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COS-Forming Reaction between CO and Sulfur: A High-Temperature Intrinsic Kinetics Study

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Carbonyl sulfide is formed in the front end (i.e., the reaction furnace and the waste heat boiler) of Claus plants which are commonly used to recover sulfur from acid gases. Moreover, COS along with CS_2, are recognized as the problematic sulfur compounds that contribute significantly to plant sulfur emissions. Further, there is limited kinetic information on the important reaction for the formation of these two compounds. Now, it is well-known that one of the important COS-forming reactions is that between CO and sulfur. In our laboratory, we conducted an experimental study to measure the intrinsic kinetics of this homogeneous gas-phase reaction in the temperature range of 600–1150 °C and over a residence time of 0.5–2.0 s. The overall reaction was found to be second order with a reaction rate constant $k_f = (3.18 \pm 0.36) \times 10^5 \exp[-(6700 \pm 108 \text{ K})/T]$ m^3/(kmol·s). In addition, a kinetic model was developed to account for both the COS formation and the COS decomposition reactions. And, finally, for the reverse reaction, the COS decomposition reaction rate constant (k_r) was regressed to match the equilibrium data of experiments at high temperatures giving a second-order reaction rate constant as $k_r = (2.18 \pm 1.12) \times 10^9 \exp[-(21630 \pm 160 \text{ K})/T]$ m^3/(kmol·s).

Introduction

Background. The modified Claus process is the most popular process employed worldwide for converting toxic hydrogen sulfide to sulfur in the hydrocarbon processing industries. The conversion of H_2S to elemental sulfur is attained in two steps. In the first (thermal) step, partial oxidation of H_2S to SO_2 is achieved at high temperatures via the following reaction:

$$H_2S + {}^3/_2O_2 \rightleftharpoons SO_2 + H_2O \tag{1}$$
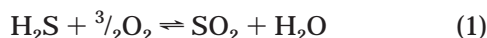
The second (catalytic) step involves a low-temperature reaction of the generated SO_2 and unreacted H_2S over fixed beds of an alumina or titania catalyst (i.e., the converters) and is represented as

$$SO_2 + 2H_2S \rightleftharpoons {}^3/_xS_x + 2H_2O \tag{2}$$
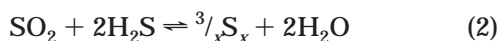
In a Claus plant, the thermal step is carried out in the reaction furnace (RF), a refractory lined cylindrical vessel attached with burners, where the temperature usually ranges from 975 to 1300 °C. The RF product is a mixture of active chemical species which are the products of combustion reactions (SO_2, CO_2, and H_2O) and of numerous side reactions (S_2, COS, CS_2, H_2, CO, and SO_3). In a Claus plant, the hot furnace product gases are cooled to approximately 250 °C in the tubes of a waste heat boiler (WHB) that follows the RF. These gases are then fed to a catalytic converter, after recovering in a condenser any sulfur produced in the RF/WHB. Sulfur produced in the catalytic converter via reaction 2 is recovered from the product gas stream in a sulfur condenser following each catalytic stage. For further recovery of sulfur, the gas stream is fed to the next catalytic stage. The gas stream resulting after the

recovery of sulfur from the last catalytic stage is termed as the tail gas. Typically, two to three catalytic stages exist in a "once through" Claus plant, achieving an overall sulfur recovery of about 96–98%. Stringent governmental environmental regulations, at present, require sulfur recovery of over 99.0%. To comply with these regulations, additional sulfur recovery is usually achieved by installing expensive tail gas cleanup units after the catalytic converters.

While many millions of dollars have been spent on developing tail gas treatment methods, little effort has been directed toward developing a clearer understanding of the Claus process chemistry at the front end of the plant. It is important to note that the front-end units of a Claus plant (i.e., RF and WHB) play a critically important role in determining the product distribution from the RF/WHB which affects not only the performance of the downstream catalytic converters but also the overall sulfur recovery efficiency of a Claus plant. Therefore, it is extremely important to develop realistic models for the RF and WHB for simulating the process better and, more importantly, to explore new operational scenarios for minimizing the sulfur emissions from Claus plants.

