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Report Number IV ✓

CHEMICAL REACTIVITY OF CYANOGEN CHLORIDE IN AQUEOUS SOLUTION

Quarterly Status Report
(June through August 1972)

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

February 1973



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

Contract DAAA15-71-C-0478

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Project LW662710A095

BROWN UNIVERSITY
Providence, Rhode Island 02912

11-16

FOREWORD

The work described in this report was authorized under Project 1W662710A095. The work described covers the fourth 3 months of study under contract DAAA15-71-C-0478. This period ran from June 1 to August 31, 1972. Dr. Maria Sauer carried out this study in the laboratory of the Principal Investigator at Brown University.

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DIGEST

We have completed our study on nucleophile attack on cyanogen chloride studying salycilhydroxamate ion and arsenate ion.

The reaction between acetaldoxime and cyanogen chloride was also studied over a wide range of pH. Activation parameters for the hydrolysis reaction were found.

The interaction between cobalt(II), manganese(II), chromium(II) has been studied spectrophotometrically and some results are included in this report.

CHEMICAL REACTIVITY OF CYANOGEN CHLORIDE IN AQUEOUS SOLUTION

I. INTRODUCTION.

→ The study on nucleophile attack on cyanogen chloride was completed and activation parameters of the hydrolysis reaction were found.

The study of the interaction between metal ions and cyanogen chloride was continued. ↙

II. EXPERIMENTATION.

A. Analytical Procedures and Methods.

The arsenate ion reaction with ClCN was studied using the colorimetric technique previously described. The salicylhydroxamate reaction was studied following the appearance of the yellow product at 400 nm in a Cary 15 Spectrophotometer. The same spectrophotometer was used to study the reactions between metal ions and ClCN.

B. Reactions Investigated.

Salicylhydroxamic Acid. The reaction was studied at pH values near and above 8, that is the compound was totally in the form of salicylhydroxamate ion. The appearance of the yellow product formed was followed at 400 nm under pseudo first-order conditions in salicylhydroxamate ion. The rate constants were calculated as usual, plotting $\log A_{\infty} - A$ against time and dividing the resulting slope by the total salicylhydroxamate ion concentration.

Arsenate Ion. This reaction was studied at pH 10 increasing the total arsenate concentration at 25°C using the colorimetric technique. At this pH the arsenate is totally in the form ASO_4H^- and the rate constant can be expressed as:

$$k_{obs} = k_{OH}[OH^-] + k_{ASO_4H}[ASO_4H^-]$$

Activation Parameters for the Hydrolysis Reaction of Cyanogen Chloride. The variation of the hydrolysis rate constant with temperature was

studied in the pH range 3-6 and the temperature range 25°C-55°C.

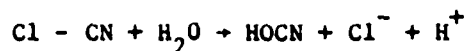
Figure I shows the Arrhenius Plot for this reaction. From the slope of the plot the activation energy was obtained. $E_a = 17.64$ kc/mol.

