Report Number III

CHEMICAL REACTIVITY OF CYANOGEN CHLORIDE IN AQUEOUS SOLUTION

Quarterly Status Report
(March through May 1972)

by
John O. Edwards, Chief Investigator
Maria Sauer, Research Associate

February 1973

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Chemical Laboratory
Edgewood Arsenal, Maryland 21010

Contract DAAA15-71-C-0478

BROWN UNIVERSITY
Providence, Rhode Island 02912

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Project 1W662710A095

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FOREWORD

The work described in this report was authorized under Project
1W662710A095. The work described covers the third 3 months of study
under Contract DAAA15-71-C-0478. This period ran from March 1 through
May 1972. Dr. Maria Sauer carried out this study in the laboratory of
the Principal Investigator at Brown University.

DIGEST

The hydrolysis of cyanogen chloride at several pH values has been studied and rate constants for acid and base catalysis are reported. The catalysis by phosphate ions has been investigated.

We have continued our study of the reaction between cyanogen chloride and different nitrogen nucleophiles. Rate constants for the reaction of cyanogen chloride with glycine, glycinamide, and benzylamine are reported. In addition a very careful study over a wider range of pH for the reactions between cyanogen chloride and several amines has been carried out. Our earlier work was covered in reports no. 1 and 2. In view of the new results, it is evident that there is a significant acid catalysis of the hydrolysis reaction at low pH values where the concentration of free amine is very small. As a consequence the rate constant values reported earlier have been corrected considering the acid catalysis of the water and the protonated amine reactions.

The interaction between cyanogen chloride and transition metal ions has been studied using nickel(II) chloride and ferrous chloride as sources of metal ions. Previous results on this matter are also included in this report.

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CHEMICAL REACTIVITY OF CYANOGEN CHLORIDE IN AQUEOUS SOLUTION

I. INTRODUCTION.

The studies of the reactions of cyanogen chloride with various nucleo-
philes were continued over a wide range of pH. We started the study of
the interaction between metal ions and cyanogen chloride using nickel(II)
chloride and ferrous chloride over the molar ration range 0-1.

II. EXPERIMENTATION.

A. Analytical Procedures and Methods.

As usual with those nucleophiles that form colorless products with
cyanogen chloride, the reaction was followed using the colorimetric procedure
based on the color formed between unreacted cyanogen chloride and
γ-(4-nitrobenzyl)pyridine. The method has been slightly modified: 0.5%
solutions of γ-(4-nitrobenzyl)pyridine in the mixed solvent system 50%
acetone - 50% water were used instead of pure acetone. This avoids preci-
pitation of the salts used in buffering the reactant solutions. Also,
when the reactions are carried out at a very low pH the γ-(4-nitrobenzyl)-
pyridine was dissolved in mixtures 50% acetone - 50% phosphate buffer, since
the yellow color fails to develop in very acid conditions. However, it
was noticed that at very low pH due probably to the presence of high
concentrations of hydrochloric acid the color tends to faint rapidly with time.
Even so, it was possible to go as far as pH 0.7 (in the reaction mixture)
without losing appreciable accuracy in the process.

The reaction was followed by taking 1 ml of the thermostated reactant
mixture at different times and adding it to 10 mls of 0.5% solution of
γ-(4-nitrobenzyl)pyridine. The absorbance of the different samples was
recorded at 420 nm using a Hitachi Spectrophotometer. Other than the changes
in the preparation of the γ-(4-nitrobenzyl)pyridine solution above mentioned

the procedure was followed exactly as it was previously described.[1]

The spectra of the products of reaction between metal ions and cyanogen chloride or sodium cyanide was studied in a Cary 15 spectrophotometer.

