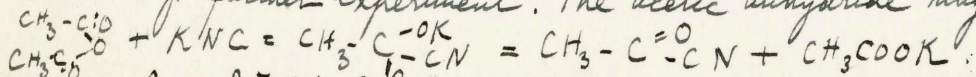
The behavior of potassium cyanide toward acid anhydrides, as well as the fact that prussic acid is converted into bis-acetyl cyanide by acetic anhydride, confirms decisively the view that acid anhydrides may be absorbed by addition to an ethylene grouping by unsaturated bodies, such as sodium-aceto-acetic ether, $CH_3-\overset{ONa}{\underset{|}{C}}=CH-COOR$, aceto-acetic ether, $CH_3-\overset{OH}{\underset{|}{C}}=CH-COOR$, etc.⁵⁷ This explains why only 10% of the normal acetate, $CH_3-\overset{OCOCH_3}{\underset{|}{C}}=CH-COOR$,

is obtained from aceto-acetic ether and acetic anhydride; the principal reaction being an absorption of the anhydride with formation of α -acetyl- β -oxycrotonic ether.⁵⁸ Such an addition by a carbonyl group takes place furthermore very generally on treatment of aldehydes with acetic anhydride.

Silver Cyanide and Chlor-carbonic Ether. On heating a mixture of 36.4 grams

⁵⁵ Hiltner, Liebig's Annalen 124, 315.

⁵⁶ There is at present (1897) another possible interpretation of this reaction which must be excluded by further experiment. The acetic anhydride may react with the $KN:C$ as follows:



⁵⁷ Liebig's Ann. 270, 333; Bernhard, Liebig's Ann. 282, 171-177. v. Peckmann, Liebig's Ann. 278, 222. (over)

can also be obtained directly from a series of consecutive products as
 sodium. The reaction is in all probability to be explained on the basis of an
 addition of the acid anhydride to the bivalent carbon atom present in the
 of potassium. The intermediate product thus formed, $KHC=OCH_3$, decomposes
 in great part, just as it is the case with the majority of the isopropyl
 addition products, with much resin formation (saponification) into the components.
 A small portion, however, splits into potassium acetate and acetyl anhydride, $C_2H_3CO-C_2H_3$,
 which in the present state contains the bivalent anhydride.
 Bivalent anhydride and potassium acetate heated in equivalent quantities
 react at 190° . A yellow substance is obtained at first and in a short time the whole
 mass becomes brown and dark brown. Other extracts from it small quantities
 (10%) of bivalent anhydride. The bivalent anhydride obtained boiled at $207.5-210^\circ$ and
 was converted into bivalent anhydride and bivalent anhydride. In
 analysis was therefore, considered unnecessary.
 The behavior of potassium acetate toward acid anhydrides, as well as
 the fact that bivalent anhydride is converted into bivalent anhydride by acetic anhydride,
 confirms decisively the view that acid anhydride may be obtained by addition to
 an ethylene grouping of unsaturated bodies, such as sodium-acetate ester.
 $CH_3-C=CH-COOR$, acetate ester, $CH_3-C=CH-COOR$, etc. This explains why
 only 10% of the normal acetate, CH_3COCH_3 ,
 $CH_3-C=CH-COOR$ is obtained from acetate ester and acetic anhydride; the principal reaction being
 an absorption of the anhydride with formation of a cyclic - β - isopropyl ester (28).
 Such an addition of a cyclic group takes place furthermore very generally in treatment
 of aldehydes with acetic anhydride.

58/Liebig's Ann. 276, 212; Berchard, Liebig's Ann. 282, 177. Compare v. Pechmann, Liebig's Ann. 278, 223;
 also 4th paper on bivalent carbon.