Using the equations

$$\Delta H^\ddagger = E_a - RT$$

$$k = \frac{k' T}{h} e^{-\Delta H^\ddagger / RT} e^{\Delta S^\ddagger / R}$$

ΔH^\ddagger and ΔS^\ddagger were calculated for the reaction



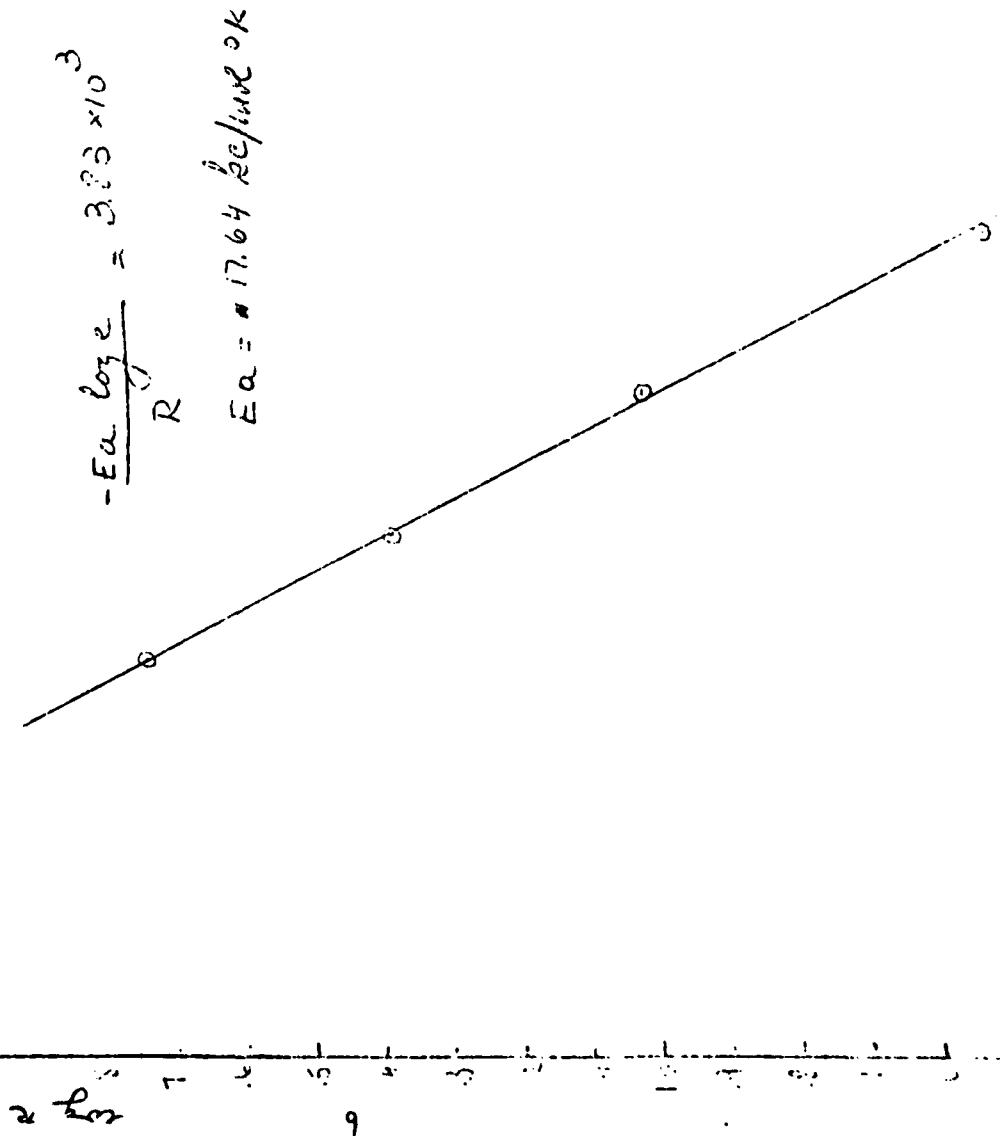
$$\Delta H^\ddagger = 17.04 \text{ kc/mol}$$

$$\Delta S^\ddagger = -29.2 \text{ cal } ^\circ\text{K mol}^{-1}$$

Reactions of Metal Ions and Cyanogen Chloride. The spectra of mixtures of cyanogen chloride and metal ions was studied in the visible and UV, at different concentration rates. All experiments were carried out in a similar way as the ones previously described for Ni(II) and Fe(II).¹ The following table shows the results of these experiments including Co(II), Cr(III) and Mn(II). Cu(II) was also studied but no absorbance was detected in the visible and UV.

1. Edwards, John O., Sauer, M., Quarterly Status Report No. 3.

Figure I
Arrhenius Plot for Hydrolysis of Cyanogen Chloride.



Table

REACTION OF METAL IONS WITH SODIUM CYANIDE AND CYANOGEN CHLORIDE SOLUTIONS

M ⁺⁺	1/X	M ⁺⁺ /NaCN ~ 1/X	M(CN) ₅ + ClCN	M ⁺⁺ /ClCN ~ 1/X	M ⁺⁺ /ClCN > 1/X	M ⁺⁺ /ClCN ~ 1/X
Ni ⁺⁺	1/4	{ 310 nm 284 nm (0.96 x 10 ⁴) = ε 267 nm (2.4 x 10 ⁴) = ε	No change	310 nm 284 nm (0.6 x 10 ⁴) = ε	Slow disappearance of absorbance	No change with time
				267 nm (1.5 x 10 ⁴) = ε	"	"
Fe ⁺⁺	1/6	U.V. absorbance goes up 350-260 mμ with no max.	blue pp - super- natant shows broad abs. 270 - 260 mμ	Broad resonance centered ~280 nm	Absorbance increases with time	No change
				No change	350 - 260 nm increases	Absorption increases
Co ⁺⁺	1/6	max. 260 mμ increases	No peak U.V. increases			Same
				No peak U.V. increases		
Mn ⁺⁺	1/5	Max. 322 mμ				

In addition the attack of CNCl on substituted phenanthroline- Fe(II) complexes was studied. Although a reaction of significant rate was observed and recorded in different conditions of pH, no conclusions can be drawn from these experiments since we cannot assure, under our experimental conditions, the absence of cyanide ion. Since we prepare cyanogen chloride by mixing equimolecular amounts of sodium cyanide and hypochlorite ion so that the ClCN they form is hundredfold in excess over the metal complex, it is evident that a small excess of either cyanide or hypochlorite ion could be in comparable concentration with the complex concentration and therefore react in a significant proportion (cyanide ion is known to attack phenanthroline iron complexes). Therefore, our experiments will be repeated using pure ClCN (gas) conveniently dissolved in water.