B. Reactions Investigated.

Nickel(II) Chloride. The spectra of acid mixtures of $NiCl_2$ and cyanogen chloride, were studied in molar fraction range 0-1 using a Cary 15 spectrophotometer. The $NiCl_2$- NaCN mixtures were also studied under similar conditions in order to compare them with the $NiCl_2$- ClCN mixtures.
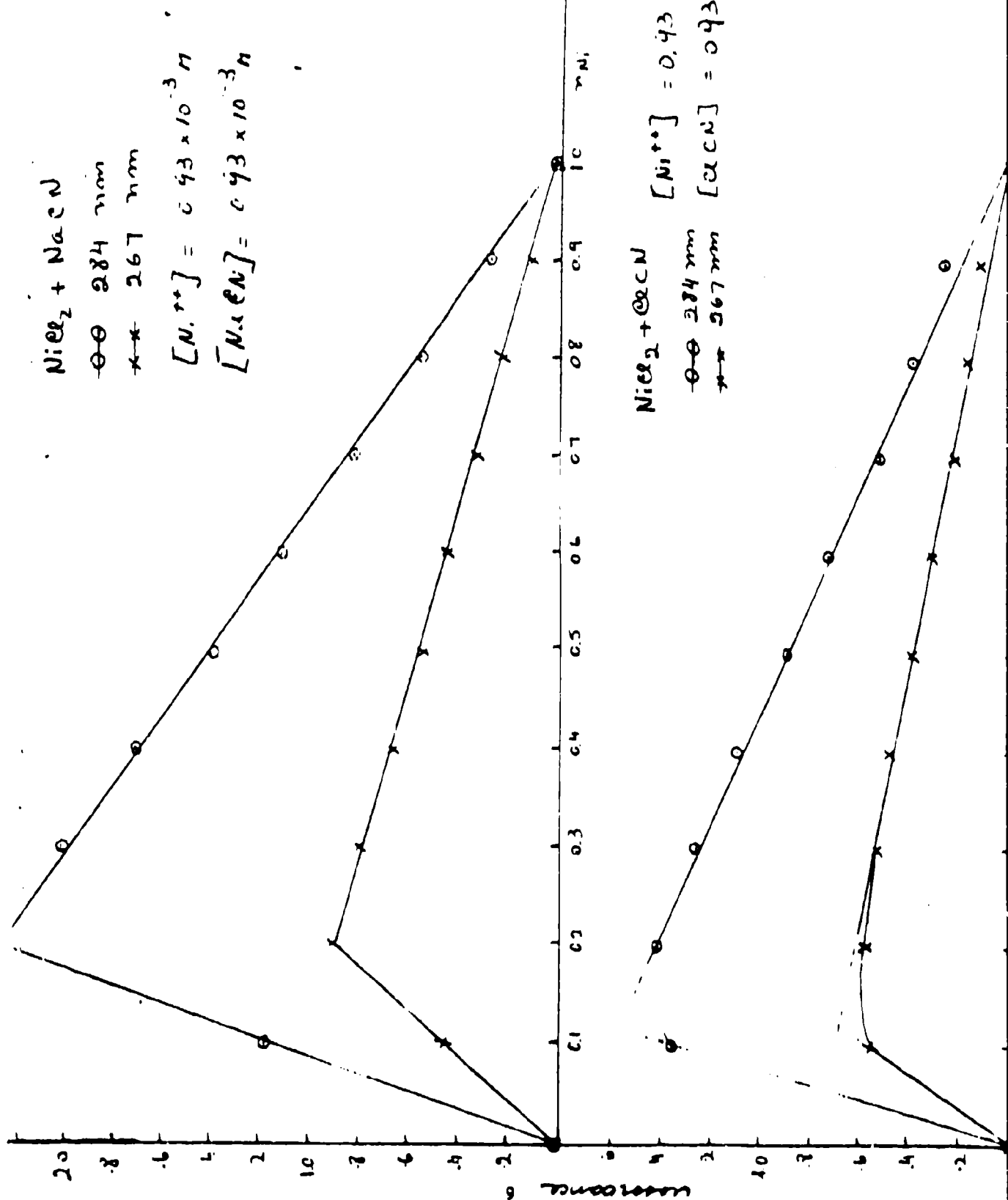
Both mixtures show no strong absorption in the visible, at concentrations 10^{-3} M, but the spectrum in the UV region shows three bands at 310 nm, 284 nm and 267 nm. Figure I shows a plot of the absorbance recorded at 284 nm and 267 nm as a function of the molar fraction for both cases $NiCl_2$- NaCN and $NiCl_2$- ClCN. As it was expected the formula of the complex formed between $NiCl_2$ and NaCN is the well known square planar $[Ni(CN)_4]^{2-}$. This is indicated by the maximum in the plot. The approximate molar extinction coefficients are in this case $\varepsilon_{310} = 0.12 \times 10^4$, $\varepsilon_{284} = 0.96 \times 10^4$, and $\varepsilon_{267} = 2.4 \times 10^4$. In the case of $NiCl_2$- ClCN mixtures under identical conditions of concentration the complex formed seems to have a similar formula as in the case of $[Ni(CN)_4]^{2-}$ although the observed extinction coefficients $\varepsilon_{284} = 0.6 \times 10^4$ and $\varepsilon_{267} = 1.5 \times 10^4$ are smaller. There are some additional experiments we have done with $NiCl_2$- ClCN mixtures.