At present, the models used for designing the RF and the WHB do not account for all key reactions that occur within. In fact, until the field study of Sames et al.,[1] it was practically unknown that reactions leading to the formation of COS and H_2S occur to a significant extent in the WHB tubes. In our laboratory, we modeled H_2S and COS formation in the WHB tubes,[2,3] using approximate reaction kinetics available in the literature for these two reactions. It was shown that rapid quenching of these two reactions could be achieved in the WHB simply by changing the WHB tube configurations. The quenching of these reactions would result in a higher sulfur recovery from the front end of Claus plants and, more importantly, enhance the overall plant

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sulfur recovery. Also, in another study from our laboratory,[4] it was shown that the presently employed methods of modeling the product composition from the RF, based either on thermodynamic equilibrium or on empirical correlation, are inadequate in predicting the concentrations of the four chemical species CO, H_2, CS_2, and COS. The failure of these models to correctly predict the composition of these components has been attributed to the kinetic limitations of the reactions involved in their formation/consumption. Accurate prediction of the concentrations of the two sulfur compounds, COS and CS_2, is especially important because they tie up a considerable amount of sulfur in the tail gas and thereby directly affect the plant sulfur balance. In fact, they are known to contribute as much as 20% to the Claus plant sulfur emissions. Obviously, from a sulfur recovery perspective, it is desirable not only to correctly predict the compositions of COS and CS_2 but also to reduce their production during the RF/WHB operations. Strategies to minimize the COS/CS_2 production in the RF/WHB demands a clearer understanding of the process chemistry and the kinetics of the key reactions. This in turn requires reliable experimental data on important reactions, occurring in the front end of a Claus plant.

In our laboratory, we are conducting reaction kinetic studies of important COS/CS_2 homogeneous gas-phase reactions.[5] In this paper, the intrinsic kinetic data are provided for one of the important COS-forming reactions between CO and sulfur.

H_2, CO, COS, and CS_2 Production in RF/WHB. There are no literature on a detailed and systematic study providing a clear understanding of the actual reaction mechanism that may be involved in the formation/consumption of H_2, CO, COS, and CS_2 in the RF and WHB of Claus plants. However, we have completed a thermodynamic feasibility study[6] of reactions that may lead to the formation and the consumption of CO, H_2, COS, and CS_2. A detailed description of the results of the thermodynamic study is beyond the scope of this paper. Nonetheless, some of the key reactions that may be involved in the formation of the four chemical species (CO, H_2, COS, and CS_2) are discussed below.

The formation of hydrogen in the Claus RF is typically attributed to the H_2S decomposition reaction because H_2S is the major H-containing species. Moreover, the presence of CO in the RF product is thought to be due to its formation from CO_2 decomposition at a high temperature in the RF flame and via the reaction of CO_2 with H_2. In Claus plants containing hydrocarbons in the RF feed, the CO formation in the RF may also be due to incomplete hydrocarbon oxidation. While CO and H_2 are considered inert species from a sulfur recovery perspective, COS and CS_2 are considered to be important sulfur species that can contribute significantly to plant emissions. Further, the formation of CS_2 is attributed mainly to the reactions of hydrocarbons with sulfur or hydrogen sulfide. However, it is not uncommon to find a citing[7] that suggests CS_2 formation from the reaction between H_2S and CO_2. This seems to be an unlikely reaction mechanism for CS_2 formation and, in fact, is not favored thermodynamically. Until recently, it was accepted that COS is formed mainly in the RF via the reaction between CO_2 and H_2S. However, it has been shown that thermodynamically COS formation is favored at low temperatures of the WHB

and not at high temperatures of the RF. Moreover, the field study of Sames et al.[1] has confirmed that the majority of COS is formed in the WHB via the reaction between CO and sulfur.

Previous Study on the CO + Sulfur Reaction. The only published results on an experimental study of the direct reaction between CO and sulfur is that by Dokiya et al.[8] They proposed a two-step process for the decomposition of hydrogen sulfide: (i) the production of hydrogen and carbonyl sulfide via the reaction of carbon monoxide and hydrogen sulfide and (ii) the decomposition of COS via the reverse of the following reaction:

$$CO + {}^{1}/_{x}S_x \rightleftharpoons COS \qquad (3)$$

They were interested in rapidly quenching reaction 3, and hence, performed experiments to obtain qualitative information on the rate of this reaction. Their experiments consisted of flowing CO over a sulfur reservoir and continuing the reaction in a Pyrex reactor. The effects of the CO flow rate, the temperature of the sulfur reservoir, and the temperature of the reactor on the COS yield were studied. The sulfur reservoir temperature was varied in a range of 200–400 °C while the reactor temperature was varied in a range of 300–550 °C. As expected, the COS yield was found to be higher for higher reactor and sulfur reservoir temperatures and lower for higher CO flow rates. It was concluded from their study that although reaction 3 is very fast, it can be quenched rapidly at higher flow rates. However, the reaction rate kinetics of reaction 3 were not reported.

Experimental Section

Description of Apparatus. Figure 1 shows a schematic of the experimental setup employed in the present study. The apparatus consisted of a coiled quartz tube reactor (coil diameter = 20 cm) placed in a Thermolyne electric furnace (internal dimensions: 47 cm × 48 cm × 71 cm) that could be operated over a temperature range of 600–1700 °C. The reactor was made up of a quartz tube of 5.0-mm diameter and available in lengths of 1.6, 3.2, 6.4, and 16 m. The gas flow rate to the reactor was controlled and metered with an eight-channel Linde mass flow controller. Carbon monoxide was obtained from Praxair, Canada at concentrations of approximately 1, 2, 5, and 10 mol % in nitrogen. The reactant stream containing sulfur was prepared by flowing pure nitrogen gas over molten sulfur contained in a heated flask. The line between the sulfur pickup flask and the reactor inlet was heated electrically with a Thermolyne heating tape to prevent the condensation of sulfur.

