Hydrolysis of Carbonyl Sulfide in a Gas-Liquid Reactor

W. R. Ernst
School of Chemical Engineering
Georgia Institute of Technology
Atlanta, GA 30332

M. S. K. Chen
Air Products and Chemicals, Inc.
Allentown, PA 18105

Carbonyl sulfide (COS) is often present in minor amounts in petroleum refinery gases and in larger amounts in coal gasification product streams. COS poses a special problem in sour gas purification processes since it is neither readily separated from the desired gas nor easily hydrolyzed by known gas treating solvents under ordinary conditions. It is a contaminant in a Claus plant feed stream which is not readily converted to sulfur. It is necessary to remove COS from fuel gases and other gases to prevent corrosion and air pollution (Graedel et al., 1981).

Sharma and Danckwerts (1964) and Sharma (1965) studied the kinetics of reactions between COS and a variety of amines in aqueous solution at 25°C. COS reacts readily with primary and secondary amine solvents to form stable thiocarbamates that are difficult to regenerate (Astarita et al., 1983; Berlie et al., 1965; Pearce et al., 1961).

Physical solvents such as sulfolane, methanol, and polyethylene glycol ethers are often used to scrub acid gases. COS is not easily removed to low levels by these solvents because COS solubility falls between those of hydrogen sulfide and carbon dioxide. Recently, the trend in the gas purification industry has been to develop new solvent systems in which the hydrolysis of COS occurs. Such solvent systems include: tetramethylene sulfone in alkanolamine aqueous solution (Sykes, 1976); aqueous solution of N-substituted pyrrolidone, piperidones, imidazole, and polyethylene glycol ethers (Bratzler and Doerges, 1976; Bratzler et al., 1977); and aqueous solution of alkyl-substituted piperazinones (Bozzelli et al., 1978), and morpholines and piperazines (Correll and Friedli, 1980).

Each of these systems has the common feature of a basic nitrogen in one of the ingredients. Since it is known that COS hydrolysis is catalyzed by bases, it is likely that base catalysis is a major reason for the effectiveness of the above solvent systems in removing COS.

An important criterion in selecting ingredients in acid-gas solvent systems is regenerability. Tertiary amines do not form stable thiocarbamates, as do primary and secondary amines, and may be suitable ingredients for these systems.

Tertiary amines also catalyze reactions of isocyanates with alcohols, water, and other compounds (Farkas and Mills, 1962). Isocyanates (R—N═C═O) are analogous in structure to carbonyl sulfide (S═C═O) and may react similarly with water. Steric hindrance as well as base strength is a factor in the catalysis of isocyanate reactions. For example, highly hindered but strongly basic penta-methylpiperidine exhibits low catalytic activity, whereas the highly accessible nitrogen on 1,4-diazabicyclo[2.2.2] octane (DABCO) makes this compound highly active in spite of low basic strength.

The purpose of this study was to examine the hydrolysis of COS in solutions of tertiary amines and an acid gas solvent. We studied DABCO and several compounds mentioned above that were reported in the patent literature to catalyze COS hydrolysis. Most of the compounds examined have about the same base strength. Large differences in catalytic activity may indicate steric effects.

Experimental Method

The liquid solution used in the reaction experiments consisted of tertiary amine (0 to 0.25 M) in a solvent consisting of a mixture of dimethyl ethers of polyethylene glycol and water (1.4 M). The Henry's law constant for COS in the solvent was calculated from data reported by Kohl and Riesenfeld (1985) to be 2.27 atm · m^3/kmol. Because our solvent purity and water concentration may have differed from that of Kohl and Riesenfeld, we measured the Henry's law constant, *H*, by injecting known quantities of a COS—CH_4—He mixture into sealed bottles con-

---

Correspondence concerning this paper should be addressed to W. R. Ernst.

taining known volumes of the solvent (without catalyst) through a septum. The bottles were placed on a shaker for several hours until equilibrium had been achieved. The gases from these bottles were analyzed on a gas chromatograph with a thermal conductivity detector. We determined an average value for H of 3.13 atm · m^3/kmol.

Two cylinders of research grade gas (Matheson) were used. One contained 2.04% CH_4 in (dry) helium. The other had a composition of 2.04% COS, 1.91% CO_2, and 2.17% CH_4 in (dry) helium. A gas mixing apparatus blended the two cylinder gases and provided feed gas with the desired COS composition. The gas mixture was bubbled through a gas saturator containing solvent (without amine) before it was fed to the reactor. COS concentration in the feed gas to the reactor ranged between 0.2 and 2%.