a. We followed the intensities of the 284 nm and 267 nm absorbance with time in mixtures where Ni^{++} was in excess to the amount required for formation of the complex, that is $\frac{[Ni^{++}]}{[ClCN]} > \frac{1}{4}$. We observed, in all cases, a slow disappearance of the complex (very rapidly formed in the beginning) as shown by the decrease of the 267 nm and 284 nm absorbancies.

1. Edwards, John O., Sauer, Maria, Quarterly Status Report No. 1.

Figure I

Concentration Plot for NiCl$_2$- NaCN and NiCl$_2$- CtCN

NiCl$_2$ + NaCN

⊖—⊖ 284 nm
x—x 267 nm

$[Ni^{++}] = 0.93 \times 10^{-3} M$

$[NaCN] = 0.93 \times 10^{-3} M$

NiCl$_2$ + CtCN

⊖—⊖ 284 nm
x—x 367 nm

$[Ni^{++}] = 0.93 \times 10^{-3} M$

$[CtCN] = 0.93 \times 10^{-3} M$

b. No change with time is observed in the spectrum in mixtures which were $\frac{[Ni^{++}]}{[ClCN]} \leq \frac{1}{4}$.

c. In case of old solutions of ClCN where HOCN is present due to hydrolysis:

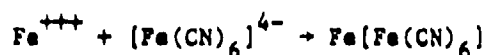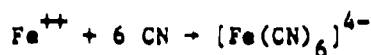$$ClCN + OH^- \rightarrow HOCN + Cl^-$$

an increase in the 267 nm absorbance is observed. In addition where very old solutions of ClCN (where all cyanogen is present as HOCN) are used, the spectrum of the mixtures consist only of a simple absorbance centered at 267 nm.

d. Solutions of $[Ni(CN)_4]^{2-}$ were prepared and an equal amount of ClCN was added. No change was observed in the spectrum during the following hour after mixing.

Ferrous chloride. The mixtures of $FeCl_2$ and ClCN behave quite differently from the mixtures of $FeCl_2$ and NaCN at least as far as the spectrum is concerned. At concentration about 10^{-3} M the slight blue colored solutions of $[Fe(CN)_6]^{4-}$ show no strong absorbance in the visible and UV.

The mixtures $FeCl_2$- ClCN on the other hand show a peculiar behavior at some concentrations. On mixing both solutions a very light blue color develops rapidly and the spectrum of this solution shows a very broad and intense absorption band centered at 265 nm. After approximately 15 minutes the clear solution turns turbid and a blue precipitate can be filtered. The spectrum of the now colorless solution shows some bond at 265 nm now with remarkable lower absorbance.

The blue precipitate could be explained by assuming formation of Prussian blue $MFe[Fe(CN)_6]$ where M is a monovalent cation by oxidation of Fe^{++} by ClCN:

$$Fe^{++} + ClCN \rightarrow Fe^{+++} + CN^- + Cl^-$$

$$Fe^{++} + 6\ CN \rightarrow [Fe(CN)_6]^{4-}$$

$$Fe^{+++} + [Fe(CN)_6]^{4-} \rightarrow Fe[Fe(CN)_6]$$

However, at this point, we cannot postulate any definite mechanism.