The hot product gas exiting the reactor was cooled in a double-pipe co-current heat exchanger called the cooler. Sulfur was partially separated from the product gas stream, as a solid, when the gas cooled to less than 100 °C in the cooler. The balance of the sulfur was removed in a sulfur trap, a 1-in. diameter quartz tube packed with glass wool. The product gas composition was analyzed by passing a stream of the sulfur-free quenched product gas to an on-line Varian gas chromatograph equipped with a thermal conductivity detector and a pulsed flame photometric detector. The separation of COS was achieved in a Hayesep Q column which was placed in series with a molecular sieve
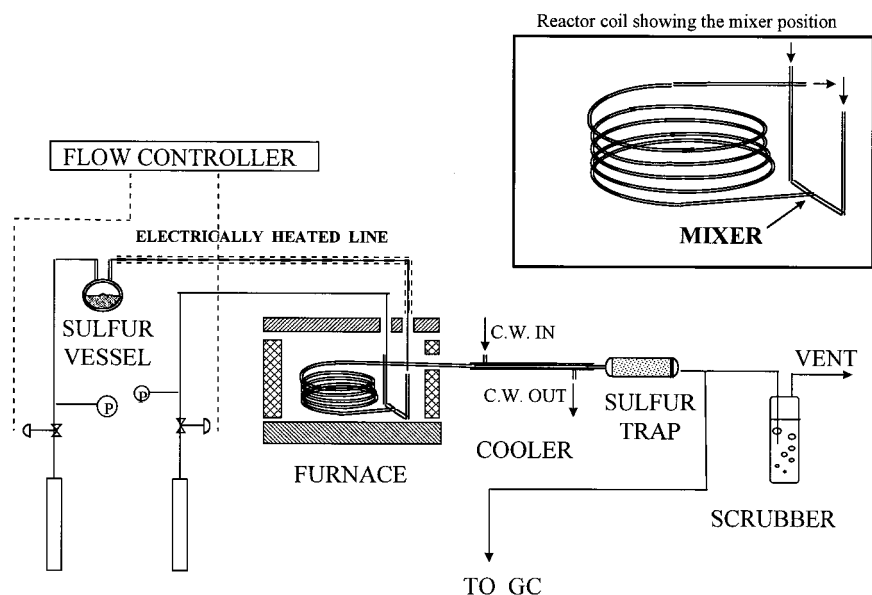
Reactor coil showing the mixer position

MIXER

Figure 1. Schematic diagram of experimental setup.
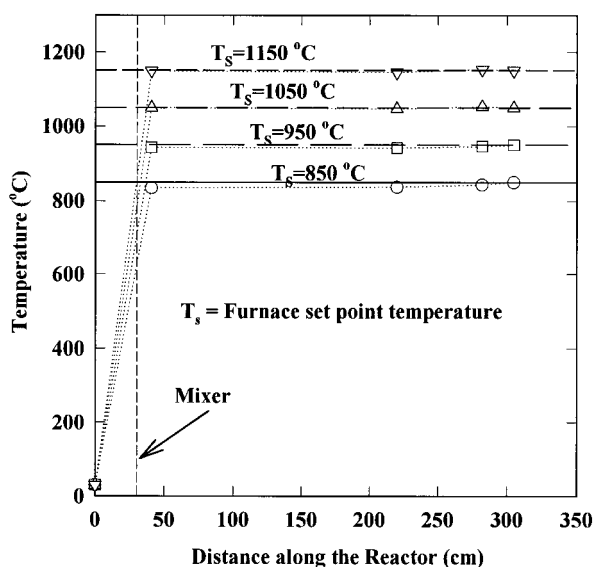

Figure 2. Gas temperature profiles along the reactor at four furnace set point temperatures (T_S).

column when the separation of CO and N_2 was required. Finally, the effluent stream from the gas chromatograph and the product gas streams were scrubbed prior to being vented to the atmosphere.

Temperature Profile in the Reactor. Inside the electric furnace, the heat flux to the cool gas entering the reactor was very high, which resulted in a rapid heatup of the reactant stream. The temperature distribution in the reactor was measured by flowing high-purity nitrogen gas in a 6.4-m-long reactor equipped with four R-type shielded thermocouples along the length of the reactor. The measured gas temperature profile along the reactor is presented in Figure 2 for four furnace set point temperatures (T_S). It can be clearly seen that the gas was heated rapidly in the preheat section, and at the mixer (i.e., where the reactants are first contacted) it reaches a temperature greater than 80% of the furnace set point temperature. This means that the reactant gases were heated close to the required reaction temperature before being mixed. The flat temperature profile along the length of the reactor,

beyond the mixer, clearly demonstrated a near-isothermal operation of the reactor at the furnace temperatures (T_S).