Weatherized carbon used in gas masks was extracted with water (0.2 grs/ml) during 24 hrs. The spectrum of the extracting solution (green, pH 8.5) was studied in the absence and in the presence of cyanogen chloride. No change was observed.

The insoluble complex $\text{Cu(NH}_3)_4 \text{CrO}_4$ was also extracted for 24 hrs (0.2 grs/ml) and the spectrum of the now pink solution (pH 7.2) was studied in the absence and in the presence of cyanogen chloride. No changes were observed. However, this does not exclude the possibility of a reaction with cyanogen chloride since changes in pH and concentration have to be taken under consideration.

III. DISCUSSION.

The metal ions-cyanogen chloride reactions require additional study in order to draw any conclusions about the nature of the interaction. This will be done during the next months.

The following table shows rate constant values obtained for all the

Table

Rate of Attack of Nucleophiles on Cyanogen Chloride at 25°C

[ClCN] = 10×10^{-3} M - 32×10^{-3} M

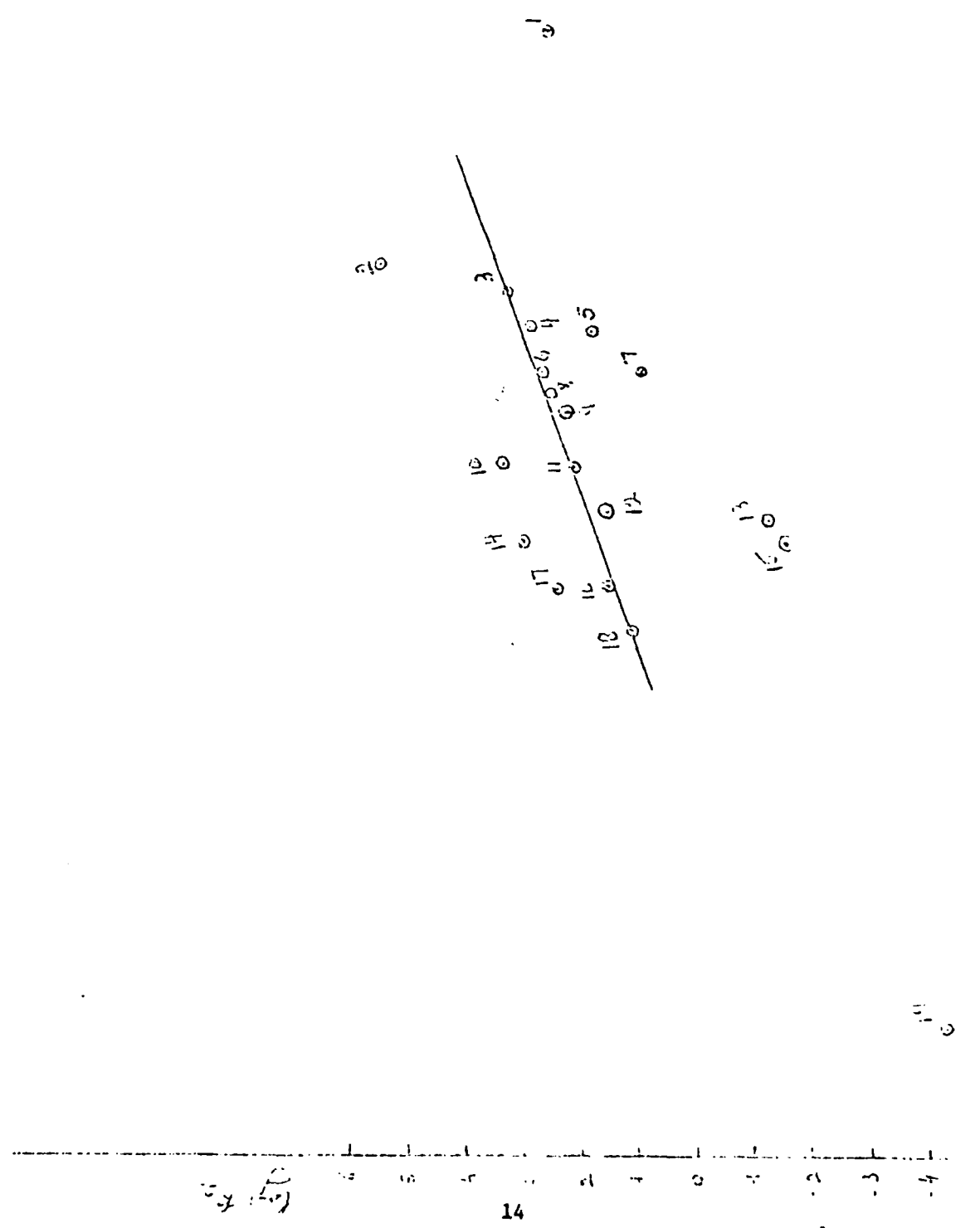
Nucleophile	[Nu] M	pH range	pKa	k_2
1 Hydroxide Ion			15.7	8×10^2
2 Hydroperoxide Ion	0.21 - 0.15	5.7 - 7	11.6	5.3×10^5
3 Piperidine	0.30 - 0.5	6.0 - 8.5	11.2	3.2×10^3
4 Methylamine	0.21 - 0.15	5.5 - 6.6	10.6	1.2×10^3
5 Sec-Butylamine	0.28	2.3 - 8.8	10.5	1.2×10^2
6 Glycine	0.11 - 0.098	5.3 - 7	9.8	8×10^2
7 Tri-Methylamine	0.20	5.8	9.74	0.15×10^2
8 Benzylamine	0.15 - 0.10	5.5 - 6.4	9.37	7.3×10^2
9 Acetaldroximate Ion	0.25 - 0.16	4.8 - 7.6	9.13	3.1×10^2
10 Hydrazine	0.3 - 0.068	1.1 - 5.9	8.1	3.6×10^3
11 Glycineamide	0.09 - 0.05	5.3 - 7	8.1	2.0×10^2
12 Salicylhydroxamate Ion	0.05 - 0.07	8	7.4	43.4
13 Phosphate (PO_4H^-)		5 - 7	7.2	8.7×10^{-4}
14 Dimethylhydrazine	0.21 - 0.15	2.4 - 4.8	6.8	1.5×10^3
15 Arsenate		10	6.77	3.2×10^{-4}
16 γ -Picoline	0.25 - 0.15	8.8 - 9.5	6.0	50.4
17 Hydroxylamine	0.21 - 0.15	3.5 - 4.0	5.96	3.7×10^2
18 Pyridine	0.15 - 0.19	6.0 - 9.7	5.23	20.4
19 Water			-1.7	6.4×10^{-5}
20 H_3O^+				2×10^{-2}