The reactor was a 3×10^{-4} m^3 stirred round-bottom flask with openings near the top for continuous gas introduction and removal. The reactor was charged with 1.5×10^{-4} m^3 of the solvent. A fritted glass sparger tube extended into the solvent for gas introduction. Product gas exited the reactor through another opening.

Gas samples were analyzed for CH_4, COS, CO_2, and H_2S on a 3.2×10^{-3} m × 2.4 m Porapak N column at 343 K in a Carle 311 gas chromatograph with thermal conductivity detector. Methane is inert and has a negligible solubility in the solvent. It was used as an internal standard. The chromatogram peak area for each gas component was corrected by the appropriate response value, listed in Table 1; the corrected peak area was divided by the corrected CH_4 peak area from the same chromatogram. This technique greatly increased the reproducibility of the gas analyses. We found that although peak areas for individual components varied slightly for multiple samples of the same gas, the ratio mol of component/mol CH_4 remained constant. For example, five chromatograms for an identical gas mixture yielded the following mol ratios: 0.940 ± 0.002 mol COS/mol CH_4 and 0.880 ± 0.002 mol CO_2/mol CH_4.

Mass transfer characteristics of the reaction system were studied in the absence of chemical reaction by unsteady state O_2 absorption and desorption experiments using a dissolved O_2 probe (Bandyopadhyay et al., 1967; Fuchs et al., 1971).

Theory

Reactor model

The purpose of the model was to describe the conversion behavior of COS in a stirred gas-liquid reactor in which gas containing COS was sparged into a stirred batch of solution. The COS is transferred to the liquid phase, where it reacts with H_2O and forms H_2S and CO_2. The H_2O concentration was the same in all experiments and in great excess. The liquid phase was assumed to be well mixed. There was no visual indication of bubble coalescence or redispersion. The best correlation of data with the model resulted when a plug flow model for the gas phase was assumed. Other workers also have used these models to describe liquid phase and gas phase mixing characteristics (Onken et al., 1985).

Table 1. CH_4 Retention and Response Values*

Component	Retention Value	Response Value
Air	41	1.62
CH_4	53	1.00
CO_2	107	0.744
H_2S	303	0.817
COS	399	0.578

*Values in 3.2×10^{-3} m × 2.4 m Porapak N Column at 343 K
Carrier gas, He; flow rate, 5×10^{-5} m^3/min

Table 2. Flow Reactor Data

Catalyst Conc. kmol/m^3	Inlet COS Conc. kmol/kmol CH_4	Frac. COS Conversion
0	0.94	~0
0	0.11	~0
0.06	0.93	0.20
0.06	0.51	0.20
0.06	0.28	0.19
0.06	0.13	0.18
0.12	0.94	0.35
0.12	0.50	0.34
0.12	0.23	0.32
0.12	0.11	0.29
0.25	0.94	0.57
0.25	0.56	0.57
0.25	0.28	0.54
0.25	0.15	0.55

The plug flow equation for the general case of an nth-order reaction in COS is:

$$C_T \cdot x \cdot y_o F df/dV_L = K\left[x \cdot y_o \frac{\pi}{H}(1-f)\right]^n \tag{1}$$

which has the solution:

$$\left[\frac{1}{(1-f)^{n-1}} - 1\right] = K \cdot \tau \cdot (n-1)\left(\frac{\pi}{H}\right)^{n-1} x^{n-1} \cdot y_o^{n-1} \tag{2a}$$

For the special case of $n = 1$, the solution is:

$$-\ln(1-f) = K\tau \tag{2b}$$

For the conditions of this study, $\tau = 469$ s.

The influence of mass transfer can be incorporated into the model for the case of $n = 1$. Previous studies (Sharma and Danckwerts, 1964), have shown that the hydrolysis of COS is relatively slow compared to that of CO_2 and that mass transfer in the gas phase is very fast. The constant K in Eq. 2b can therefore be represented as:

$$\frac{1}{K} = \frac{1}{k_L a} + \frac{1}{k \cdot C_c} \tag{3}$$

Results and Discussion

Study of DABCO

During the reaction experiments the system was assumed to be at steady state when the effluent concentrations of COS, CO_2, and H_2S remained constant for at least one hour. COS

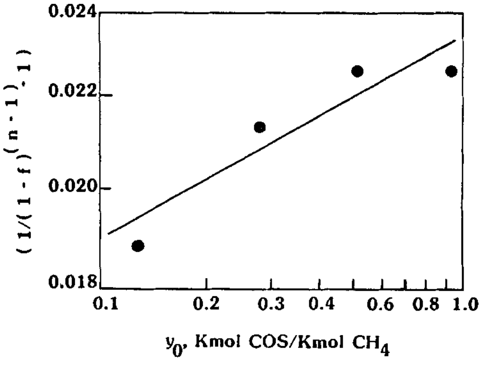

Figure 1. Determination of COS reaction order for catalyst concentration = 0.06 kmol/m^3.

achieved a constant concentration usually within one hour after startup whereas three or four hours were required for CO_2 and H_2S.

