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CHEMICAL REACTIVITY OF CYANOGEN CHLORIDE IN AQUEOUS SOLUTION.(U)

JAN 73 J O EDWARDS, M SAUER

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Report Number II ✓

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Quarterly Status Report
(December 1971 through February 1972)

1 Nov 71 - 29 Feb 72

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

January 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 second 3 months of study under Contract DAAA15-71-C-0478. This period ran from 1 December 1971 to 29 February 1972. Dr. Maria Sauer carried out this study in the laboratory of the Principal Investigator at Brown University.

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DIGEST

Studies of the chemical reactivity of cyanogen chloride with various nucleophiles in aqueous solutions were continued. Spectrophotometric techniques, as well as the colorimetric technique described in the previous report, were used for analysis. Nucleophiles investigated were pyridine, piperidine, trimethylamine, α -picoline, sec-butylamine, acetaldoxime, and hydriodic acid. A Bronsted plot with all nucleophiles thus far studied is included.

Summary

CHEMICAL REACTIVITY OF CYANOGEN CHLORIDE IN AQUEOUS SOLUTION

I. INTRODUCTION.

The studies of the reactions of cyanogen chloride with various nucleophiles were continued. Some of the reactions were complicated by the formation of colored reaction products which interfered with the colorimetric analyses. Other studies were complicated by secondary reactions of the products which made the rate determinations of the primary reactions more difficult.

II. EXPERIMENTATION.

A. Analytical Procedures and Methods.

With those nucleophiles that formed a colorless product with cyanogen chloride, the reaction was followed using the colorimetric procedure based on the color formed between cyanogen chloride and γ -(4-nitrobenzyl)-pyridine.

This method has been already described in our previous report. However, there are limitations, and the accuracy of the method is a subject of worry since several runs (especially below pH 5) had been discarded due to a lack of reproducibility.

When pyridine and γ -picoline were the nucleophiles, the reactions were studied by following the appearance of the colored product in a Cary 15 spectrophotometer. The reaction between hydriodic acid and cyanogen chloride was studied following the appearance of iodine in a Durrum Stopped-Flow apparatus.

All calculations of pseudo first-order rate constants were carried out using a least-squares program on APL code as previously described.¹

B. Preparation.

Cyanogen chloride solutions were prepared as previously described

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

(Report 1). The liquid nucleophiles were purified by distillation, and their aqueous solutions prepared freshly before use.

C. Reactions.

The reactions were assumed to follow the stoichiometry



where Nu^- represents the nucleophile. The rate law

$$\frac{-d[\text{Cl-CN}]}{dt} = k_2 [\text{Cl-CN}] [\text{Nu}^-]$$

was also assumed initially. With nucleophile in considerable excess, the law can be written as

$$\frac{-d[\text{Cl-CN}]}{dt} = k' [\text{Cl-CN}]$$

where

$$k' = k_2 [\text{Nu}^-]_0$$

When the colorimetric procedure was used, the second-order rate constants, k_2 , were found as described in Report No. 1.¹ When the appearance of a colored product was followed in the Cary 15 Spectrophotometer the logarithm of the difference ($A_\infty - A_t$), where A = absorbance of product, was plotted against time. Since

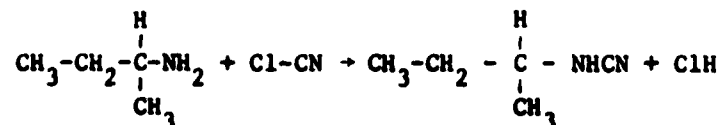
$$[\text{Nu-CN}]_\infty - [\text{NuCN}]_t = [\text{CNCl}]_t$$

then $\log (A_\infty - A_t) = k't$. k' and k_2 were then found in a way similar to that in the colorimetric procedure.

III. RESULTS OF NUCLEOPHILES INVESTIGATED.

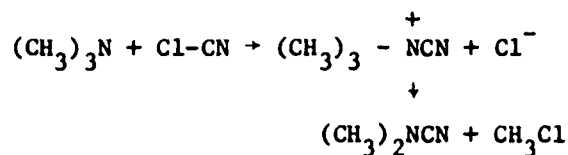
A. Sec-Butylamine.

The sec-butylamine reaction with cyanogen chloride was studied in the pH range 7.3-8.8 using the colorimetric procedure. The reaction was assumed to be:



B. Trimethylamine.

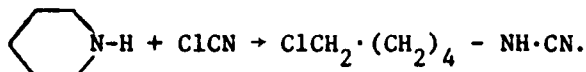
The reaction between trimethylamine and cyanogen chloride was studied at pH 5.8 using the colorimetric procedure. It has been postulated² that the reaction between cyanogen halides and tertiary bases proceeds in two stages. Addition of cyanogen chloride to the amine forms a quaternary base. The quaternary base then decomposes to a halide and cyanamide.



