FE-2496-32
Distribution Category UC-90c

KINETICS OF REACTIONS OF CYANIDE AND REDUCED SULFUR SPECIES TO FORM THIOCYANATE

Richard G. Luthy
Samuel G. Bruce, Jr.

Department of Civil Engineering
Environmental Studies Institute
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Date Prepared: August 1978
Date Published: January 1979

Prepared for the United States Department of Energy

Under Contract No. EX-76-S-01-2496

rb

PROLOGUE

In July of 1976, the Department of Energy initiated a comprehensive program for environmental assessment of its high-BTU coal gasification pilot plant installations. The overall objective of the program is to develop the methodology and data base necessary for meaningful assessment of the environmental impact of the coal gasification processes. The environmental characterization efforts at each pilot plant are focused on scalable process units, with the goal of establishing rules and strategy for scaleup to commercial-size installations.

Carnegie-Mellon University, in its role as assistance, coordination and evaluation contractor for the DOE environmental assessment program, has prepared a series of technical documents in support of program objectives and activities within and across the coal gasification facilities. This report represents one in that series. Reports are also available describing the unique C-MU role and summarizing program activities.

ABSTRACT

Interactions of cyanide and reduced sulfur species in aqueous solution can produce thiocyanate. Kinetics of reaction of cyanide and polysulfide, and cyanide and thiocyanate were investigated. Initial rate kinetic data for reaction of cyanide and polysulfide showed the reaction is mixed order and that the order decreases from 1.91 to 1.18 as pH increases from 8.2 to 12; this was largely accounted for by a decrease in reaction order with respect to cyanide as pH increases above the pK_a for hydrogen cyanide. Catalysis and inhibition studies showed that high concentrations of ammonia were inhibitory and that coal char fines were catalytic. The rate of reaction of cyanide and polysulfide is approximately three or more orders of magnitude faster than reaction of cyanide and thiosulfate depending on pH value. A neutral or slightly alkaline solution containing on the order 10^{-3}M or more total sulfide can form polysulfide on exposure to oxygen, and in the presence of cyanide there should be reaction to yield thiocyanate.

TABLE OF CONTENTS

INTRODUCTION

Cyanide, sulfide, and thiocyanate are environmentally significant pollutants in industrial wastewaters from coke manufacturing and iron making, and from coal gasification and liquefaction. These species plus complexes of cyanide and thiocyanate comprise an important group of constituents with regard to treatment and reuse of wastewaters from these industries. Effluent limitation guidelines have been specified for cyanide and sulfide in coal coking, iron making, and related industries (Luthy, Massey, and Dunlap, 1977). Cyanide and thiocyanate can enter into corrosion and deposition reactions with steel process lines and equipment, and therefore have important implications for development of wastewater reuse strategies. The purpose of this paper is to present some aspects of aqueous chemistry of cyanide and sulfur in order to better understand how cyanide may react with sulfide oxidation products to form thiocyanate.

FORMATION OF CYANOGEN COMPOUNDS

Wastewater Characteristics

The occurence of cyanide, sulfide, and thiocyanate in coal coking effluents results from pyrolysis of coal at high temperature. Coke is manufactured in by-product recovery ovens where coal is heated without air at temperatures ranging from 1500 to 2000°F. Coal volatiles are collected in a gas main and cooled, which results in the condensation of tars and flushing liquor. The tar and liquor are separated, and a portion of the liquor is recirculated to flush the gas main. The process produces water which originates from moisture in the coal; the excess liquor is called weak ammonia liquor and may be processed for by-product recovery of ammonia, phenol, and light oils comprised predominately of benzene, toluene, and xylene. Table 1 shows general characteristics of coke plant weak ammonia liquor, and the characteristics of this liquor after processing for ammonia recovery by steam distillation with addition of lime.

At present there are no large commercial scale coal gasification plants or coal liquifaction facilities in this country. However, increased emphasis on augmenting natural gas and petroleum supplies via coal conversion has stimulated a number of research projects, some of which have advanced to substantial pilot plant testing programs. Coal gasification entails the reaction of coal, steam, and air for low BTU gas or oxygen for medium and high BTU gas to convert coal carbon to gaseous constituents. Present process research activity is focused on evaluation of improved efficiencies by use of pressure, bed fluidization, and catalysts (Mills, 1977). Coal liquefaction entails the reaction of coal and hydrogen under temperature and pressure to produce liquid hydrocarbons from coal. Coal gasification and coal liquefaction produce foul condensates which contain many of the same constituents as found in coke plant weak ammonia liquor. The amount of organic contaminants in coal gasification raw product gas quench condensates is dependent on operating variables and coal type. Highest temperature reactors, 2000-3500°F, produce the cleanest product gas and condensates relatively free of organic contamination. Other factors that affect effluent quality are: gas residence time, coal heatup rate, and gas solid mixing (Massey, Luthy, and Pochan, 1978).

Table I

Characteristics of Coal Coking and Coal Conversion Effluents

Parameter mg/ℓ	Coke Plant Weak Ammonia Liquor[1]	Coke Plant Ammonia Still Effluent[2]	Synthane Process By-Product Water[4]	Hygas Process Wastewater[5]	H-Coal Liquefaction Foul Water[6]
COD	2500-10,000	3400-5700	15,000-43,000	3000-5100	88,000 (26,500)
Phenol	400-3000	620-1150	1700-6600	560-900	6800
NH_3-N	1800-6500	22-100	7200-11,000	2600-4600	17,000
NO_3^--N	-----	< 0.2	-----	1-5	< 1
Kjeldhal-N	-----	21-27	-----	4-10	50
P	< 1	0.9	-----	0.5-1.8	-----
CN^-	10-100	1.6-6	0.1-0.6	0.1-0.7	-----
SCN^-	100-1500	230-590	22-200	17-45	-----
$S^=$	200-600	8	-----	60-220	29,000
$SO_4^=$	-----	325-350	-----	60-180	-----
Alkalinity (as $CaCO_3$)	3800-4300[3]	525-920	10,000-20,000	9800-15,000	-----
Conductivity (μmhos/cm)	-----	3500-6000	-----	30,000	-----
pH (units)	7.5-9.1	9.3-9.8	8.5-9.3	7.8-8.0	9.5

Notes:
1. Data Sources: Rubin and McMichael, 1975; Wong-Chong, et al., 1978; Kostenbader and Flecksteiner, 1969; EPA, 1974
2. Luthy and Jones, 1978. Free and fixed leg stripping with addition of lime.
3. Calculated from data of Jablin and Chanko, 1972
4. Johnson, et al., 1977
5. Luthy and Tallon, 1978. Hygas wastewater was comprised of equal volumes of cyclone and quench effluents.
6. Reap, et al., 1977. Stripped foul water with sulfide removed had an average COD of 26,500 mg/ℓ.

Table 1 compares effluent composition for two hydrocarbon bearing coal gasification condensates and a coal liquefaction effluent with coal coking wastewaters. This comparison shows that cyanide, sulfide, and thiocyanate are common to coal coking and coal conversion effluents.

Source of Cyanide and Thiocyanate

At present little specific information is available to explain mechanisms for formation of cyanide or thiocyanate during coal coking or coal conversion. Various authors (Hill, 1945; Nakles, 1977) believe that under conditions existing during coal carbonization and gasification that ammonia released from the coal may be converted to cyanide. Ammonia is formed as a result of release of amino or substituted amino type side chains from the coal structure. Nitrogen which remains in the coal after release of amino compounds is thought to be much more refractory than amino type nitrogen. Hydrogenation conditions during gasification results in more ammonia formation than during carbonization, probably as a result of hydrogen attack of ring bound nitrogen. Cyanide may form during coal coking as a result of reaction of ammonia with C, CH_4, C_2H_2, C_2H_4, and/or CO (Hill, 1945). Thus cyanide production is the result of secondary reactions. Its production is enhanced by high temperatures, as it has not been observed in low temperature ($\sim 400^{\circ}F$) treatment of coal whether by extraction of distillation. It may be derived to a minor extent by pyrolysis of nitrogenous products obtained as a result of coal decomposition, such as from pyridine.