An important feature of the reactor was its two L-shaped vertical preheat sections of length 30 cm each which were joined at the *mixer* (see inset Figure 1). This design ensures that the two reactant streams were mixed (at the mixer) only after attaining a significantly high temperature, thereby preventing any reaction in the heat-up zone (preheat sections).

Quenching of Hot Product Gas. The quenching of the hot product gas was achieved in the reactor system by a combination of free and forced convection cooling. From the temperature measurements in the quench zone, it was found that the hot gases are naturally cooled from 1200 °C to less than 500 °C, in the 20-cm long part of the reactor that extended outside the furnace wall. The gases were cooled further from less than 500 °C to below 100 °C in the 45-cm long double-pipe co-current heat exchanger or cooler. The cooler, designed originally as the hot gas quench, was made of quartz and had an inside diameter of 3 mm. The hot gases pass through the inside tube while cold water runs on the outside. The residence time of the gases in the 20-cm reactor extension has been calculated to be less than 20 ms. Since the reaction is essentially quenched at temperatures below 500 °C, it can be concluded that a rapid quench exists for the hot product stream from the reactor.

Sulfur Pickup. The reactant stream containing sulfur was prepared by passing nitrogen gas over molten sulfur contained in a 2.0-L round-bottom flask which was heated by an electric mantle. Pure sulfur powder (from BDH Chemicals) supplied by VWR Canlab was used in the experiments. The amount of sulfur picked up by the nitrogen gas was a function of the flask temperature. The flask temperature, in turn, was fixed by the input power to the heating mantle which was controlled by a variac power controller. To determine the amount of sulfur picked up, nitrogen was flowed for 10–20 min and the sulfur condensed in a sulfur trap was measured gravimetrically. The amount of sulfur, expressed as S_2, picked up at three different variac power controller settings corresponded to 1.8, 3.2, and

4.9 mol % in N_2. It must be pointed out that these values are an average of 10−12 experiments with a standard deviation of approximately 10%. The flask temperatures at the three variac settings were 230, 280, and 330 °C. At these temperatures, the sulfur vapor is composed mainly of higher sulfur allotropes (i.e., S_6, S_7, and S_8). Assuming an average of 7 sulfur atoms/molecule in saturated vapor of sulfur, it can be calculated that the degree of saturation for sulfur in the nitrogen stream is approximately 45, 20, and 10% expressed at stream temperatures (equal to the flask temperatures) of 230, 280, and 330 °C, respectively.

Experimental Conditions. Experiments were conducted with dilute concentrations of reactants (dilution > 90%) in a temperature range of 600−1150 °C using 6.4- and 16-m long reactors. The flow rate of each reactant stream (i.e., N_2-diluted CO and N_2 diluted sulfur) was maintained at 2.0 L/min (measured at room temperature and atmospheric pressure) which gave an actual residence time of 0.5−1.0 and 1.1−2.1 s for the 6.4- and 16-m long reactors, respectively. These residence times were calculated at the furnace set point temperature assuming plug flow of the gases. The total inlet pressure varied from 115 to 130 kPa. To study the effect of CO concentration on COS formation, experiments were conducted with a fixed S_2 concentration of 0.90 mol % while the CO concentration was varied to 0.5, 2.5, and 5.0 mol %. Similarly, the effect of sulfur concentration on COS formation was studied experimentally with a fixed composition of 5.0 mol % CO and by changing the S_2 concentrations to 0.90, 1.60, and 2.45 mol % in N_2.

Reactor Verification Study. To verify the operational characteristics of the reactor system, propane pyrolysis experiments were conducted in our laboratory.[5] Propane pyrolysis was selected as a model reaction because it has been extensively studied over the last 35 years, and hence, reliable kinetic information is readily available in the published literature. A computer program was written to simulate the propane pyrolysis reactions.[5] The molecular reaction scheme proposed by Sundaram and Froment[9] comprising ten reactions (i.e., Model I of their paper) was incorporated in the computer program.