Hydrolyses of Cyanogen Chloride. Cyanogen chloride hydrolyzes in basis media according to reaction:

$$Cl - CN + OH^- \rightarrow HO - CN + Cl^-$$

The rate of base hydrolysis was studied by Price et al who found $k_{OH} = 6 \times 10^2\ M^{-1}\ min^{-1}$. Deviations from this value at pH 7.5 were attributed entirely to catalysis by phosphate ion.
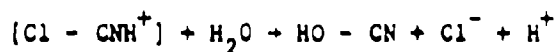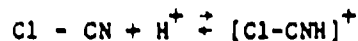
We have studied the hydrolysis of cyanogen chloride between pH 0.7 - 10.5. Dependence of rate of hydrolysis on pH is shown in Figure II. It can be seen that there is a definite "water reaction" (as indicated in the bottom part of the plot) and a small catalysis by the phosphate buffer. The phosphate catalysis contribution can be seen from the experimental deviations of the calculated values.

The rate for the basic reaction was calcualted from the values at pH 10.5 and 10 giving $k_{OH} = 8 \times 10^2\ M^{-1}\ min^{-1}$. The rate of the water reaction was calculated from the bottom part of the plot (considering $[H_2O] = 55\ M$) giving $k_{H_2O} = 6.45 \times 10^{-5}\ M^{-1}\ min^{-1}$. The reaction would be

$$ClCN + H_2O \rightarrow HOCN + Cl^- + H^+$$
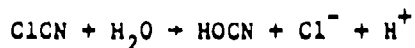
Between pH 0.7 and 1.3 the value of k_H was calculated considering $k_{obs} = k_{H_2O}[H_2O] + k_H[H^+]$ and the reaction

$$Cl - CN + H^+ \rightleftharpoons [Cl-CNH]^+$$

$$[Cl - CNH^+] + H_2O \rightarrow HO - CN + Cl^- + H^+$$

so that $k_H = 2 \times 10^{-2}\ M^{-1}\ min^{-1}$.

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Figure II

Hydrolysis of ClCN, 25°C.

- - Experimental values
-×-×- Calculated values considering
only k_{OH} and k_{H_2O}.

pH 0.7 - 1.3   HCl
pH 2.2 - 3.6   Acetate Buffer
pH 4.6 - 10.5   Phosphate Buffer

$3 + \log k$,

pH

2
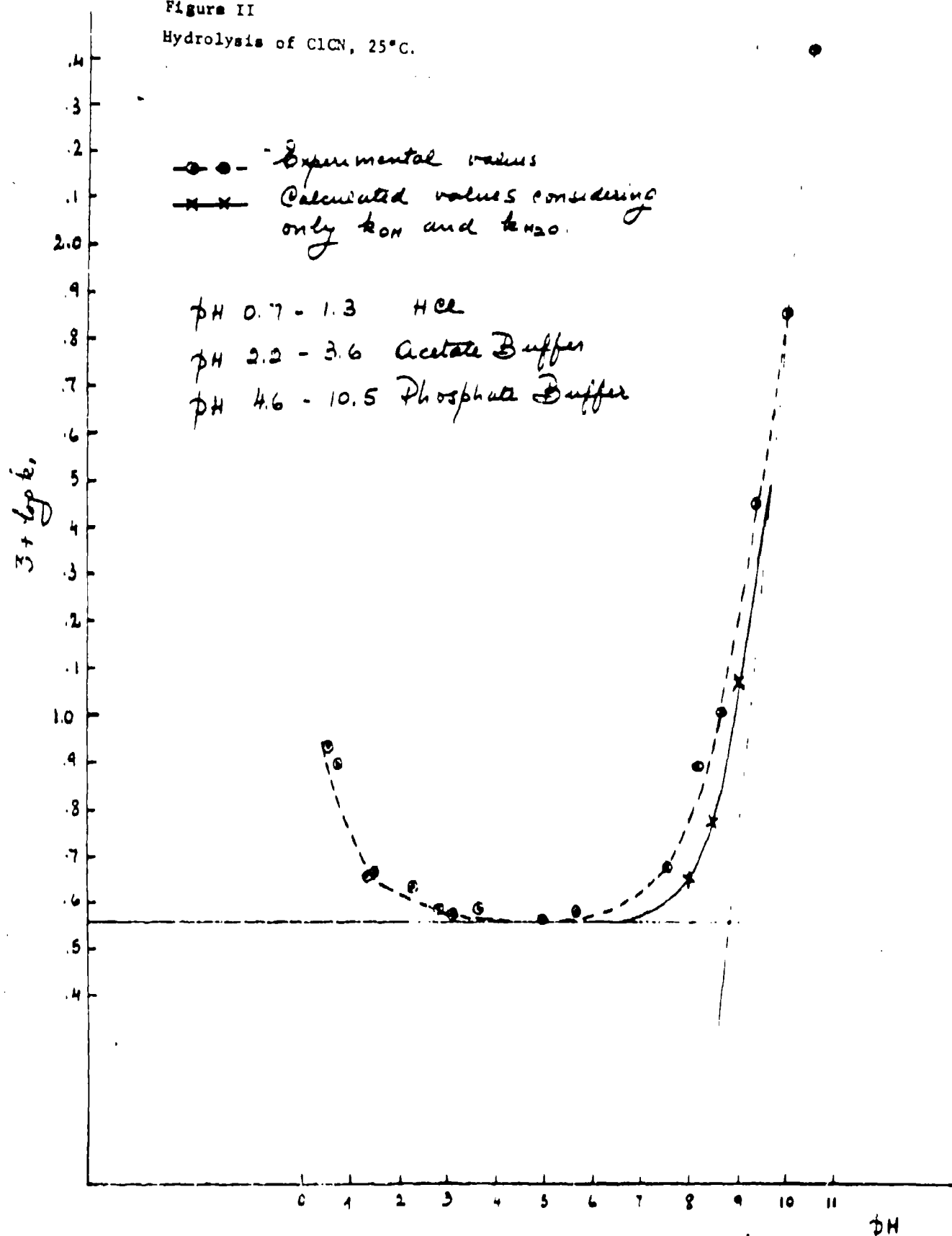
At low pH values the reaction was very difficult to study due to the analytical technique used.