There is at present (1897) another possible interpretation of the reaction of the acetate ester with the KHC as follows:
 $CH_3CO-C=CH + KHC=OCH_3 \rightarrow CH_3CO-C=CH + CH_3COOK$
 28) Liebig's Ann. 278, 223; Berchard, Liebig's Ann. 282, 177-178; v. Pechmann, Liebig's Ann. 278, 223.

of silver cyanide and 28.5 grams of chlor-carbonic ether to $130-140^{\circ}$ for six hours a considerable interaction takes place. A little ethyl chloride and carbon dioxide are given off and a strong odor of isonitrile is observed on opening the sealed tube. 15 grams of a dark brown oil boiling between 90° and 120° were obtained. From this by means of fractional distillation and treatment of the high boiling fraction with dilute hydrochloric acid 3 c.c.m. of pure cyan-carbonic ester, boiling at 116° were obtained. The low boiling fractions ($93-105^{\circ}$) consist of a mixture of chlor-carbonic ester and isocyan-carbonic ether ⁵⁹ which were not separated.

The formation of two isomeric esters is the most interesting result of this experiment. To draw inferences from this fact concerning the constitution of cyanide of silver on the basis of the substitution hypothesis must lead, as has already been emphasized in the introduction, to utterly absurd conclusions: for cyanide of silver yields on the one hand with ethyl iodide exclusively ethyl isocyanide, $C_2H_5-N:C$, and on the other, with benzoyl chloride exclusively benzoyl cyanide $C_6H_5CO-C:N$. This question can only be solved by an exhaustive study of the whole subject: we must determine most carefully whether substitution or addition reactions really take place and whether singly or side by side. The isonitriles are known to react most violently by addition with halogens and acid chlorides; with alkyl iodides, on the other hand, they react at high temperatures and only with resin formation. It is consequently clear that silver cyanide as a derivative of isocyanogen, $Ag N:C$ might react with halogens and acid chlorides preferably by addition to the unsaturated carbon atom present. A molecule may be susceptible to attack at two or more points and the question in every instance is only which is preferred; in many cases, e.g. where two esters are formed from one salt the molecule must be attacked simultaneously at two points. During the last few years I have discovered countless instances of this character. When silver cyanide, $Ag N:C$, on the other hand is treated with alkyl iodides preferably a direct replacement of the metal with formation of ethyl isocyanide must take place.

Potassium Cyanide and Chlor-carbonic Ether.

50 grams of chlor-carbonic ether are added quickly to a solution of 32 grams potassium cyanide in 96 grams water and 25 grams alcohol; care must be

⁵⁹ Salomon, Journ. f. pract. Chem. [2] 9, 298.

The University of Chicago

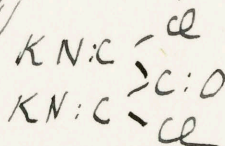
taken to shake the solution constantly, and before starting it must be cooled to -13° . The temperature of the mixture rises to -2° ; a dark red coloration and an odor of prussic acid are noticed. After 40 minutes water is added and the solution extracted with ether. After drying with calcium chloride and distilling off the ether 27 grams of oil are obtained; this oil is distilled first at reduced, then at ordinary pressure. The yield is 18 grams, boiling from $116-124^{\circ}$ (the greater part at $116-118^{\circ}$). The oil consists chiefly of cyan-carbonic ether; it contains, however, small quantities of ethyl carbonate.

If this experiment is carried out at the room temperature much less cyan-carbonic ether is formed; the intermediate product first arising

$$\text{KN}:\text{C} \begin{array}{l} \diagup \text{Cl} \\ \diagdown \text{COOC}_2\text{H}_5 \end{array}$$

breaks down for the most part ⁶⁰⁾ into prussic acid (or azulmic acid), potassium chloride, carbon dioxide and alcohol. This, as has already been repeatedly emphasized, is a favorite mode of decomposition for all isocyanogen addition products in the presence of water or alkalis.

Potassium Cyanide and Phosgene. When phosgene is added slowly to a solution of potassium cyanide (three molecules) in six parts of water, care being taken to cool to $-10^{\circ}-15^{\circ}$ and to shake constantly, interaction begins at once with considerable evolution of heat; a very strong odor of prussic acid is noticed; the solution turns yellow, red, dark brown and much azulmic acid separates out as dark resin. On adding acetic acid a violent evolution of carbon dioxide occurs and phenyl-hydrozene then gives no precipitate. This shows clearly that the addition product first formed ⁶¹⁾

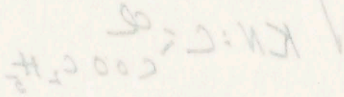


breaks down spontaneously into prussic acid (or azulmic acid), potassium chloride and potassium carbonate. To isolate carbonyl cyanide, ⁶²⁾

⁶⁰⁾ This explains the earlier results of Wilm and Wischin, Liebig's Ann. 147, 153; compare also Weddige, Journ. f. pract. Chemie [2] 10, 197.
⁶¹⁾ Compare Liebig's Ann. 270, 286, 298.