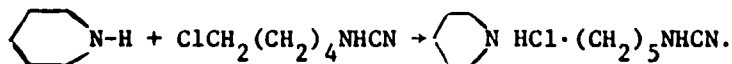
C. Piperidine.

The reaction between piperidine and cyanogen chloride was studied at pH 6.0 using the colorimetric technique.

The reaction was assumed to be:

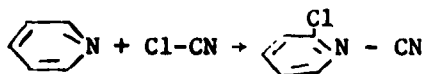


It has been postulated² that the resulting compound reacts with the unconverted cyclic base to form a quaternary compound



D. Pyridine.

The reaction between pyridine and cyanogen chloride has been known for a long time and has been applied to develop analytical methods for detection of cyanogen chloride.³ We have studied the primary reaction



by following the formation of the yellow product at 400 nm where the maximum

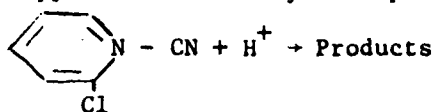
2. Migrdichian, V. The Chemistry of Organic Cyanogen Compounds. Reinhold Publishing Corporation, New York, N. Y.

3. Epstein, J., Anal. Chem. 19, 272 (1947).

extinction coefficient is observed.

The reaction was studied in the pH range 6.0-9.7 and in the range of pyridine concentration 0.15-0.19 M.

A secondary reaction, catalyzed by H^+ , was also observed and was studied by following the disappearance of the yellow product after it was formed.



In poorly buffered solutions, a production of H^+ was observed which indicates the formation of H^+ during the reaction. This secondary reaction was studied by mixing the yellow product formed at pH 9.5 with 5% solutions of phosphate buffer. So far, however, the reaction has been studied only at pH 5.6 and 6.0.

The rate law was assumed to be

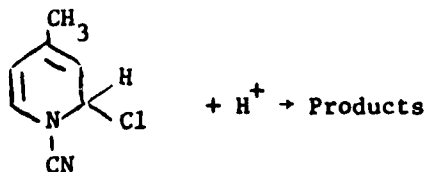
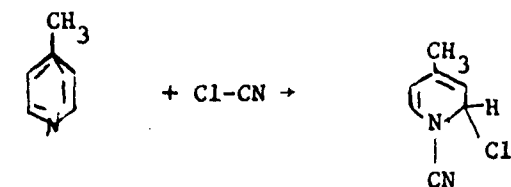
$$\frac{-d(I)}{dt} = k'[I]$$

where $k' = k_2[H^+]$.

From plots of $\ln [I]$ as a function of time, pseudo first-order constants k' were obtained. k_2 was calculated by dividing by $[H^+]$. $k_2 = 1.76 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$.

E. α -picoline and γ -picoline.

α -picoline (2-methylpyridine) does not seem to react with cyanogen chloride. γ -picoline reacts readily with cyanogen chloride forming a yellow compound with maximum extinction coefficient at 415 nm.

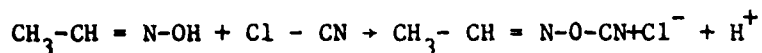


The primary reaction was studied in the pH range 8.8-9.5 following the formation of product. The secondary reaction was studied at pH 7.4 and 8.8 by following the disappearance of product formed in alkaline media when the product was mixed with 5% phosphate buffer. $k_2 = 1.0 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$.

At pH values of the order of the pKa of pyridine, the primary reaction is impossible to observe since, at these pH values, the secondary reaction becomes very important.

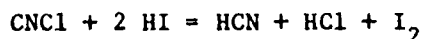
F. Acetaldoxime.

The reaction between acetaldoxime and cyanogen chloride was studied at pH 4.8. The reaction was assumed to be:



G. Hydriodic acid.

It has been reported that hydroiodic acid reacts with cyanogen chloride liberating iodine.⁴



However, it also has been reported that there is no apparent reaction between cyanogen chloride and hydriodic acid.² On mixing solutions of HI and cyanogen chloride when HI is in considerable excess, we did observe the very rapid formation of iodine followed by a very slow disappearance of iodine. The disappearance of iodine was probably due to reaction with the HCN.

So far the data obtained on this reaction are not understood, and no numerical values for the rate constants have been obtained.

4. Sartori, M. The War Gases. D. Van Nostrand Co., Inc., p 190, 1939, New York, N. Y.

IV. SUMMARY AND CONCLUSIONS.

The results of these studies are tabulated in the table. These data are also presented graphically in the form of a Bronsted plot.

Our data to date indicate that the rate constants for the reactions of cyanogen chloride with amines generally follow the basicities of the amines. The slope for the line drawn on the figure is 0.5. We will soon have enough data to confirm (of deny) the position and the slope of the line on this Bronsted plot.

There is a significant trend with the alpha-nucleophiles. In all five cases, the points are distinctly above the line drawn.

