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Report Number I

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Quarterly Status Report
September through November 1971

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

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December 1972

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Chemical Laboratory
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Quarterly Status Report

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Maria Sauer

December 1972

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DEPARTMENT OF THE ARMY
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Contract DAAA15-71-C-0478

Project 1W662710A095

BROWN UNIVERSITY
Providence, Rhode Island 02912

FOREWORD

The work described in this report was authorized under Project IW662710A095. The work described covers the first three months of study under Contract DAAA15-71-C-0478. This period ran from 1 September 1971 to 30 November 1971. 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 initiated. Colorimetric analyses for cyanogen chloride were performed using *p*-(4-nitrobenzyl)pyridine. The nucleophiles investigated were hydroperoxide anion, methylamine, hydroxylamine, hydrazine, and dimethylamine. Second-order rate constants were determined for these reactions.

CHEMICAL REACTIVITY OF CYANOGEN CHLORIDE IN AQUEOUS SOLUTION

I. INTRODUCTION.

The compound cyanogen chloride Cl-CN is in common use, yet its presence in significant quantity cannot be tolerated by the human body. In order to understand better the behavior of this compound, a study of its aqueous chemistry was initiated. Of particular importance to this contract are the reactions with nucleophiles. As we had not previously worked with the compound, it was necessary to acquaint ourselves with the material and with the analytical procedures to be used in following the reactions. This has been accomplished, and our reactivity studies have been initiated.

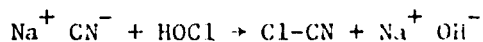
II. EXPERIMENTATION.

A. Analytical Procedures.

The compound itself presents no visible nor ultraviolet absorption of satisfactory intensity for monitoring the decrease in concentration with time. Further, the nucleophiles to be studied were so variable in nature that no common feature presented itself as a basis for an analytical procedure. We therefore chose to use the sensitive and accurate colorimetric procedure based on the color formed between cyanogen chloride and γ -(4-nitrobenzyl)-pyridine. With the exception of such colored materials as chromate ion, this analytical procedure is practical for our needs.

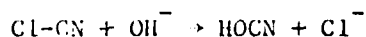
B. Preparation.

Cyanogen chloride solutions were prepared using equimolar amounts of sodium cyanide and sodium hypochlorite in the presence of phosphate buffer at pH 8.2.



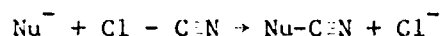
The reaction is practically instantaneous as can be seen spectro-

photometrically by the complete disappearance of the hypochlorite ultra-violet absorption. The cyanogen chloride solutions were freshly prepared immediately before use, since the rate of hydrolysis at that pH is quite significant.¹



C. Reactions.

The several reactions which we have investigated 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; however, the values of the constants k_2 were checked for consistency.

With nucleophile in considerable excess, the law can be written as

$$\frac{-d(\text{Cl-CN})}{dt} = k' (\text{Cl-CN})$$

where $k' = k_2 (\text{Nu}^-)_0$

that is, $\ln(\text{CN-Cl})_t = \ln(\text{CN-Cl})_0 - k't$.

The logarithm of the absorbance of the complex formed between the cyanogen chloride and γ -(4-nitrobenzyl)pyridine was plotted against time and the slope found by applying the least squares method. Both graphical and mathematical calculations were programmed on APL (A Programming Language developed for the IBM 360 computer) code, and the experimental data were fed into a time-sharing terminal of the computer. The second-order rate constant, k_2 , was then obtained by dividing the slope by the concentration of unprotonated nucleophile previously calculated using the corresponding

1. Price, C. C., et al. Hydrolysis and Chlorinolysis of Cyanogen Chloride. J. Amer. Chem. Soc. 69, 1640 (1947).

PKb. It was found, in most of the cases that, in order to have measurable rates of reactions, it was necessary to work at low pH; at high pH values, the reactions are too fast.

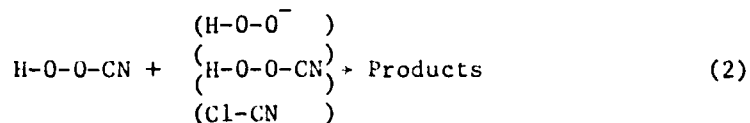
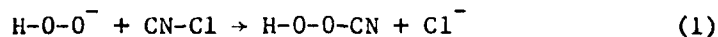
To 10 ml of 1% or 0.5% acetone solutions of γ -(4-nitrobenzyl)pyridine, depending on the initial concentration of cyanogen chloride, was added 1 ml of the reaction mixture. The tubes were stoppered, and immediately afterward, mixed by inversion. The absorbance at 420 nm was recorded no sooner than 30 minutes later since it was found that the yellow color reaches a constant intensity in this time.

III. RESULTS.

A. Nucleophiles Investigated.

1. Hydrogen Peroxide. The reaction between hydrogen peroxide and cyanogen chloride has not been reported in the literature although it is known that hydrogen peroxide reacts with HCN and cyanides to give oxamide ($O = CNH_2$)₂.

Also, the kinetics of the reaction between hydrogen peroxide and benzonitrile was studied by Wiberg, who showed the rate to be dependent on the hydrogen peroxide anion concentration. We have studied the reaction between hydrogen peroxide and cyanogen chloride over a wide range of pH. The reaction proceeds in several stages with a mechanism still not completely clear.