Less is known about the formation of thiocyanate during coal coking and coal gasification. It is not known if thiocyanate may form as a result of gas phase reactions, as there is no documentation showing the presence of gas phase thiocyanate (Hill, 1945; Luthy, et al, 1977). Ammonia and carbon disulfide will react under pressure to produce thiocyanate (Williams, 1948). However, this may not be applicable to coal coking or gasification, because carbon disulfide is a minor component of product gas.

As explained in this paper, it is known that cyanide can react with oxidized products of sulfide to produce thiocyanate in the aqueous phase. The extent to which these reactions may occur in the gas phase are unknown. These reactions presuppose the existence of an oxidizing agent and presumably if there were no oxidizing agent, then the reactions can not proceed to yield thiocyanate. Hence, at present it is not possible to predict the extent to which gas phase cyanide may be converted to thiocyanate. Careful gas phase sampling programs are required in order to answer this question.

Regardless if thiocyanate can be formed in significant quantities as a result of gas phase reactions, there is no question that thiocyanate is found in coal gasification raw product gas quench condensates, coke plant ammonia liquors, and in coke oven gas distribution line condensates and deposits (Luthy, et al,1977; Massey, et al, 1976). A review of possible aqueous phase reaction pathways for production of thiocyanate in coke plant ammonia liquors and in coal gasification plant quench waters was presented in Luthy, et al, 1977. That paper reviewed possible reactions of cyanide with sulfur, and discussed these reactions in light of studies on the oxygenation of sulfide in aqueous solution. A conclusion from that work was that the dominate reaction pathways for formation of thiocyanate with sulfide oxidation products entails reaction of cyanide with polysulfide (S_x^{2-}) or thiosulfate ($S_2O_3^{2-}$). The following discussion interprets those findings in view of sulfur oxidation chemistry and kinetics.

SULFUR-CYANIDE INTERACTIONS

Recent kinetic studies on the oxygenation of sulfide in aqueous solution have revealed the complex nature of these reactions. The stoichiometry of sulfide-oxygen reactions depends on pH, concentration of reactants, and the existence of inhibitory or catalytic substances. In the pH range of 6.5 to 8.0 Chen and Morris (1972a) found that at high sulfide concentration there is maximum polysulfide formation. Thiosulfate is the principal product in laboratory solutions at pH greater than 8.5 regardless of the sulfide to oxygen ratio. Some sulfite (SO_3^{2-}) may form and is slowly oxidized to sulfate, or sulfite may react with sulfur of polysulfide to form thiosulfate. Eventually all sulfur and its oxyanions will be oxidized to sulfate in the presence of oxygen. O'Brien and Birkner (1977) concluded that a high total sulfide to oxygen ratio, S^{2-}_{tot}/O_2, along with a residual total sulfide concentration of more than 10^{-3}M leads to the formation of polysulfide.

The second dissociation constant for sulfite, $HSO_3^- = H^+ + SO_3^{2-}$, has pK_2 of 7.2. Thus sulfite becomes dominate as pH increases. Also the equilibrium shown in equation (1) shifts to favor thiosulfate rather than sulfite and sulfur at increasing pH values.

$$HSO_3^- + S = S_2O_3^{2-} + H^+ \tag{1}$$

Hence the lack of polysulfide as an oxidation product of sulfide at pH greater than 8.5 may result from its consumption to form thiosulfate.

Polysulfide ions, S_x^{2-}, form through sequential combinations of neutral sulfur atoms with sulfide. Schwarzenback and Fisher (1960) have found that the polysulfuration index, x, can be 2 to 5, but tetra- and pentapolysulfide dominate in aqueous polysulfide solutions. The second dissociation constants for H_2S_4 and H_2S_5 are $10^{-6.3}$ and $10^{-5.7}$ respectively (Schwarzenbach and Fisher), 1960). Thus at pH values greater than 7.3, S_4^{2-} and S_5^{2-} are the principal forms of the polysulfide ion.

As a result of these studies it is concluded that possible reactions of cyanide with sulfide oxidation spieces may proceed according to the reactions summarized in Figure 1. This figure incorporates the sulfide oxygenation pathway proposed by Chen and Morris (1972a) and cyanide chemical reactions with sulfur compounds reviewed in Luthy, et al., (1977) and the equilibrium represented by equation 1. Data presented in Table 1 shows that coke plant weak ammonia liquors and coal conversion quench waters typically have total sulfide concentration ranging from 5 x 10^{-3} to more than 10^{-2}M. This condition should favor the formation of polysulfide upon contact with oxygen at near neutral or slightly alkaline conditions.

The reaction of cyanide with polysulfide shown in Figure 2 may be described as

$$S_xS^{2-} + CN^- \rightarrow S_{x-1}S^{2-} + SCN^- \tag{2}$$

In this reaction one polysulfide-sulfur atom, poly-S^o, is reduced from oxidation state 0 to -1 while the cyanide-carbon atom is oxidized from oxidation state +2 to +3.

Cyanide is also reactive with thiosulfate. This reaction may be described as

$$S_2O_3^{2-} + CN^- \rightarrow SO_3^{2-} + SCN^- \tag{3}$$

One thiosulfate sulfur atom undergoes oxidation from oxidation state +2 to +4 while the other thiosulfate sulfur atom is reduced from the +2 to the -1 oxidation state.

Thus, there are two predominate pathways for the reaction of cyanide with sulfide oxidation products to yield thiocyanate. The experimental portion of this study presents results of investigation of the kinetics of these reactions.

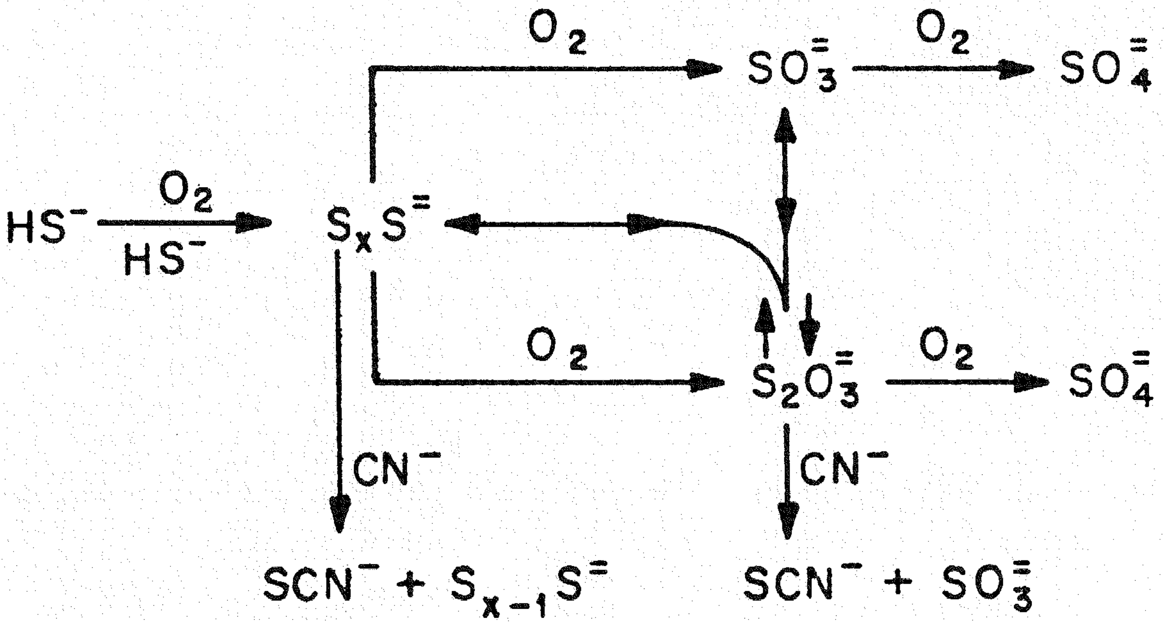

Figure 1 Possible reactions of cyanide with reduced sulfur species in aqueous solution to yield thiocyanate.

EXPERIMENTAL

Reagents:

All stock solutions were prepared using certified analytical salts, acids and bases. Each solution was prepared in laboratory distilled water and stored under refrigeration.

Buffer solutions were prepared at pH 8.2, 10, and 12 at 0.1M strength. The pH 12 buffer was prepared with 10.6 g/ℓ Na_2CO_3; the pH 10 buffer with 4.2 g/ℓ $NaHCO_3$ and 5.3 g/ℓ Na_2CO_3; the pH 8.2 buffer with 8.4 g/ℓ $NaHCO_3$. Hydrochloric acid (6N) was used for adjusting pH to the appropriate value.