Phosphate Ion. The attack of phosphate ion on cyanogen chloride was studied in the pH range 5 to 7. In the solutions at pH 5 where the phosphate ion is in the form $PO_4H_2^-$, no catalysis of the hydrolysis reaction was observed upon increase of the total phosphate concentration. However at pH 6.5 to 7 where the $[PO_4H^=]$ becomes significant an increase in the rate of hydrolysis with the phosphate concentration was observed. That is $k_{obs} = k_{OH}[OH^-] + k_{phosp}[Phosp] + k_{H_2O}[H_2O]$. Where

$$k_{phosp} = \frac{k_{obs} - k_{OH}[OH^-] - k_{H_2O}[H_2O]}{[Phosp]}$$

If we consider the total phosphate concentration, in order to compare our values with the one reported by Price et al, we have $k_{phosp} = 1.6 \times 10^{-2} \ M^{-1} \ min^{-1}$ Since we know that the active form involved in the catalysis is $PO_4H^=$ then $k_{PO_4H} = 2.9 \times 10^{-2} \ M^{-1} \ min^{-1}$ is higher since they are including also the water reaction in the phosphate rate constant -- that is, according to them: $k_{obs} = k_{OH}[OH^-] + k_{phosp}[Phosp]$ disregarding the term $k_{H_2O}[H_2O]$.

Nitrogen Nucleophiles. The reaction between 4-chloropyridine and cyanogen chloride was studied spectrophotometrically. The yellow product of reaction shows a maximum absorbance at 375 nm. However, it was difficult to obtain a reproducible value of the rate constant since the chloropyridine alone seems to undergo decomposition in aqueous solution becoming quite yellow. The study of reactions with other pyridines were attempted without much success due mainly to analytical problems. Among them the 3-ethylpyridine

and 4-ethylpryidine (quite insoluble in aqueous solution) and 4-amino-

pyridine were tried unsuccessfully. Using the colorimetric technique the

reaction between benzylamine and cyanogen chloride was studied at pH 5.5

to 6.4; glycinamide and glycine were studied in the range of pH 5.3 to

7. The reactions were assumed to be:

$$R - NH_2 + ClCN \rightarrow ClH + RNH - CN$$

in all cases as it was previously discussed.[1] The calculated second-order

rate constants are shown in the table.