Experiments were conducted for five residences times at a furnace set point temperature (T_S) of 850 °C. The reactant stream comprised 1.97 mol % propane in nitrogen. The product gases at the reactor exit were analyzed for five major chemical species: H_2, CH_4, C_2H_4, C_3H_6, and C_3H_8. Also, the product composition from our tubular reactor was predicted from the computer program, assuming plug flow of gases and isothermal operation. The isothermal temperature was equal to the furnace set point temperature of 850 °C. A comparison of the product composition obtained from the experiments in our reactor and that from the simulator has been presented in Figure 3. The solid line represents the parity line and the dashed lines correspond to 10% variations. It can be observed from Figure 3 that there is a good agreement between the experimentally measured and the predicted gas composition with deviations remaining within 10%. This validated the experimentally obtained isothermal temperature profile (Figure 2) and also showed that the gas flow could be approximated as plug flow.
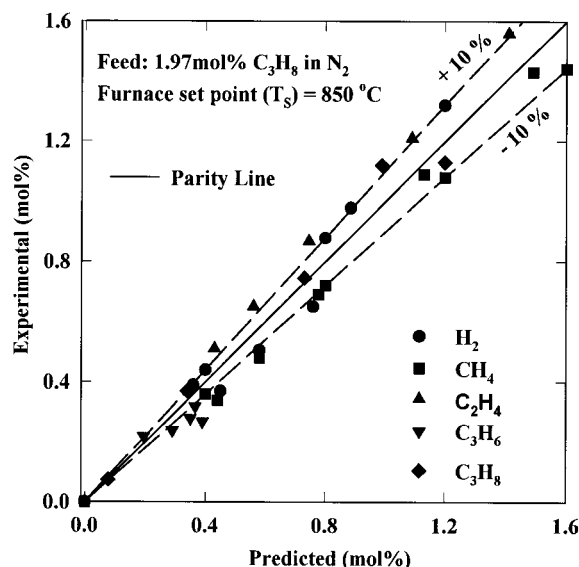

Figure 3. Comparison of experimental and predicted product gas composition for pyrolysis of 1.97 mol % C_3H_8 in N_2. (Predicted at T = 850 °C assuming plug flow of gas.)
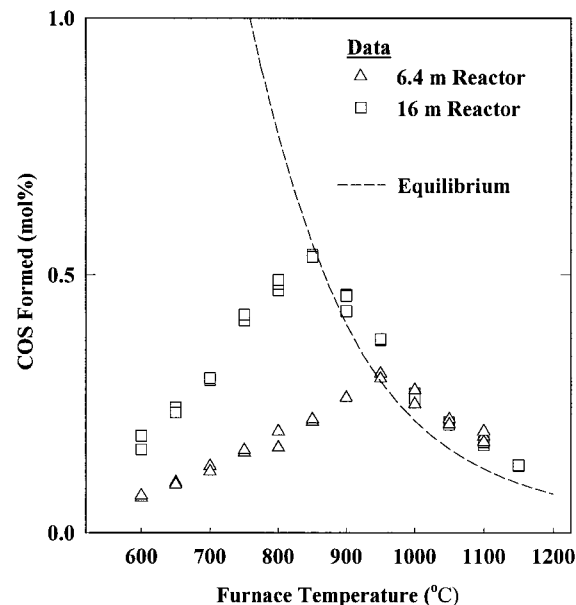

Figure 4. Variation of COS produced with temperature in two quartz reactors (6.4- and 16.0-m long). (Feed: 5.0 mol % CO, 0.90 mol % S_2, balance N_2.)

Results and Discussion

Effect of Temperature on COS Formation. Experiments were conducted by reacting 5.0 mol % CO with 0.90 mol % S_2 in the temperature range of 600−1150 °C. The results of these experiments are presented in Figure 4 as the amount of COS produced at various furnace temperatures. The two sets of data represent the COS formed in experiments using reactors of lengths 6.4 and 16 m. Additionally, the equilibrium COS concentration are also plotted as a dashed line in Figure 4. The equilibrium concentration of COS in a CO−COS−N_2−S_i (i = 1, 2, ..., 8) system was computed from a program written to minimize Gibbs free energy of an ideal gas reacting mixture. The free energy of formation data for all the relevant species were taken from JANAF thermochemical tables.[10]

It can be observed from Figure 4 that the COS formation is favored thermodynamically at lower tem-

peratures, with the COS equilibrium concentration decreasing as the temperature increases. The two distinct features of the experimental plots are the occurrence of a maximum in the COS formed and the greater than equilibrium yield of COS at higher temperatures. The occurrence of maxima in the COS formed is due to the interplay between reaction kinetics and thermodynamic equilibrium.

The experimental COS conversions are limited by chemical thermodynamic equilibrium for temperatures greater than 850 and 950 °C for the longer and shorter reactor, respectively. At lower temperatures (600–950 °C), the experimentally realized conversions are lower than the equilibrium conversion and kinetically limited under our experimental conditions. Within this temperature range, an increase in temperature results in an increased reaction rate and, therefore, in a larger COS conversion. At higher temperatures (>950 °C), the gas residence time or reaction time in either of the reactors is sufficient for the attainment of equilibrium conversions. The experimentally obtained conversions are determined by the equilibrium conversion limits which decrease with the temperature; hence, the experimentally realized conversions are found to decrease with the temperature.