A 10 g/ℓ stock cyanide solution (CN^-) was prepared by diluting 25.1 g KCN and approximately 2 g NaOH pellets to one liter. This solution was standardized regularly through the course of the experimentation.

A strong solution of polysulfide was prepared by placing 10 to 20 g of sodium tetrapolysulfide (Ventron-Alfa Products) in one liter of buffer solution. A portion of the polysulfide solution was analyzed immediately following preparation to determine the concentration. The solution was then diluted with buffer as required for the experiment. It was found that the polysulfide salt was unstable when exposed to air and moisture, and that the polysulfide solution would gradually degrade even when refrigerated in a closed container. For these reasons, polysulfide solutions were prepared fresh daily and standardized immediately before use.

Standard thiosulfate solutions were prepared by dissolving $Na_2S_2O_3$ in pH 12 buffer solution.

Analytical Procedures:

Cyanide concentrations were measured as total cyanide after distillation with magnesium chloride reagent. The pyridine-barbituric acid colorimetric procedure was used to measure cyanide in the distillate. Stock syanide solution was standardized by the silver nitrate titrimetric method (APHA, 1975).

Polysulfide was measured by a procedure adopted from Krachner (1970). In this procedure polysulfide is reacted with excess cyanide under anaerobic conditions in boiling boric acid to form one molecule of thiocyanate for each polysulfide sulfur atom at oxidation state zero, poly-S^o. Fifty mℓ of 200 g/ℓ boric acid solution were placed in a 125 mℓ beaker, covered with a watch glass and brought to a strong boil to expel oxygen. While the solution was still hot, there was then added a measured amount of polysulfide containing not more than 200 mg poly-S^o followed immediately by 2 mℓ of 10% cyanide. The solution was brought to a second boil and the reaction went to completion in about five minutes owing to the rapid rate at elevated temperature and the presence of excess cyanide. Boiling was continued for another 10 minutes to volatize excess cyanide. The procedure must be performed in a laboratory hood to assure no contact with highly toxic hydrogen cyanide gas evolved. The sample was cooled and analyzed for thiocyanate.

The thiocyanate analytical method used in the kinetic studies with polysulfide is based on a copper-pyridine method developed by Kruse and Mellon (1951) and Danchik and Boltz (1968). This method has been discussed in Luthy et al, (1977); details of the procedure are provided in Luthy (1977). Thiocyanate is reacted with cupric copper and pyridine to form dithiocyanatopyridine

$$\begin{aligned} 2\,SCN^- + Cu^{2+} &\rightarrow Cu(SCN)_2 \\ Cu(SCN)_2 + 2\,C_5H_5N &\rightarrow Cu(C_5H_5N)_2(SCN)_2 \end{aligned} \qquad (4)$$

This forms a light green precipitate which is extracted with chloroform. The reaction is stoichiometric and the resulting color of the chloroform adheres to Beer's law to permit spectrophotometric determination at 407 nm against a chloroform blank. The first step in this procedure is addition of 1:1 HNO_3 to lower sample pH to 3.0 to 3.5. This results in precipitation of polysulfide in the sample as a cloudy white precipitate. The sample is coarse filtered after pH adjustment, and then filtered through 0.45 μ membrane filter to remove sulfur prior to addition of reagents.

The thiocyanate analytical procedure has proved successful on a variety of wastewaters; the method was checked for interferences from the reactants and oxidation products encountered in this study. No problems were identified except with solutions containing on the order of 0.2M thiosulfate. This solution resulted in a cloudy sulfur precipitate in the chloroform which could not be removed easily by filtration. In this case thiocyanate was measured instead by the ferric nitrate procedure (APHA, 1975).

Thiosulfate solutions were standardized by titrating against KI and standard bi-iodate.

Approach:

The reaction order was determined with respect to each constituent in the cyanide-polysulfide reaction at pH 8.2, 10, and 12. These values were chosen somewhat arbitrarily; however, it should be noted that pH values of 10 and 12 are above the pK_a for hydrogen cyanide, $pK_a = 9.2$, and a pH value of 12 is that recommended for sample preservation for analysis of cyanide and thiocyanate (APHA, 1975). A pH value of 8.2 was selected because it is representative of the pH of coal conversion gas quench waters; this pH is above pK_2 for tetrapolysulfide and below pK_a for hydrogen cyanide.

The determination of the order and reaction rate for the cyanide-polysulfide reaction was performed by the Van't Hoff (differential) method. This procedure is based on the following assumption of a general kinetic equation

$$\frac{dSCN^-}{dt} = R_i = k_{a+b} \, (CN_{tot})_o^a \, (poly\text{-}S^o)_o^b \tag{5}$$

where

R_i = initial reaction rate, M/ℓ - min

k_{a+b} = specific rate constant

CN_{tot} = molar concentration of HCN + CN^-

poly-S^o = molar concentration of polysulfide-sulfur. The molar ratio of poly -S^o to total sulfur in tetrapolysulfide (Na_2S_4) is 3 to 4; but because Na_2S_4 decomposes, polysulfide solutions must be standardized regularly prior to use.

a = reaction order with respect to CN_{tot}

b = reaction order with respect to poly-S^o

This expression written in logarithmic form becomes:

$$\log R_i = \log k_{a+b} + a \log (CN_{tot})_o + b \log (poly\text{-}S^o)_o \tag{6}$$

The equation shows the sum of linear terms for each component of the reaction. The value of <u>a</u> can be determined from initial rate tests in which the concentration of poly-S^o is held constant and different concentrations of cyanide are used. Thus equation (6) can be written as:

$$R_i = k_a \, (CN_{tot})_o^a \tag{7}$$

where k_a is the rate constant with the same initial poly-S^o concentration and varying cyanide levels. Similarily, the value of b can be obtained by conducting tests in which the concentration of cyanide is kept at the same level with different initial poly-S^o concentrations.

$$R_i = k_b \, (\text{poly-}S^o)_o^b \tag{8}$$

where k_b is the rate constant with same initial cyanide concentration and different initial poly-S^o concentrations.

The order of reaction obtained by the differential method entails the determination of slopes of initial production rates. The change in concentration of reactants is small in the initial stages of the reaction; therefore, equations (7) and (8) will not change materially even if the reactant held at the same initial concentration is not in excess. In logarithmic form equation (7) becomes:

$$\log R_i = \log k_a + a \log (CN_{tot})_o \tag{9}$$

Thus by plotting measured values of R_i logarithmically against $(CN_{tot})_o$, linear plots should be obtained with slope equal to a. Likewise, the logarithmic form of equation (8) is:

$$\log R_i = \log k_b + b \log (\text{poly-}S^o) \tag{10}$$

a logarithmic plot of variation of initial rate with different poly-S^o levels should yield a straight line with a slope b.

The overall specific rate constant, k_{a+b}, in equation (5) can be found by substituting experimental data for R_i, CN_{tot}, and poly-S^o, and using values of a and b as established from the logrithmic plots.

Six different sets of experimental kinetic studies were performed to determine the rate and order of the reaction with respect to each reactant at three pH values. The experimental technique employed concentrations of cyanide and polysulfide to yield in a short interval an easily determined amount of thiocyanate.

The polysulfide solution was standardized and diluted with the proper buffer to 138 mg/ℓ as poly-S^o (4.3×10^{-3} M poly-S^o). Two hundred mℓ of this solution was placed in a 250 mℓ Erlenmeyer flask. Cyanide was added at concentrations ranging from 26 to 780 mg/ℓ (1×10^{-3} to 3×10^{-2}M) by pipeting stock solution into the flask. This operation insured an accurate measure of initiation time and prevented volatilization of cyanide since only small amounts of stock cyanide were required and no pH adjustment had to be made to the stock solution prior to the experiment. The reaction was allowed to proceed for five minutes, during this period the flasks were swirled several times to assure a uniform mixture. The reaction was stopped by adding several mℓ of 1:1 HNO_3 to lower sample pH to a value between 3.0 and 3.5. This caused the polysulfide solution to change from a characteristic golden brown color to a milky yellow and then to a white precipitate. The precipitate was removed by coarse filtering and then by filtering through 0.45 μ membrane filter to yield a clear sample which was analyzed for thiocyanate.