Table 2 shows the fractional conversion of COS for four inlet concentrations and three catalyst concentrations. No COS conversion or product formation was found in the two blank runs in which no catalyst was added to the reactor solution. The uncertainty in gas analysis was equivalent to a fractional conversion of about 0.01.

The order of reaction with respect to COS was determined at each catalyst concentration by finding the value of n that best fit the experimental data to an nth-order rate expression, Eq. 2a. In Figure 1, for an assumed value of $n = 1.1$, linear regression yielded a slope of 0.094, from which a value $n = 1.094$ was calculated. Table 3 shows that the order determined at each catalyst concentration is slightly greater than 1. To simplify further analysis of the data, the reaction order was set equal to 1 and Eq. 2b was used to calculate experimental rate constants. Figure 2 shows the implication of this assumption: the first-order rate constants show a slight increase with COS inlet concentration. However, this assumption had little effect on the conclusions drawn from this study.

Thompson et al. (1935) showed that the rate constant for COS hydrolysis in an uncatalyzed aqueous system is 2×10^{-5} m^3/kmol · s. Assuming that the reaction is first order in H_2O concentration, the first-order rate constant for the reaction of COS with pure liquid H_2O would be 0.001 s^{-1} (Sharma and Danckwerts, 1964). In the current study, in a nonaqueous system the water concentration was only 1.4 kmol/m^3. Assuming that there is no effect of solvent on the reaction, the predicted rate constant for the uncatalyzed system in our studies should have been 2.8×10^{-5} s^{-1}. This rate constant is equivalent to a COS fractional conversion for the uncatalyzed experiments of 0.013. This value was above the level of uncertainty in COS conversion for the blank experiments; therefore, the rate constant must have been lower than 2.8×10^{-5} s^{-1}. We suspect that the solvent does affect the reaction and the assumption of first-order dependence on water cannot be used to extrapolate the data of Thompson et al. to a nonaqueous system.

Table 3. COS Reaction Order

Catalyst Conc. kmol/m^3	COS Order
0.06	1.09
0.12	1.10
0.25	1.04

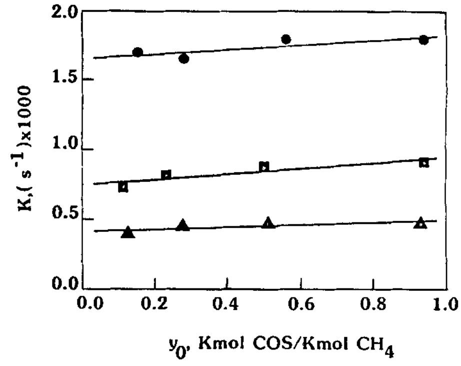

Figure 2. Influence of inlet COS concentration on first order rate constant for various catalyst concentrations.
● 0.25, ■ 0.12, ▲ 0.06 kmol/m^3

The volumetric mass transfer coefficient, k_La, for O_2 in the reaction liquid, measured under nonreaction conditions was 0.022 s^{-1}. A k_La value was estimated for COS in the reaction liquid by assuming that k_L is proportional to $D^{0.5}$ (Higbie, 1935). Sharma (1965) reported $D(COS—H_2O) = 1.9 \times 10^{-9}$ m^2/s; Arnold (1930) reported $D(O_2—H_2O) = 2.4 \times 10^{-9}$ m^2/s. The Wilke-Chang correlation predicts that the ratio of diffusion coefficients for two species measured in one solvent system should equal the ratio of diffusion coefficients in another solvent system. Applying this prediction leads to an estimate of $k_La = 0.019$ s^{-1} for COS.

Figure 3 shows the first-order rate constants plotted according to Eq. 3 for the reaction data in Table 2. Also plotted at $[COS]^{-1} = 0$, is the reciprocal of k_La estimated from the O_2 absorption-desorption experiments. The solid line is a linear least-squares fit of the kinetic data. From slope and intercept, the values of the constants in Eq. 3 were found to be $k = 7.7 \times 10^{-3}$ m^3/s · kmol, and $k_La = 1.3 \times 10^{-2}$ s^{-1}. This latter value is in reasonable agreement with the value from the O_2 absorption-desorption experiments.