Rate of Attack of Nucleophiles on Cyanogen Chloride			
Nucleophile	pKa	k_2	Observations
1. Hydroperoxide ion	11.6	5.3×10^5	to be repeated
2. Piperidine	11.2	3.2×10^3	
3. Methylamine	10.6	1.2×10^3	
4. Sec-Butylamine	10.5	1.2×10^2	
5. Tri-Methylamine	9.74	0.15×10^2	
6. Benzylamine	9.37	7.3×10^2	
7. Acetaldoximate Ion	9.13	5.1×10^3	to be repeated
8. Hydrazine	8.1	3.6×10^3	
9. Glycineamide	8.1	2.07×10^2	
10. Hydroxylamine	5.96	3.7×10^2	
11. Dimethylhydrazine	6.8	1.5×10^3	
12. γ-Picoline	6.0	50.4	
13. Pyridine	5.23	20.4	
14. OH^-	15.7	8×10^2	
15. H_2O	- 1.7	6.4×10^{-5}	
16. Glycine	9.8	8×10^2	
17. $PO_4H^=$	2.23	8.7×10^2	
18. H_3O^+		2×10^{-2}	

In view of the acid hydrolysis and the magnitude of the water reaction

it was necessary to apply a correction to the rate constants for amines

previously reported,[1,2] depending on the pH at which they were studied.

2. Edwards, John O., Sauer, Maria, Quarterly Status Report No. 2.

Although the ideal situation would be to study the attack of amines on cyanogen chloride under conditions where they are totally free bases ($R-NH_2$), that is at a pH > pKa, the fact that amine attack on ClCN is so fast makes this impossible under our experimental conditions when the colorimetric method is used. Thus, at the pH where the reactions are studied the amines are mostly in the protonated form and the proportion of free base has to be calculated considering the Ka of the amine

$$R - NH_3^+ + H_2O \overset{Ka}{\rightleftharpoons} R - NH_2 + H_3O^+$$

$$\frac{[R - NH_2][H_3O^+]}{[R - NH_3^+]} = Ka$$

$$[R - NH_2] = \frac{Ka[R - NH_3^+]}{[H_3O^+]}$$

and the $[R - NH_2] + [R - NH_3^+] = [amine]_T$. In this way the reaction takes place at a measurable rate since free amine is present in small concentration Then, it is necessary to study the reaction in a wide range of pH to see if there is any attack by the protonated form of the amine.

Figure III shows the variation of k_{obs} as a function of pH for hydrazine and piperidine.

As can be seen in the specified range of pH the attack by the amine and other nucleophiles on cyanogen chloride can be expressed:

$$k_{obs} = k_H[H^+] + k_{H_2O}[H_2O] + k_{RNH_3} + [RNH_3^+] + k_{RNH_2}[RNH_2] + k_{OH}[OH]$$

It is evident that at pH < 3 $k_{obs} = k_H[H^+] + k_{RNH_3} + [RNH_3^+]$ at 3 < pH < 6 if pKa > 6 $k_{obs} = k_{H_2O}[H_2O] + k_{RNH_3} + [RNH_3^+] + k_{RNH_2}[RNH_2]$ and at pH > 6
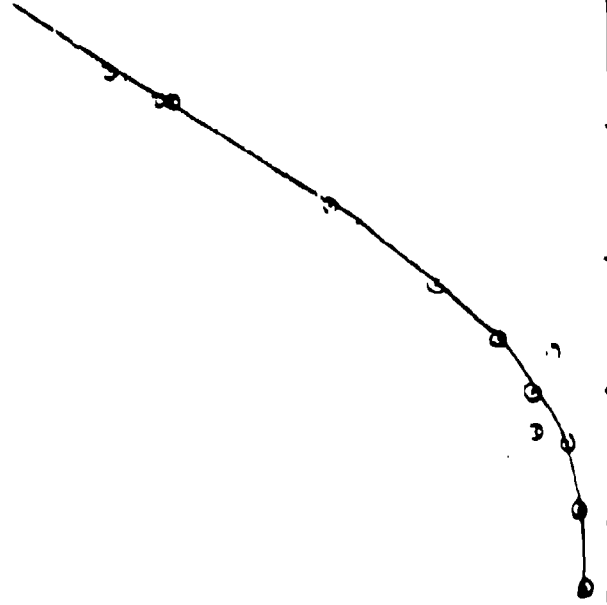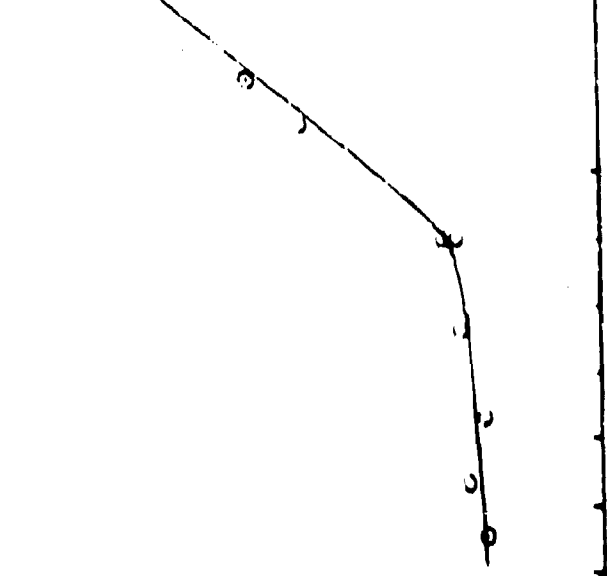
Figure III