A special series of tests were performed at pH of 8.2 to check for cyanide losses by votatilization. These tests consisted of adding cyanide to samples containing no polysulfide, waiting for five minutes, and then analyzing for cyanide. This test showed that there was no loss of hydrogen cyanide over the time interval employed here. Another set of tests were performed to ensure that the reaction was indeed stopped by acidification and filtration. Replicate kinetic test samples were acidified and filtered and allowed to stand from several minutes up to four hours prior to analyzing for thiocyanate. Analysis showed that there was no increase in thiocyanate over this period.

Catalysis and Inhibition:

Additional kinetic studies were performed at pH of 8.2 to evaluate potential catalytic and inhibitory effects of inorganic and organic species. Compounds selected for this work were chosen by their prevalence in coal coking and coal conversion wastewaters and by reported effects on sulfur oxidation kinetics. Chen and Morris (1972b) studied the effects of addition of various metal ions and organic compounds on sulfide oxidation. Other studies in this area have been performed by Krebs (1929), Bulfer, et. al. (1936), and Cline and Richards (1969). As a result of this work, the following compounds were selected for study of the effect of small additions on cyanide-polysulfide reaction kinetics: B, Ba^{2+}, Ca^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, NH_4^+, Zn^{2+}, phenol, ferricyanide, and coal char fines. Coal char fines were obtained from Hygas coal gasification pilot plant Run 72.

It is recognized that cyanide can form a variety of complex compounds with species such as copper, nickle, and zinc. This introduces another factor which may have significant effects on cyanide-polysulfide kinetics. It was not the intent of this study to separate these possible effects. The studies presented here are perhaps purely abstract in nature since little is understood about interactions leading to catalysis or inhibition. The final results are at least indicative as to the importance that these substances may have on thiocyanate production.

RESULTS

Cyanide-Polysulfide Reaction:

Experimental results for estimation of initial reaction rates and order or reaction for formation of thiocyanate from reaction of cyanide and polysulfide are presented in Figures 2, 3, and 4 for pH values 8.2, 10, and 12 respectively. These data conform to the straight line relationship given by equations (9) and (10). The order of the reaction with respect to each constituent is given by the slopes of the initial reaction rate plots, and the rate constant for the reaction at each pH value can be computed according to equation (6). Emperically determined kinetic coefficients for the cyanide-polysulfide reaction system are summarized on Table II. The reaction kinetics are approximately overall first order at pH of 12. The reaction order increases with decreasing pH value; at pH of 8.2 the reaction is close to second order.

The catalysis and inhibition studies with the cyanide-polysulfide reaction system were performed in the same manner as for the initial rate studies with the only difference being the addition of a new agent. The results of this work are presented in Table III as R/Ro where Ro is the initial rate of reaction without the agent and R is the rate of reaction with the agent present at the specified concentration. These studies were performed at pH of 8.2 and further study is required to determine if pH may have a large effect on catalysis and inhibition.

Because of the noticeable effect of ammonia and coal char fines, additional tests were performed with a range of concentration of ammonia as an inhibitor and with a range of concentration of coal char fines as a catalysis agent. Figure 5 is a plot of percent decrease of thiocyanate production versus ammonia

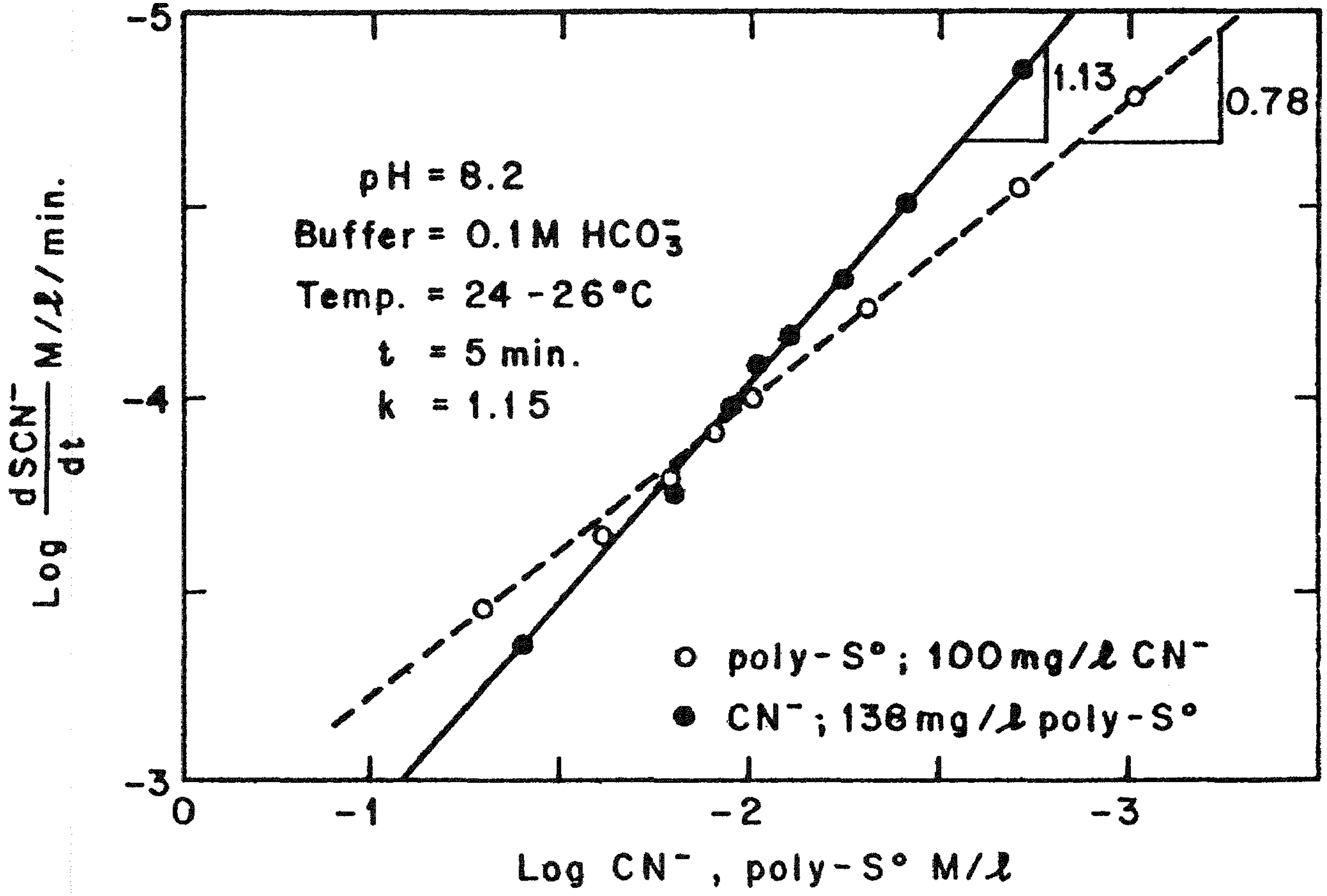

Figure 2 Initial rate kinetic data for the polysulfide-cyanide reaction at pH = 8.2