Forcing the line in Figure 3 through the origin (i.e., assuming that k_La is very large) had only a slight influence on the slope. The resulting rate constant decreased by only 4%, to 7.4×10^{-3} m^3/s · kmol. Thus in spite of the substantial improvement in COS hydrolysis rate due to the presence of the catalyst, it can be concluded that the reaction falls into the very slow regime of Danckwerts (1970) where mass transport effects can be neglected. Similar conclusions have been reached for COS hydrolysis in other catalyst-solvent systems (Sharma and Danckwerts, 1964).

Studies of other amines

Several other tertiary amines were studied in this reactor. Table 4 summarizes the results of these studies. Activity did not correlate with base strength for these compounds. DABCO, which showed high activity in isocyanate reactions (Farkas and Mills, 1962), showed highest activity in this study. Dimethylpi-

Table 4. Relative Activities of Tertiary Amines in COS Hydrolysis

Amine	pK_B	Ref.*	$k \times 1{,}000$ $m^3/kmol \cdot s$
1,4-diazabicyclo[2.2.2] octane (DABCO)	5.4	(a)	7.7
1,2-dimethylimidazole	6.3	(d)	2.1
1-methylimidazole	7.4	(d)	1.1
1,4-dimethylpiperazine	5.5	(b)	1.3
Triethanolamine	6.2	(c)	0.03

*References
(a) Farkas and Mills (1962)
(b) Christensen, et al. (1976)
(c) Huber (1967)
(d) Estimated from pH measurements of aqueous amine solutions

perazine, which has about the same base strength as DABCO, has only one-sixth the activity of DABCO. Triethanolamine, which is the most sterically hindered of the amines, has a base strength similar to 1,2-dimethylimidazole but is two orders of magnitude lower in activity.

Determining a reaction mechanism was beyond the scope of this investigation; however, one might consider two likely candidates:

1. Catalysis by hydroxyl ions produced by proton transfer from water to the basic amines
2. Direct interactions between the basic nitrogen group of the amines and COS to form a complex that subsequently reacts with H_2O

In dilute aqueous solution mechanism 1 would predominate since it is well established that OH^- reacts rapidly with COS; however, it is less obvious in the present study because of the low concentration of water: the hydroxyl ions should be less active in the nonaqueous environment. If mechanism 1 were predominant, a correlation between activity and base strength should have been observed.

Mechanism 2 is analogous to a mechanism proposed by Baker and coworkers (1947, 1949) for the reaction of isocyanates with alcohols. They supported this mechanism by demonstrating that steric hindrance of the amine structure plays a major role in determining activity. The surprisingly high activity of DABCO compared with activities of other compounds may be the result of the sterically favored structure of DABCO, which would facilitate the complexing of COS with DABCO.

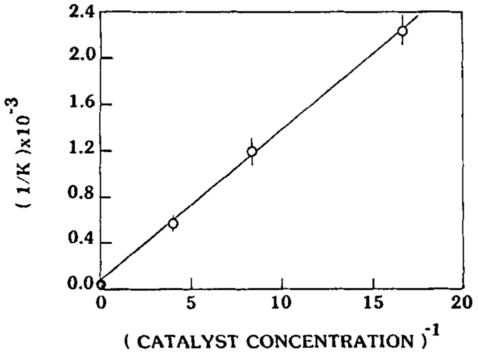

Figure 3. Effect of catalyst concentration on first-order rate constant.

Influence of mass transfer on reaction rate

Acknowledgment

The authors express appreciation to E. J. Greskovich, J. T. Edwards, and D. Mitchell for helpful suggestions throughout this work.

Notation

C_c = catalyst concentration, kmol/m^3
C_T = molar density of gas = $(24.45)^{-1}$ kmol/m^3
F = gas flow rate, m^3/s
f = COS fractional conversion
H = Henry's law constant, atm · m^3/kmol
k = rate constant, m^3/kmol · s
K = pseudofirst-order rate constant, Eqs. 1, 2, 3, s^{-1}
k_La = volumetric mass transfer coefficient, s^{-1}
V_L = reactor liquid volume, m^3
x = mol fraction CH_4 in gas
y_o = inlet gas mol ratio of COS to CH_4
π = total pressure = 1 atm
τ = space time = $(V_L\pi/C_TFH)$s · kmol dissolved COS/kmol COS in gas

Literature Cited

Arnold, J. H., "Studies in Diffusion. II: A Kinetic Theory of Diffusion in Liquid Systems," *J. Am. Chem. Soc.*, **52**, 3937 (1930).