TABLE

SECOND-ORDER RATE CONSTANTS FOR THE NUCLEOPHILIC ATTACK ON CYANOGEN CHLORIDE

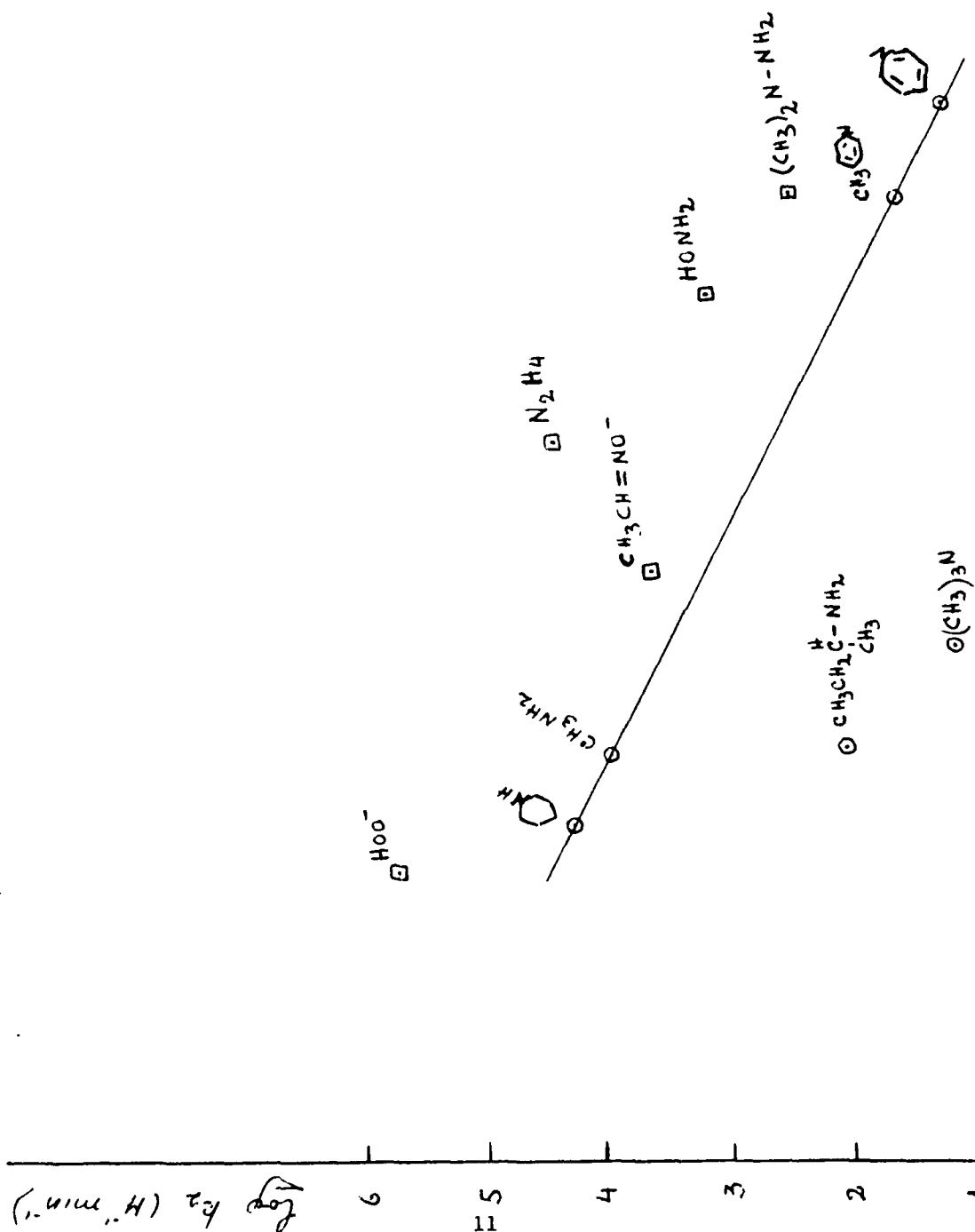
$[Cl-CN] = 0.0085 \text{ M} = 8.5 \times 10^{-3} \text{ M}$

$t = 25^\circ\text{C}$

Nucleophile	[Nu]	$k_2 (\text{M}^{-1} \text{min}^{-1})$	pKb
Pyridine	0.15-0.19	20.4	8.77
γ -Picoline	0.15-0.25	50.4	8.0
Piperidine	0.30	2×10^4	2.79
Sec-Butylamine	0.28	1.2×10^2	3.44
Trimethylamine	0.20	0.15×10^2	4.26
Acetaldoximate Ion	0.25	5.12×10^3	4.87

Figure

Bronsted Plot for the Attack of Nucleophiles on Cyanogen Chloride at 25°C



The two amines below the line, along with the nonreactive alpha-picoline, suggest that steric hindrance must be important in the transition state.

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13. ABSTRACT

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