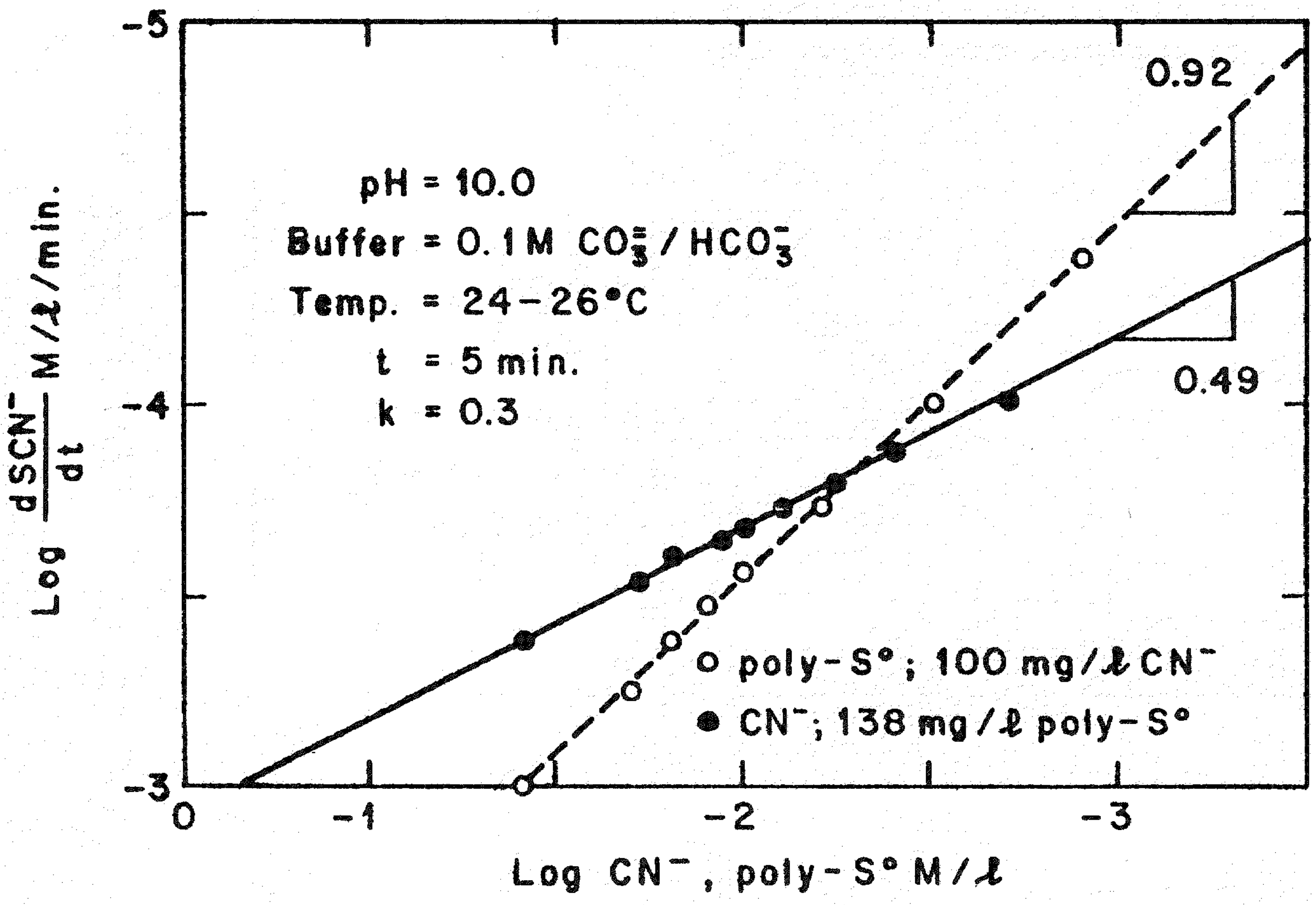

Figure 3 Initial rate kinetic data for the polysulfide-cyanide reaction at pH = 10

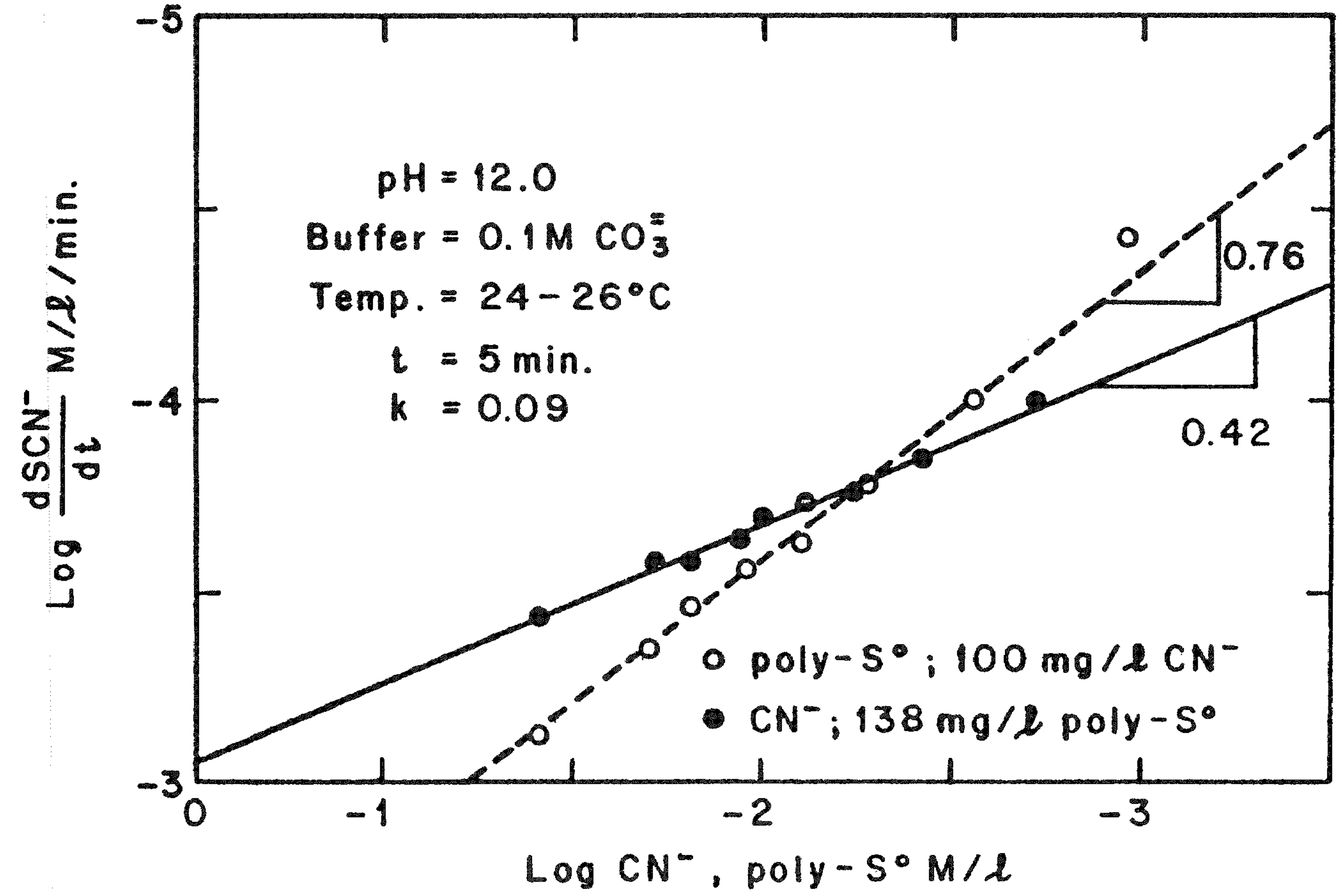

Figure 4 Initial rate kinetic data for the polysulfide-cyanide reaction at pH = 12

Table II

KINETIC COEFFICIENTS FOR THE CYANIDE-POLYSULFIDE REACTION SYSTEM

KINETIC PARAMETER	pH VALUE		
	8.2	10.0	12.0
Order with respect to CN_{tot}, a	1.13	0.49	0.42
Order with respect to poly-S^{o}, b	0.78	0.92	0.76
Overall order, a + b	1.91	1.41	1.18
Specific rate constant k_{a+b}	1.15	0.30	0.09

Notes: Temp. = 24-26°C, 0.1 M carbonate buffers, units are consistent with M/ℓ - min reaction rate.