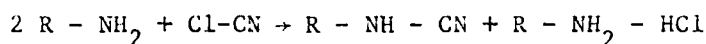
Reaction (1) was studied in the pH range 5.7-6.5 under pseudo-first-order

conditions following the disappearance of CNCl with 4-(nitrobenzyl)pyridine as described above. The table shows the second-order rate constant obtained at different hydrogen peroxide anion concentrations.

The several reactions of the second stage were studied following the disappearance of the hydroperoxide absorption at 240 nm, with different values of the ratio $(\text{H}_2\text{O}_2)/(\text{CNCl})$. The results so far obtained show that the H-O-O-CN formed reacts slowly with the hydrogen peroxide (when present in excess), or with another molecule of H-O-O-CN, or with CN-Cl (when present in excess) according to the different initial values of the ratio $(\text{H}_2\text{O}_2)/(\text{CNCl})$.

However, further studies on this secondary stage are necessary in order to understand better the mechanisms involved in each case.

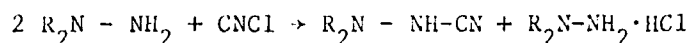
2. Methylamine and Hydroxylamine. Reports of reactions of amines with cyanogen chloride have been confirmed.



It has been reported that methylamine and cyanogen chloride react in ether forming symmetrical dimethylguanidine $(\text{CH}_3\text{NH})_2:\text{NH}$.

We have observed in both cases a rapid disappearance of cyanogen chloride. The methylamine reaction was studied in the pH range 5.5-6.0; and the hydroxylamine reaction, in the pH range 3.3-3.7. Both reactions were studied under pseudo-first-order conditions. Second-order rate constants for each are summarized in the table. Secondary reactions, such as those for guanidine formation, have not yet been investigated.

3. Hydrazine and Dimethylhydrazine. The reaction of hydrazine with cyanogen halides has been reported in the literature to give aminoguanazo and diaminoguanidine as final products.



The hydrazine reaction with cyanogen chloride was studied in the pH range 2.9-3.1 and the dimethylhydrazine reaction in the pH range 2.4-4.8, in both cases under pseudo-first-order conditions. (The secondary reactions have not yet been studied.) The calculated second-order constants are again given in the table.

Table

Second-Order Rate Constants Obtained

(CNCl) = 0.010 to 0.022 M.

(Nucleophile) = 0.21 to 0.15 M.

Temperature = 23°C $\pm$ 1°C.

Nucleophile	pKb	$k_2 (\text{min}^{-1} \text{M}^{-1})$
HOO^-	2.4	5.3×10^5
CH_3NH_2	3.38	1.0×10^4
HO-NH_2	8.04	3.7×10^2
$\text{H}_2\text{N-NH}_2$	5.93	3.1×10^4
$(\text{CH}_3)_2\text{N-NH}_2$	7.2	1.8×10^3

IV. SUMMARY AND CONCLUSIONS.

The method of analysis works satisfactorily, albeit we have found it appropriate for our study to use somewhat larger quantities of the colorimetric reagent than we had hoped.

In the table, our second-order rate constants for reaction of cyanogen

chloride with five nucleophiles are presented. For comparison the constants for OH^- and OCl^- are $6 \times 10^2 \text{ min}^{-1} \text{ M}^{-1}$ and $16 \times 10^2 \text{ min}^{-1} \text{ M}^{-1}$.¹ As expected for nucleophilic attack on the digonal carbon, the anionic alpha-nucleophiles HOO^- and OCl^- are very reactive, and the neutral alpha-nucleophiles show a small "alpha-effect" (defined as an abnormal nucleophilic reactivity relative to the proton basicity). The rate ratio of 10^3 for $(\text{HOO}^-)/(\text{OH}^-)$ is somewhat smaller than that for nitriles,^{2,3} however, the cyanogen chloride because of its greater reactivity would be expected to show lower discrimination as is indeed the case.

It is clear that decontamination of cyanogen chloride solutions is very simple. Treatment with 3% hydrogen peroxide plus a bit of base will destroy the chloride in the time of mixing (a few seconds). For dilute solutions of cyanogen chloride such as are required for our experiments, the facile preparation and destruction reactions have allowed us to do these experiments without ever having to prepare significant quantities or to store any at all.

2. Wiberg, K. B. The Mechanisms of Hydrogen Peroxide Reactions. I. The Conversion of Benzonitrile to Benzamide. *Ibid*, 75, 3961 (1953).
3. Wiberg, K. B. The Mechanisms of Hydrogen Peroxide Reactions. II. A Comparison of the Reactivity of Hydroxyl Ion and Hydroperoxide Ion toward Benzonitrile. *Ibid*, 77, 2519 (1955).

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Studies of the chemical reactivity of cyanogen chloride with various nucleophiles in aqueous solutions were initiated. Colorimetric analyses for cyanogen chloride were performed using γ-(4-nitrobenzyl)pyridine. The nucleophiles investigated were hydroperoxide anion, methylamine, hydroxylamine, hydrazine, and dimethylamine. Second-order rate constants were determined for these reactions.		

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