Astarita, G., D. W. Savage, and A. Bisio, *Gas Treating with Chemical Solvents*, Wiley, New York (1983).

Baker, J. W., and J. B. Holdworth, "The Mechanism of Aromatic Side-chain Reactions with Special Reference to the Polar Effects of Substituents," *J. Chem. Soc.*, 713 (1947).

Baker, J. W., M. M. Davies, and J. Gaunt, "The Mechanism of the Reaction of Aryl Isocyanates with Alcohols and Amines," *J. Chem. Soc.*, **9**, 19, 27 (1949).

Bandyopadhyay B., A. E. Humphrey, and H. Taguchi, "Dynamic Measurement of the Volumetric Oxygen Transfer Coefficient in Fermentation Systems," *Biotechnol. Bioeng.*, **9**, 533 (1967).

Berlie, E. M., J. W. Estep, and F. J. Ronicker, "Preventing MEA Degradation," *Chem. Eng. Prog.*, **61**(4), 82 (1965).

Bozzelli, J. W., G. D. Shier, R. L. Pearce, and C. W. Martin, "Absorption of Sulfur Compounds from Gas Streams," U.S. Pat. 4,112,049 (Sept. 5, 1978).

Bratzler, K., and A. Doerges, "Process for the Desulfurization of Gases," U.S. Pat. 3,966,875 (June 29, 1976).

Bratzler, K., A. Doerges, and M. Kriebel, "Process of Purifying Gases Produced by the Gasification of Solids or Liquid Fossil Fuels," U.S. Pat. 4,011,066 (Mar. 8, 1977).

Christensen, J. J., and L. D. Hansen, and R. M. Izatt, *Handbook of Proton Ionization Heats and Related Thermodynamic Quantities*, Wiley, New York (1976).

Correll, G. D., and H. R. Friedli, "Hydrolysis of Carbonyl Oxysulfide with Morpholine and Piperazine," Eur. Pat. 0,008,449 (May 3, 1980).

Danckwerts, P. V., *Gas-Liquid Reactions*, McGraw-Hill, New York (1970).

Farkas, A., and G. A. Mills, "Catalytic Effects in Isocyante Reactions," *Adv. Catal.*, **13**, 393 (1962).

Fuchs, R., D. D. Y. Ryu, and A. E. Humphrey, "Effect of Surface Aeration on Scale-up Procedures for Fermentation Processes," *Ind. Eng. Chem. Process Des. Dev.*, **10**, 190 (1971).

Graedel, T. E., G. W. Kammlott, and J. P. Franey, "Carbonyl Sulfide—Potential Agent of Atmospheric Sulfur Corrosion," *Science*, **212**, 663 (May 8, 1981).

Higbie, R., "The Rate of Absorption of a Pure Gas into a Still Liquid During Short Periods of Exposure," *Trans. AIChE*, **31**, 365 (1935).

Huber, W., *Titrations in Nonaqueous Solvents*, Academic Press, New York (1967).

Kohl, A. L., and F. C. Riesenfeld, *Gas Purification*, 4th ed., Gulf, Houston (1985).

Onken, U., R. Sick, and P. Weiland, "Determination of Gas-Liquid Mass Transfer by Oxidation of Hydrazine," *Chem. Eng. Sci.*, **40**(10), 1990 (1985).

Pearce, R. L., J. L. Arnold, and C. K. Hall, "Studies Show Carbonyl Sulfide Problem," *Hydrocarb. Proc. Pet. Refiner,* **40**(8), 121 (Aug., 1961).

Sharma, M. M., "Kinetics of Reactions of Carbonyl Sulphide and Carbon Dioxide with Amines and Catalysis by Brönsted Bases of the Hydrolysis of COS," *Trans. Faraday Soc.,* **61,** 681 (1965).

Sharma, M. M., and P. V. Danckwerts, "Absorption of Carbonyl Sulfide in Amines and Alkalis," *Chem. Eng. Sci.,* **19,** 991 (1964).

Sykes, J. A., Jr., "Selective Removal of Sulfur Compounds from Acid Gas Mixtures Containing Significant Quantities of Carbonyl Sulfide," U.S. Pat. 3,965,244, (June 22, 1976).

Thompson, H. W., C. F. Kearton, and S. A. Lamb, "The Kinetics of the Reaction between Carbonyl Sulfide and Water," *J. Chem. Soc.,* 1003 (1935).

Manuscript received May 5, 1987 and revision received Aug. 27, 1987.