TABLE III

INHIBITORY AND CATALYTIC EFFECTS OF VARIOUS COMPONENTS ON THE CYANIDE-POLYSULFIDE REACTION SYSTEM

SUBSTANCE	SALT USED	CONCENTRATION M/ℓ	R/Ro	Notes
Boron (B)	H_3BO_3	9.25×10^{-4}	1.06	
		9.25×10^{-3}	.83	
Calcium (Ca^{2+})	$CaCl_2$	2.5×10^{-4}	1.03	
		2.5×10^{-3}	.99	
Magnesium (Mg^{2+})	$MgCl_2 \cdot 6H_2O$	4.11×10^{-4}	1.12	White cloudiness
		4.11×10^{-3}	.99	
Ferricyanide ($Fe(CN)_6^{3-}$)	$K_3Fe(CN)_6$	4.72×10^{-5}	.99	A strong color imparted
		4.72×10^{-4}	.50	
Barium (Ba^{+2})	$BaCl_2 \cdot 2H_2O$	7.28×10^{-7}	1.03	
		7.28×10^{-5}	1.03	
Manganese (Mn^{2+})	$MnSO_4 \cdot H_2O$	1.82×10^{-6}	1.03	
		1.82×10^{-4}	1.02	
Zinc (Zn^{2+})	$ZnSO_4 \cdot 7H_2O$	1.53×10^{-6}	1.29	A white precipitate formed
		1.53×10^{-4}	1.06	
Nickle (Ni^{2+})	$NiCl_2 \cdot 6H_2O$	1.70×10^{-6}	1.19	Dark color developed
		1.70×10^{-4}	.86	
Copper (Cu^{2+})	$CuSO_4 \cdot 5H_2O$	1.57×10^{-6}	1.12	Initial yellow color then returning to normal
		1.57×10^{-4}	.99	
Phenol	C_6H_5OH	1.06×10^{-2}	.99	
		5.31×10^{-2}	.92	
Ammonia (NH_4^+)	NH_4Cl	5.54×10^{-2}	.70	
		2.77×10^{-2}	.63	
Char	Gasification coal char fines	1000 mg/ℓ	.79	
		10000 mg/ℓ	1.89	

Notes: pH = 8.2, 0.1 M HCO_3^- buffer

$CN_{tot} = 3.85 \times 10^{-3}$ M

poly-$S^o = 4.31 \times 10^{-3}$M

concentration, and Figure 6 is a plot of percent increase in production of thiocyanate versus concentration of char fines.

Cyanide-Thiosulfate Reaction:

An extensive analysis of kinetics of reaction of cyanide and thiosulfate was not performed owing to data presented on this reaction by Bartlett and Davis (1958). These authors measured the rate of reaction between sodium cyanide and sodium thiosulfate in water and found that the reaction proceeded irreversibly, and that the cyanide ion is a stronger thiophile than the sulfite ion. The reaction at 25°C with an ionic strength of 0.09M was second order with a rate constant of 2.3×10^{-3} ℓ/M-min.

The value of this rate constant was confirmed in this study within a factor of two by conducting initial rate studies with equimolar solutions of cyanide and thiosulfate at a pH of 12 in 0.1M carbonate buffer. Here cyanide and thiosulfate were reacted at 0.19M concentration for twenty minutes. In these tests the production of thiocyanate was measured by the ferric nitrate procedure after lowering pH and filtering precipitated sulfur.

DISCUSSION

In a previous paper (Luthy, et.al., 1977) initial observations on the formation of thiocyanate from the cyanide-polysulfide aqueous reaction were investigated. Those studies were preliminary batch test reactions and provided only general information about the reaction rate. The present study was performed in order to better understand the complexities of this system and to increase knowledge about interactions between sulfur and cyanide chemical systems. The data presented here involves initial rate kinetic studies on the cyanide-polysulfide reaction pathway and also entails observations on a

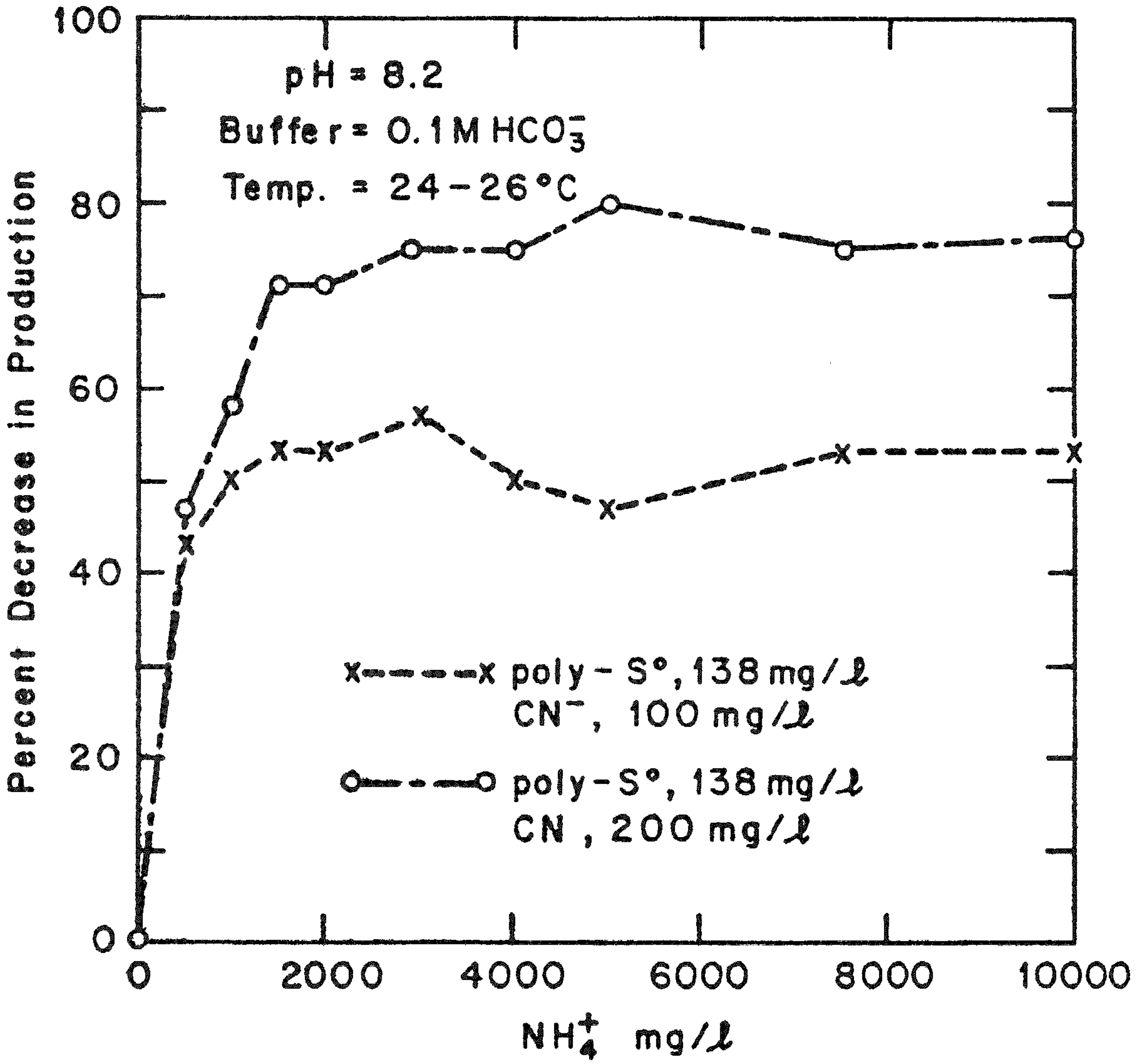

Figure 5 Inhibitory effect of ammonium on thiocyanate production via the polysulfide-cyanide reaction pathway.