From Figure 4, it can be seen that the experimental conversions in the 16.0- and 6.4-m-long reactors exceed the thermodynamic equilibrium conversion for temperatures greater than 900 and 1000 °C, respectively. This seemingly odd behavior can be attributed to a combination of experimental errors and limitation of complete reaction quenching. The experimental errors involved in the measurement of COS composition (<5%) and in the determination of sulfur concentration (<10%) only partially account for the higher than equilibrium conversion. The major reason for this observation lies in the fact that although we have an extremely rapid quenching of hot product gases (quenching from over 1200 to 500 °C in less than 20 ms), it is not instantaneous. The lower temperatures in the quench zone shift the equilibrium of COS-forming reaction 3 toward the right (i.e., toward higher COS concentrations). Thus, in the quench zone, because of the shift in equilibrium, the CO and sulfur react to some extent before being quenched completely.

Effect of Sulfur Concentration. To study the effect of sulfur concentration on the COS formation and to determine the order of reaction with respect to the sulfur concentration, experiments were conducted in a 6.4-m-long reactor at three temperatures of 600, 700, and 800 °C with a fixed CO concentration of 2.5 mol % and by varying the S_2 concentration to 0.9, 1.6, and 2.45 mol %. It must be pointed out, once again, that the sulfur vapor was considered to be composed entirely of S_2. Equilibrium calculations have verified that more than 90% of the sulfur is present as S_2 at low partial pressures and high temperature (>500 °C).

At compositions far removed from equilibrium, the reversible reaction is negligible, and under such conditions, the rate of formation of COS can be expressed by the following empirical relation:

$$r_{COS} = k_f C_{CO}{}^n C_{S_2}{}^m = k_f P_{CO}{}^n P_{S_2}{}^m / [RT]^{m+n} \quad (4)$$

where n and m are reaction orders with respect to CO and S_2 concentrations. Below 800 °C, the conversion of CO was less than 20%, and thus, its concentration
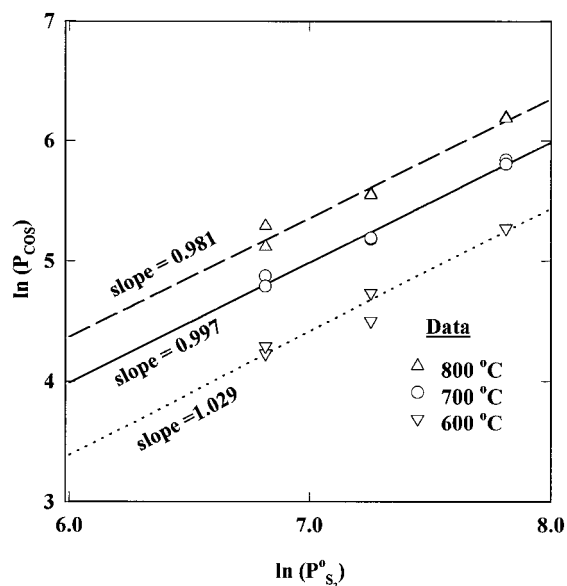

Figure 5. Order of dependency with respect to S_2 concentration for COS formation reaction.

can be assumed to be constant (i.e., $P_{CO} = P_{CO}^{\circ}$). Additionally, the sulfur conversions calculated from the COS formed were calculated to be less than 30%. Thus, for the sake of simplicity, if it is assumed that both the reactants were in excess compared to the product, the relationship $\ln(P_{COS}) = \ln(K' t_{res}) + m \ln(P_{S_2}^{\circ})$ can be derived, where K' is equal to k_f times $(P_{CO}^{\circ})^n/[RT]^{m+n-1}$ Hence, the slope (m) of a plot of $\ln(P_{COS})$ versus $\ln(P_{S_2}^{\circ})$ would give the order of reaction with respect to the S_2 concentration.

In Figure 5, $\ln(P_{COS})$ is plotted against $\ln(P_{S_2}^{\circ})$ for three different temperatures. The slopes (m) of the straight lines correlating the data points are also reported on Figure 5 and are 0.981, 0.997, and 1.029 corresponding to the temperatures of 800, 700, and 600 °C, respectively. These slopes are close to unity which implies that the order of the reaction with respect to the S_2 concentration is unity.

Effect of CO Concentration. The effect of CO concentration on the COS production rate was studied in a manner similar to that employed for studying the effect of the S_2 concentration on the COS formation. Experiments were conducted in a 16-m-long reactor with CO concentrations of 0.5, 2.5, and 5.0 mol % with a fixed S_2 concentration of 0.90 mol %. The amount of COS formed corresponds to conversions of less than 10% for both CO and S_2. Thus, with the assumption that the reactants were in excess compared to the product, the relationship between COS and CO concentration can be derived from eq 4 to be $\ln(P_{COS}) = \ln(K'' t_{res}) + n \ln(P_{CO}^{\circ})$, where K'' is equal to k_f times $P_{S_2/[RT]^{m+n-1}}^{\circ}$. In Figure 6, the straight line fitted through the data points yields slopes (n) of 1.053, 0.997, and 1.107 for the reaction temperatures of 800, 700, and 600 °C, respectively. The order of reaction with respect to the CO concentration is, therefore, equal to unity.