pH Dependence of the Rate of Reaction for Nitrogen

Nucleophiles—Cyanogen Chloride Reactions.

Piperidine [3.15 n]

$pka = 11.2$

Hydrazine 0.008 M

$pka = 8.1$

$2 + log k_{obs}$

$k_{obs} = k_{OH}[OH] + k_{RNH_2}[RNH_2]$. Usually when the reaction is studied at pH > pKa - 3 all corrections due to water reaction or protonated amine reaction are practically negligible.

With this in mind we have recalculated the rate constants already reported,[1,2] and the new results are shown in the table (page 14).

A Brönsted plot of the nucleophiles so far studied is included. (Figure IV)

III. DISCUSSION.

The mechanism of reaction between transition metal ions and cyanogen chloride is at the moment not very well understood.

If the complex formed between Ni^{++} and ClCN is actually $[Ni(CN)_4]^{2-}$ some oxidation of Ni^{++} must take place in order to account for the presence of cyanide ion

$$Ni^{++} + ClCN \rightarrow CN^- + Ni^{+++} + Cl^-$$

$$Ni^{++} + 4 CN^- \rightarrow [Ni(CN)_4]^{2-}$$
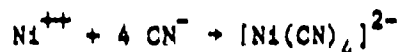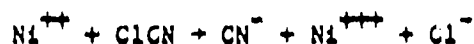
On the other hand, the formation of a complex between Ni^{++} and ClCN cannot be excluded. It would appear that also HOCN forms a complex with Ni^{++} with a completely different spectrum than $Ni(CN)_4{}^{2-}$. At this point, a kinetic study of the rapid complex formation would actually provide some clue as to the mechanism of the reaction.

In addition, there is no way by which we can explain the decomposition of the complex by excess of Ni^{++}. Some kinetic studies on these mixtures will probably help us in finding some possible mechanism.

In the $FeCl_2$- ClCN mixtures the facts seem to be easier to explain and the actual oxidation of Fe^{++} by ClCN appears to take place at a measurable rate. Again we will need some kinetic studies in order to prove this point.