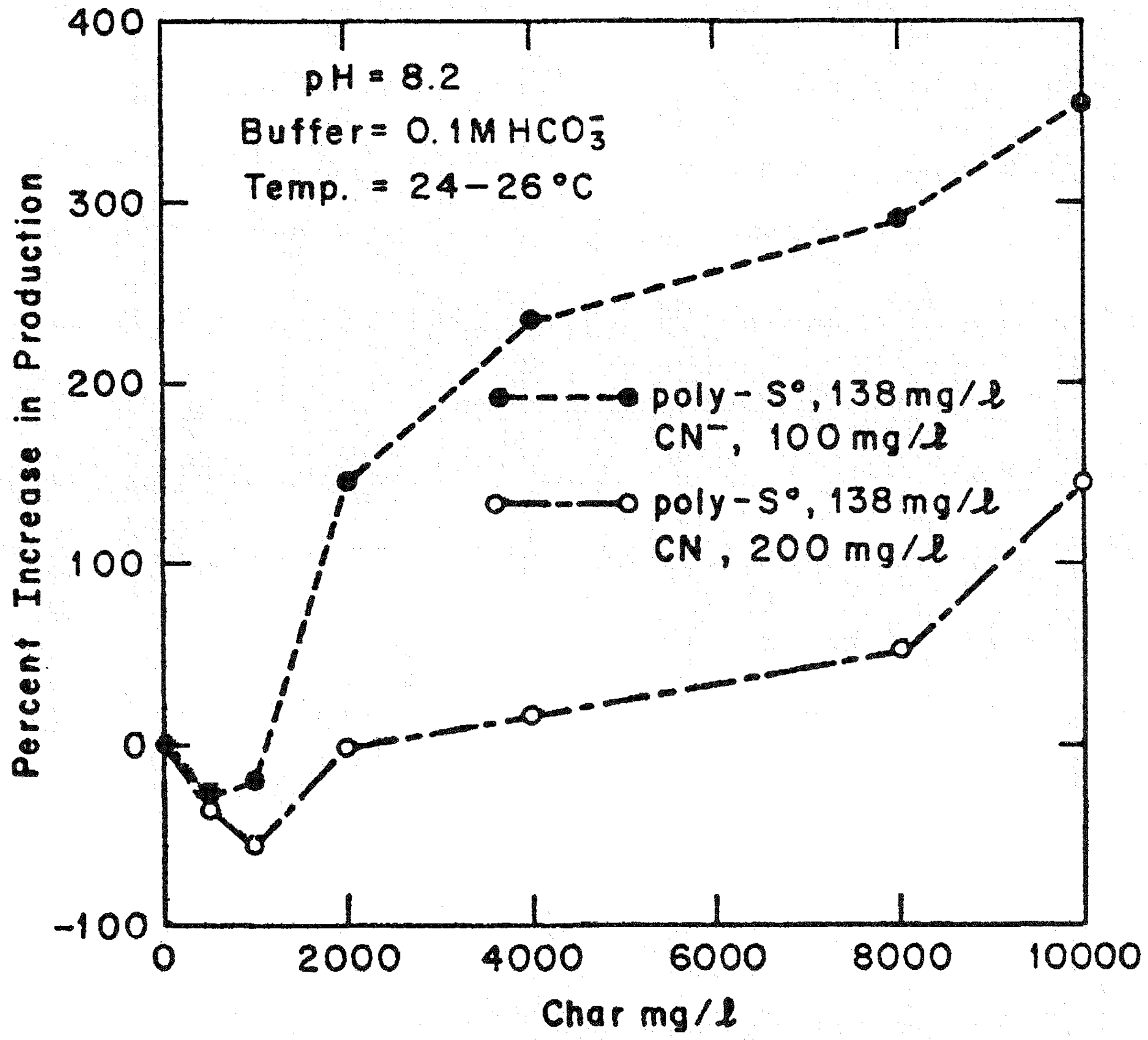

Figure 6 Catalytic effect of coal char fines on thiocyanate production via the polysulfide-cyanide reaction pathway.

small group of possible catalytic and inhibitory agents.

The initial rate kinetic data for the cyanide-polysulfide reaction showed the reaction is mixed order and that the order decreases from 1.91 to 1.18 as pH increases from 8.2 to 12.0. This is largely accounted for by a pronounced decrease in the reaction rate with respect to cyanide as pH is increased above the pK_a for hydrogen cyanide. The rate constant for cyanide is observed to decrease from 1.13 to 0.42 over the pH range from 8.2 to 12. The specific rate constant for the cyanide-polysulfide reaction decreases from 1.15 to 0.09 over this pH range. These findings show that cyanide-polysulfide reaction is rapid, and that the reaction rate increases with pH.

Screening studies on the cyanide-thiosulfate reaction generally confirmed the second order specific rate constant presented by Bartlett and Davis (1958). The significance of the rates of reaction of cyanide with polysulfide and with thiosulfate is shown in Figure 7 which compares predicted initial rates of reaction of cyanide with polysulfide at pH of 8.2 and 12.0 with predicted rates of reaction of cyanide with thiosulfate. These data show that the reaction rate with polysulfide at pH of 8.2 is approximately three order of magnitudes faster than that with thiosulfate. Note also that the rate of reaction of cyanide with polysulfide is sensitive to pH at low concentration levels of reactants.

These findings indicate that the cyanide-polysulfide reaction pathway can dominate over the cyanide-thiosulfate reaction pathway to form thiocyanate. However, in a system initially containing cyanide and sulfide the thiocyanate production kinetics must be viewed in light of sulfide oxygenation pathways. In a system containing on the order of 10^{-3} M or more sulfide in a slightly alkaline solution, the sulfide oxygenation pathway as discussed in Figure 1 should prevail. In this case polysulfide exists as a sulfide oxidation product, and results of

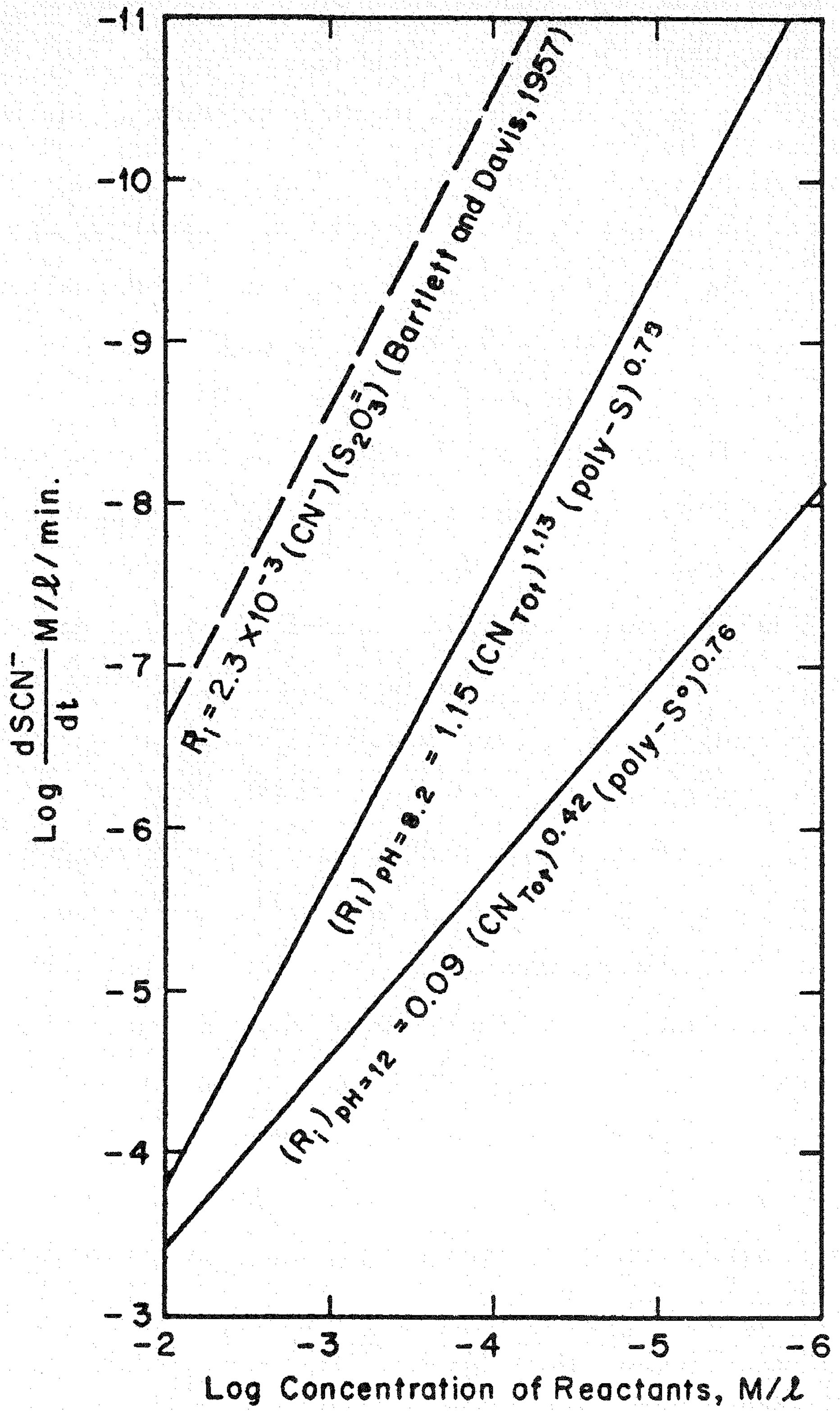

Figure 7 Comparison of production rates for formation of thiocyanate from reaction of equimolar concentrations of cyanide and polysulfide, and cyanide and thiosulfate.

this study show that as polysulfide is produced it can react rapidly to form thiocyanate. If thiosulfate were the predominate sulfide oxidation product, the production of thiocyanate from cyanide would be greatly reduced.