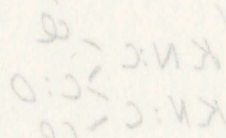
When to shake the solution for starting it must be cooled to -15° . The temperature of the mixture rises to -2° , a dark red coloration and an odor of fusaric acid are noticed. After 40 minutes water is added and the solution extracted with ether. After drying with calcium chloride and distilling off the ether 27 grams of oil are obtained; the oil is distilled first at reduced, then at ordinary pressure. The yield is 18 grams, boiling from $115-124^{\circ}$ (the greater part at $115-118^{\circ}$). The oil consists chiefly of α -pinene-carbonic ether; it contains, however, small quantities of other carbonates.

If the experiment is carried out at the room temperature much α -pinene-carbonic ether is formed; the intermediate product first arising



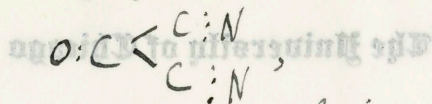
breaks down for the most part into fusaric acid (or α -pinene acid), potassium chloride, carbon dioxide and alcohol. This is the already repeatedly emphasized is a favorite mode of decomposition for all isopropylidene derivatives in the presence of water or alcohol.

Potassium cyanide and Propene. When propene is added slowly to a solution of potassium cyanide (three molecules) in six parts of water, care being taken to cool to -10° and to shake constantly, interaction begins at once with evolution of heat; a very strong odor of fusaric acid is noticed; the solution turns yellow, red, dark brown and much α -pinene acid separates out as dark resin. On adding acetic acid a violent evolution of carbon dioxide occurs and phenyl-hydroperoxide then gives its precipitate. The above clearly that the intermediate product first formed is



breaks down spontaneously into fusaric acid (or α -pinene acid), potassium chloride and potassium carbonate. To isolate carbonic cyanide

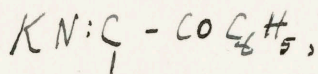
60) This explains the earlier results of Hill and Whistler, *Chicago Jour.* 147, 128; compare also Whistler, *Journ. of Physical Chemistry* [2] 10, 197. 61) *Chemical Abstracts* 1910, 228, 298.



it is consequently necessary to carry out experiments in the absence of water; since it has been found that phosgene does not react with cyanide of silver below 150° , it is more likely that the object in question can be attained through the use of carbonyl bromide which has recently been isolated by Besson ⁶².

In the above mentioned action of aqueous potassium cyanide on chloro-carbonic ester or benzoyl chloride the addition product first formed is split for the most part into the components; when an aqueous solution of potassium cyanide or mercury cyanide is shaken with benzoyl chloride at the room temperature there occurs exclusively a decomposition into prussic acid (or acylinic acid), benzoic acid and potassium chloride or mercuric chloride.

At a lower temperature, as was shown above, the intermediate product



splits in part into potassium chloride and bis-benzoyl cyanide; the chief reaction is, however, here also decomposition into the components.

The most striking and peculiar result of my earlier work on the bivalent carbon atom is the discovery of the perfectly general fact, namely: that the isocyanides unite energetically with acid chlorides to form complex molecules which in their turn break down with the greatest ease into the components from which they were formed ⁶³.

It was, therefore, to be expected that the salts of prussic acid, if they are derivatives of isocyanogen, would show a similar behavior, and from the above it will be seen that this expectation has been fully realized.

III. The Chemistry of Cyanogen.

The Cyanetholines of Cloëz, i. e. the Esters of Normal Cyanic Acid, $\text{RO} \cdot \text{C}:\text{N}$, Do not Exist.

A long time ago, in 1857, Cloëz ⁶⁴ gave an account of a substance which is formed

⁶² Besson, Compt. rend. 120, 190.