Determination of Rate Constant (k_f). For an isothermal plug flow of gases in a tubular reactor under diluted conditions, the concentrations of a product or a reactant along the reactor length can be tracked in terms of the actual gas residence time {i.e., $dC_{COS}/dz = A/Q(r_{COS})$ can be replaced by $dC_{COS}/dt = r_{COS}$}. The reaction rate constant (k_f) for the reaction between CO
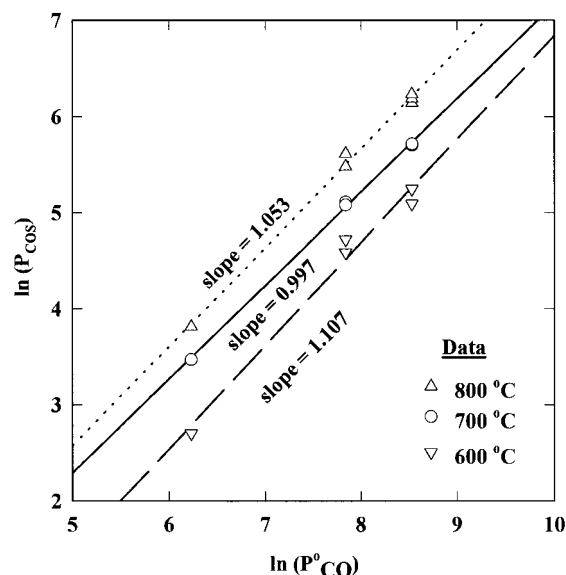
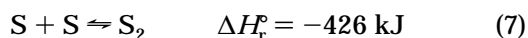**Figure 6.** Order of dependency with respect to CO concentration for COS formation reaction.

Figure 7. Arrhenius plot of rate constant (k_f) for reaction between CO and S_2 to form COS.

and S_2 was determined by integrating eq 4 with both "n" and "m" taken as unity. For the evaluation of the rate constant (k_f), selected data corresponding to a COS conversion of less than 80% of the equilibrium value were used. The calculated rate constants are presented as an Arrhenius plot of the rate constant (k_f) in Figure 7. The plot demonstrates linearity for the range of temperatures investigated. The activation energy, computed from the slope of the plot, was found to be 55.8 kJ/mol. A least-squares minimization of the calculated second-order rate constants yielded (k_f in m^3/(kmol·s))

$$k_f = (3.18 \pm 0.36) \times 10^5 \exp[-(6700 \pm 108 \text{ K})/T] \quad (5)$$

Possible Reaction Mechanism. Since the apparent orders of reaction with respect to the CO and S_2 concentrations are unity, a plausible reaction mechanism for COS formation can be proposed on the basis of the following set of reactions:

$$\text{CO} + \text{S}_2 \rightleftharpoons \text{COS} + \text{S} \qquad \Delta H_r^o = 120 \text{ kJ} \quad (6)$$

$$\text{S} + \text{S} \rightleftharpoons \text{S}_2 \qquad \Delta H_r^o = -426 \text{ kJ} \quad (7)$$

$$\text{CO} + \text{S} \rightleftharpoons \text{COS} \qquad \Delta H_r^o = -305 \text{ kJ} \quad (8)$$