Inhibition and catalysis studies demonstrated the effect of various compounds on the cyanide-polysulfide reaction. Of the metal ions studied, Ca^{2+}, Mg^{2+}, Ni^{2+}, and Zn^{2+} had the greatest catalytic effect at their lower concentration, when larger concentrations were employed metal ions inhibited the reaction rate slightly. Though these compounds had an effect on the reaction rate, their effect was relatively small at the concentrations employed here. Metals such as zinc, nickle, and copper can form complexes with cyanide and it would be expected that extensive complexation would reduce the reactivity of cyanide with polysulfide. The metal ion concentrations used in the catalytic-inhibitory tests were on the order of a factor of twenty or less than the total analytical concentration of cyanide. This may explain the relatively small effect on reaction rate. Screening studies showed that complexed cyanides may not be reactive with polysulfide as no reaction was observed between polysulfide and ferricyanide. This finding is consistent with Bartlett and Davis's (1959) observation that ferricyanide or ferrocyanide ions do not attack elemental (S_8) sulfur at a measurable rate.

The cyanide-polysulfide reaction was inhibited by approximately 50 to 80% at pH of 8.2 in the presence of more than 2000 mg/ℓ ammonia-nitrogen. Small concentrations of coal char fines also had an inhibitory effect, but at concentrations greater than several thousand mg/ℓ, coal char fines had a pronounced catalytic effect. This effect appears to be more pronounced for lower cyanide concentrations. Phenol was the only soluble organic constituent investigated and it showed little effect on the reaction of cyanide and polysulfide.

Though not evaluated here, the reaction of cyanide with thiosulfate is expected to show a pH dependency. Equation (1) shows that, as pH is decreased, thiosulfate equilibrium shifts to favor sulfite and sulfur (Latimer and Hildebrand, 1951; Chen and Morris, 1972a). In the presence of HS^- this would result in the formation of polysulfide as indicated by equation 1.

CONCLUSIONS

Procedures and data have been presented for the study of aqueous phase formation of thiocyanate resulting from interactions between cyanide and polysulfide, and cyanide and thiosulfate. Experimental data were used to describe the production of thiocyanate from polysulfide; it was found that the reaction order decreases and rate increases as pH is varied from 8.2 to 12. The rate of production of thiocyanate from polysulfide is shown to be approximately three orders of magnitude or more faster, depending on pH, than the rate of formation of thiocyanate from thiosulfate.

These experiments have implications for describing quality changes which may result when processing wastewaters containing sulfide and cyanide in the pH range of 6.5 to 8. Upon exposure to oxygen, sulfide may be oxidized to polysulfide if S^{2-}_{tot} is on the order of 10^{-3}M or more. This would cause reaction of cyanide to form thiocyanate. Thus, cyanide would be converted from a highly toxic and volatile compound to a relatively non-toxic, strongly ionic specie. If it is desired to process wastewaters for reuse, thiocyanate can present problems owing to its tendency to enter into corrosion and deposition reactions with steel process units.

ACKNOWLEDGEMENT

This work was sponsored by the Department of Energy in conjunction with C-MU's efforts to assist, help coordinate, and provide evaluative services in the DOE coal gasification environmental assessment program.

Dennis Mialki and James C. Cook assisted with the experimental studies.

REFERENCES

American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 14th Ed, APHA, Washington, D. C. (1975)

Bartlett, P. D. and R. E. Davis, J. Am. Chem. Soc., 80, pt. 2, 2513 (1958)

Bulfur, G., A. J. Boyle, and L. H. Baldinger, J. Am. Pharmaceutical Soc., 25, 1104 (1936)

Chen, K. Y. and J. C. Morris, Env. Sci. and Tech., 6 (6), 529 (1972a)

Chen, K. Y. and J. C. Morris, J. San. Eng. Div., Am. Soc. of Civil Eng., 98: SA1, 215 (1972b)

Cline, J. D. and F. A. Richards, Env. Sci. and Tech., 3 (9), 838 (1969)

Danchik, J. M. and D. F. Boltz, Anal. Chem., 40 (14), 2215 (1968)

EPA, Development Document for Effluent Limitations Guidelines and Performance Standards for the Steel Making Segment of the Iron and Steel Manufacturing Point Source Category, EPA-44011-74-024a, Washington, D. C. (1974)

Hill, W. H., "Recovery of Ammonia, Cyanogen, Pyridine, and Other Nitrogenous Compounds from Industrial Gases" in Chemistry of Coal Utilization, Vol 2, H. H. Lowry, Ed., J. Wiley and Sons, N.Y. (1945)

Jablin, R. and G. P. Chanko, paper presented at AICHE Advances in Water Pollution Control Meeting, New York (1972)

Johnson, et al., Pittsburgh Energy Research Center Report, DOE/PERC/RI-77/13, November (1977)

Kostenbader and Flecksteiner, J. Water Pol. Control Fed., 41 (2), part 1, 199 (1969)

Krachner, J. K., Analytical Chemistry of Sulfur and Its Compounds, Wiley-Interscience N.Y. (1970)

Krebs, H. A., Biochim. Z, 204, 343 (1929)

Kruse, J. M. and M. G. Mellon, Sewage and Indus Wastes, 23, 1402 (1951)

Latimer, W. M. and J. H. Hildebrand, Reference Book of Inorganic Chemistry, 3rd Ed., Macmillan Co., New York (1951)

Luthy, R. G., "Manual of Methods: Preservation and Analysis of Coal Gasification Wastewaters," ERDA, NTIS No. FE-2496-8 (1977)

Luthy, R. G. and L. D. Jones, "Biological Treatment of Coke Plant Wastewater," Center for Energy and Environmental Studies, Carnegie-Mellon University, Dec. (1978)

Luthy, R. G., S. G. Bruce, Jr., R. W. Walters, and D. V. Nakles, "Identification and Reactions of Cyanide and Thiocyanate in Coal Gasification Wastewaters, 50th Annual Conf. Water Pol. Control Fed., to appear Jour. WPCF (1977)

Luthy, R. G., M. J. Massey, and R. W. Dunlap, "Analysis of Wastewaters from High BTU Coal Gasification Plants," Proc. 32nd Purdue Industrial Waste Conf., Purdue Univ., Lafayette, Ind. (1977)

Luthy, R. G. and J. T. Tallon, "Experimental Analysis of Biological Oxidation Characteristics of Hy gas coal Gasification Wastewater," DOE, NTIS FE-2496-27 (1978)

Massey, M. J., R. G. Luthy, and M. J. Pochan, "C-MU Technical Contributions to the DOE Environmental Assessment Program," DOE FE-2496-39 (1978)

Massey, M. J., F. C. McMichael, and R. W. Dunlap, Chem. Eng., Aug. 30, 109 (1976)

Mills, G. A., CHEMTECH, July, 418 (1977)

Nakles, D. V., Ph.D. Thesis, Dept. of Chem. Eng./Engineering and Public Policy, Carnegie-Mellon University (1977)

O'Brien, D. J. and F. B. Birkner, Env. Sci. and Tech., 11 (12), 114 (1977)

Rubin, E. S. and F. C. McMichael, Env. Sci. and Tech., 9 (2) 112 (1975)

Reap, E. J., G. M. Davis, M. J. Duffy, and J. H. Koon, paper presented at the 32nd Purdue Industrial Waste Conf.,Purdue University, Lafayette, Ind. (1977)

Schwarzenbach, G. and A. Fisher, Helv. Chem. Acta, 169, 1365 (1960)

Williams, H. E., Cyanogen Compounds, 2nd Ed., Edward Arnold and Co., London, (1948)

Wong-Chong, G. M., S. C. Caruso, and T. G. Patarlis, paper presented at 84th National Meeting AICHE, Atlanta, Feb. (1978)

☆U.S. GOVERNMENT PRINTING OFFICE: 1979–640-014/4564