Figure IV
Bronsted Plot, 25 C.
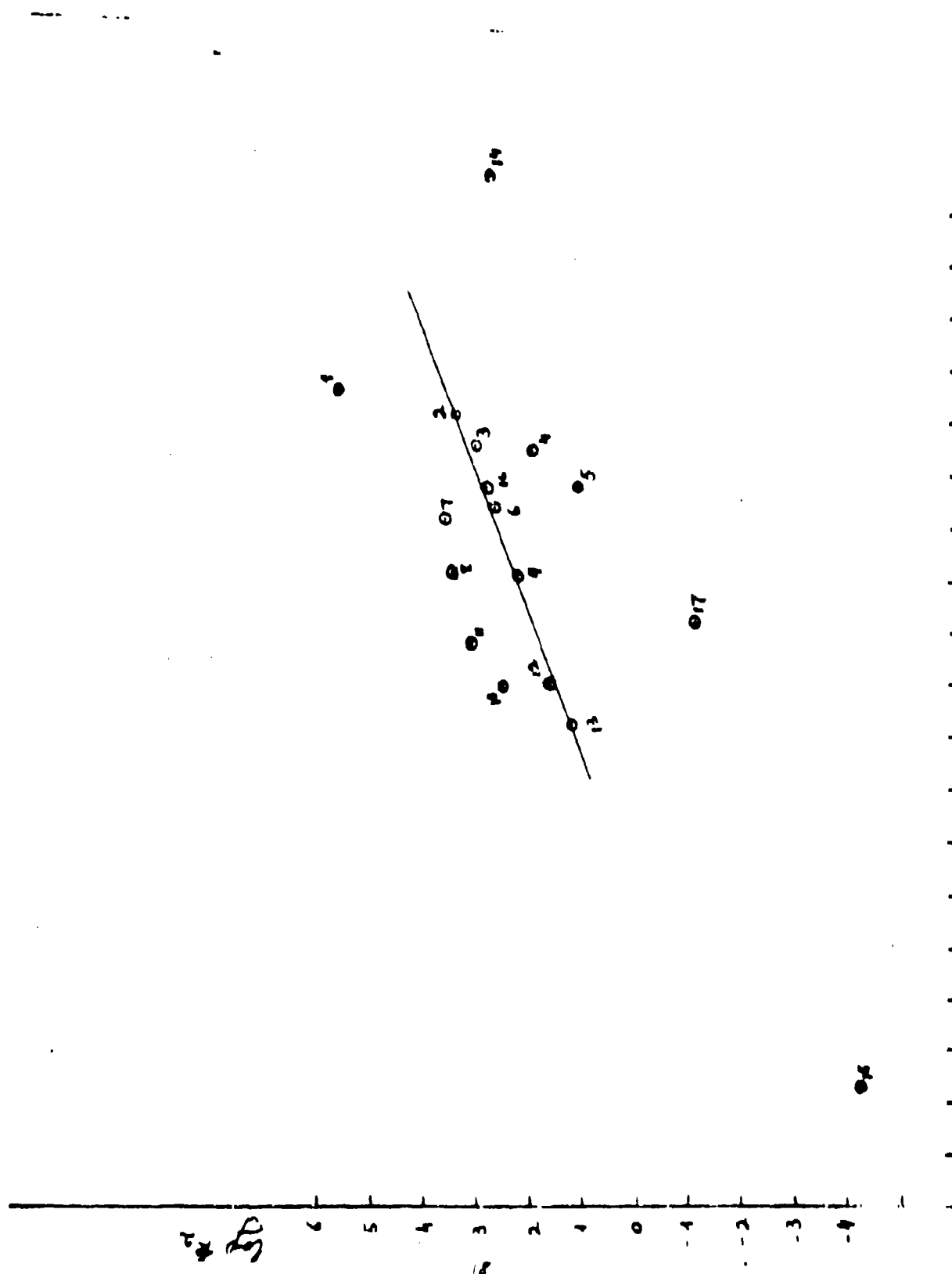
The study of the hydrolysis of cyanogen chloride became absolutely necessary since we are studying the aqueous chemistry of ClCN. In general our results in basic solutions agree roughly with the value obtained by Price et al: $k_{OH} = 6 \times 10^{-2}$ M^{-1} min^{-1}. The acid hydrolysis is assumed to be a catalysis of the water reaction although it is known that nitriles decompose in concentrated acid solutions giving the corresponding amide:

$$R - CN + H_2O \xrightarrow{H^+} R - C \overset{NH}{\underset{OH}{\diagdown}} \quad \rightarrow \quad R - C \overset{NH_2}{\underset{O}{\diagdown}}$$
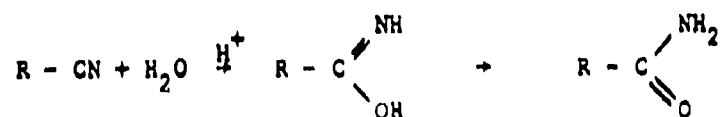
In case of Cl-CN, however, the Cl-C bond is weak enough to make the Cl-CN decompose according to a hydrolysis mechanism before the above reaction takes place.

The correction applied to the nitrogen nucleophiles rate constants previously found change slightly the slope of the Brönsted plot to 0.37.

Actually, the mechanism of attack on cyanogen chloride by protonated amines remains unknown, however our primary concern so far has been to find reliable constants for the free amine rate constants.

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13. ABSTRACT

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Hydrolysis of Cyanogen Chloride						