⁶³ Liebig's Ann. 280, 299.

⁶⁴ Compt. Rend. 44, 482.

it is consequently necessary to carry out experiments in the absence of water; since it has been found that phosphorus does not react with oxygen at 150°; it is more likely that the first reaction can be obtained through the use of carbonyl bromide which has recently been isolated by Pearson & I. In the above mentioned reaction of carbon monoxide and carbon dioxide or carbonyl chloride the relative product first formed is split for the most part into the components; when an excess, solution of potassium cyanide or sodium cyanide is shaken with carbonyl chloride at the same temperature there occurs exclusively a decomposition into prussic acid (or cyanic acid), hydrogen cyanide and potassium chloride or sodium chloride. At a lower temperature, as was shown above, the intermediate product $KN:C - CO_2H$.

splits in part into potassium chloride and the carbonyl cyanide; the chief reaction is, however, the decomposition into the components. The most striking and peculiar result of my earlier work on the violent carbon atom is the discovery of the perfectly general fact, namely: that the isocyanides unite vegetatively with carbonyl chloride to form complex molecules which in their turn break down with the greatest ease into the components from which they were formed &c. It was, therefore, to be expected that the salt of prussic acid, if they are derivatives of isocyanogen, would show a similar behavior, and for the above it will be seen that this expectation has been fully realized.

III. The Chemistry of Cyanogen.

The Synthesis of Carb. i. e. the Ester of Normal Cyanic Acid.

A long time ago, in 1857, Cläij gave an account of a substance which is found

84) Pearson, Confr. Rend. 120, 190.
83) Cläij, Rend. 280, 189.
82) Confr. Rend. 77, 185.

when chlor-cyanogen is led into alcoholic sodium ethylate; it separates out on addition of water as an oil, which, after washing with water and drying in a desiccator, gave analytical figures corresponding to the formula C_2H_5OCN . Cloëz, therefore, concluded at first that an ester of nitril cyanic acid had been formed. Gal afterward studied the behavior of this oil toward alcoholic potash and found that potassium cyanate is formed, which, however, is transformed at once into potassium cyanurate⁶⁵. Hydrochloric acid also converts it into cyanuric acid.

Cloëz presented his complete investigation of this subject in the form of a thesis to the Scientific Faculty of Paris in August 1866. This paper, which has been ignored by all those who afterward worked in the same field⁶⁶, (Hofmann, Ponomareff, and Mulder), I too was unable to consult. I had access only to an extract published in Würtz, *Dictionnaire de Chimie*. Cloëz modified his method of preparing cyanetholin in so far that he used exactly molecular quantities of chlor-cyanogen and sodium ethylate and carried out the experiment in ethereal solution; the filtrate was then freed from alcohol and ether by heating on the water bath. According to Cloëz cyanetholin decomposes when heated to $120-150^\circ$ with formation of alcohol and of two oils only one of which is soluble in water. The insoluble oil boils at 195° and gives on analysis figures corresponding to C_2H_5OCN ; it is converted by alcoholic potash into potassium cyanurate.

Cloëz prepared also the corresponding methyl-, propyl- and amyl-ester. By treatment with alcoholic potash, with ammonia or with hydrochloric acid he obtained from all the esters exclusively cyanuric acid, a result which Gal confirms⁶⁷. He, therefore, is in doubt⁶⁸ whether the esters obtained are derivatives of cyanic or of cyanuric acid, though he inclines to the latter opinion.

The experiments of Hofmann and Oshausen⁶⁹ contain nothing new and confirm in every respect the earlier experiments of Cloëz⁷⁰. Afterwards Mulder undertook an exhaustive study of ~~the~~ Cloëz's substance, as well as of ethyl cyanurate

⁶⁵ Liebig's Ann. 137, 127.

⁶⁶ Compt. Rend. 70, 1172.

⁶⁷ Bull. Soc. Chim. 6, 439.

⁶⁸ Compt. Rend. 70, 1172.

⁶⁹ Ber. d. Chem. Ges. 3, 269.

⁷⁰ Compt. Rend. 70, 1172.