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nucleophiles studied during the past year. A Brønsted plot of some compounds is also included (Figure II). As can be seen, in general, the pattern of reaction is close to the one expected including the abnormal reactivity of some alpha-nucleophiles.

A quantitative index of the alpha effect can be estimated considering the rate constants of hydrazine and glycinamide that have the same $pK_a = 8.1$: $k_{hyd}/k_{glyc} = 18$. This alpha effect index and the Brønsted plot slope ($\beta = 0.37$), agreed fairly well with the correlation found between these two values by Dixon and Bruice. (The alpha effect index interpolated from their plot for a β value 0.37 is 17. These facts suggest a transition state where there is a considerable amount of bond formation between substrate and nucleophiles. In addition, the activation parameters found for the hydrolysis reaction, in particular $\Delta S = -29$ eu also agree with a substantial amount of bond formation in the transition state.

Figure II
 Bronsted Plot, 25°C.



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DOCUMENT CONTROL DATA - R & D

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1. ORIGINATING ACTIVITY (Corporate author) BROWN UNIVERSITY Providence, Rhode Island 02912		2a. REPORT SECURITY CLASSIFICATION UNCL	
		2b. GROUP NA	
3. REPORT TITLE CHEMICAL REACTIVITY OF CYANOGEN CHLORIDE IN AQUEOUS SOLUTION			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) 4th Quarterly Report - June 1972 - August 1972			
5. AUTHOR(S) (First name, middle initial, last name) John O. Edwards and Maria Sauer			
6. REPORT DATE February 1973		7a. TOTAL NO. OF PAGES 18	7b. NO. OF PERS 1
8a. CONTRACT OR GRANT NO. DAAA15-71-C-0478		9a. ORIGINATOR'S REPORT NUMBER(S) None	
b. PROJECT NO. 1W662710A095		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.			
d.			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Chemical Laboratory, Edgewood Arsenal, Maryland 21010 (CPT L. Eng, 301-671-3753/ 3860	
13. ABSTRACT <p>We have completed our study on nucleophile attack on cyanogen chloride studying salicylhydroxamate ion and arsenate ion.</p> <p>The reaction between acetaldoxime and cyanogen chloride was also studied over a wide range of pH. Activation parameters for the hydrolysis reaction were found.</p> <p>The interaction between cobalt(II), managanes(II), chromium(II) has been studied spectrophotometrically and some results are included in this report. ←</p>			

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	ROLE	WT	ROLE	WT	ROLE	WT
Cyanogen Chloride Decontamination C.K. reactivity Hydrylsis of Cyanogen Chloride						