The initial step involves reaction of CO and S_2 to form COS and atomic sulfur via reaction 6. The sulfur atom can subsequently react with another sulfur atom or with CO according to reactions 7 and 8, respectively. Association of two atoms or an atom and a diatomic molecule are known to proceed via rapid reactions.[11−12] Hence, it is expected that a sulfur atom produced from reaction 6 will react rapidly, and therefore, the rate-limiting step for the three reactions' (6−8) mechanism is expected to be reaction 6. Using the steady-state hypothesis for the sulfur atom, it can be derived that the rate constant for the COS-forming reaction 6 will be one-half the observed rate constant (k_f), if reaction 8 dominates as the subsequent reaction, and will be equal to the observed rate constant (k_f), if reaction 7 dominates as the subsequent reaction. Since CO concentrations are expected to be greater than 2 orders of magnitude than S atom concentrations, reaction 8 will dominate.
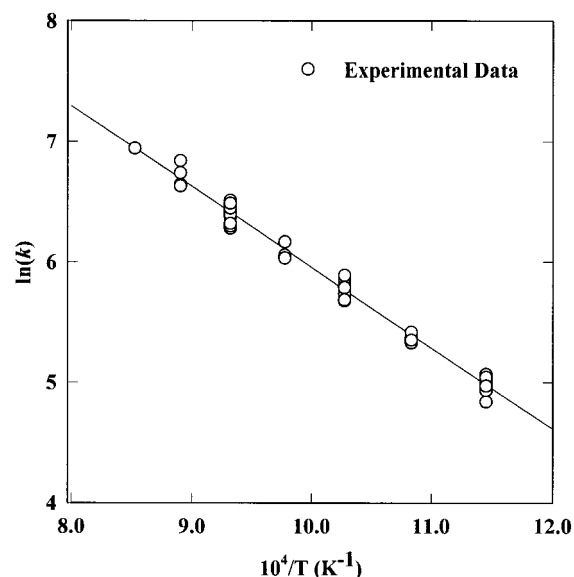
The reverse of reaction 6 has been studied recently by Oya et al.[13] and Woiki et al.[14] who reported activation energies of 23.8 and 37 kJ/mol, respectively. Therefore, the activation energy of the forward reaction would be expected to be in the range of 140−160 kJ/mol (=$\Delta H_r^o - \Delta nRT + E_r \sim$ 120+24 or 37 kJ/mol). However, the observed activation energy is approximately 40% of that expected. This suggests that the reaction possibly proceeds via the formation of the reaction intermediates which have a lower energy barrier. Also, it is possible that the reaction in the reverse and the forward direction proceeds along different reaction pathways which involve the formation of different reaction intermediates. For example, the reaction intermediate formed during the forward reaction could be [O=C=S- - - -S]$^\#$ while that formed during the reverse reaction could be [O=C- - - -S=S]$^\#$. Clearly, the location of a single bond associated with the sulfur atom is different in the two postulated reaction intermediates; hence, the energy required to form or to break the relevant bond is expected to be different. This may be a possible explanation of the observed activation energy for reaction 6 being less than the expected value of 160 kJ.

The low preexponential factor also needs some discussion. We calculated the preexponential or the frequency factor from the collision theory[15] to be of the order 10^{11} m^3/(kmol·s) for the reaction between S_2 and CO. The observed frequency factor is about 0.3×10^6 m^3/(kmol·s), which implies that the steric factor is of the order 10^{-5} or 10^{-6}. This steric factor may seem to be an extremely low value. According to the statistical theory,[15] the steric factor for a reaction involving two diatomic molecules to form a nonlinear complex is in the range 10^{-3} to 10^{-6} and that for the reaction between two diatomic molecules forming a linear complex is 10^{-4} to 10^{-8}. Since the observed steric factor lies in the range predicted by the statistical theory, the low preexponential factor should not be considered to be an anomaly.

Development of a Kinetic Model for the COS Reaction. The overall reaction for COS formation can be represented according to the following stoichiometric equation:

$$2\text{CO} + \text{S}_2 \rightleftharpoons 2\text{COS} \quad (9)$$

We have seen earlier that the COS-forming reaction between CO and S_2 is equilibrium-limited, especially at high temperatures when both the forward rate and the reverse rate for reaction 9 become rapid and lead quickly to attainment of the equilibrium. Hence, in the development of a kinetic model for COS formation, the reverse of reaction 9 must be included to predict the equilibrium. At first, we attempted to account for the reverse reaction by adding a second term in eq 4 to satisfy the chemical reaction equilibrium (i.e., $K_{eq} = C_{CO}^2 C_{S_2}/C_{CO}^2$); the rate of formation of COS was represented as

$$r_{COS} = k_f[C_{CO}C_{S_2} - (C_{COS}^2/C_{CO})/K_{eq}] \qquad (10)$$

where K_{eq} is the equilibrium constant for reaction 9. Although this rate expression yielded the correct equilibrium composition for the reacting mixture, there was an inherent problem in the manner that the equilibrium had been forced into the equation. An inspection of eq 10 clearly shows that for a reaction mixture containing only COS or a zero amount of CO, numerical problems will result as the second term will approach infinity.

To overcome this problem, we modified the second term on the right-hand side of eq 10 as follows:

$$r_{COS} = K_F C_{CO}C_{S_2} - 2k_r C_{cos}C_t \qquad (11)$$

The new term represents the rate of decomposition of COS into CO and elemental sulfur. The kinetics of this reaction has been studied in shock tubes at high temperatures by a number of researchers.[13,16-19] Among these works, the lowest temperature investigated was that by Scheker and Wagner[18] who report the kinetic data up to a temperature of 1227 °C. The rate constants of a COS decomposition reaction reported in the more recent studies[13,16] was extrapolated to the temperatures of our experimental study. Simulations were performed to predict the COS formation in the tubular reactor at the experimental conditions used in our experiments. The predictions of COS formed in both our reactors were significantly higher for temperatures exceeding 900 °C. This implied that the reverse reaction was much faster than that being predicted by the kinetic model. Thus, we decided to obtain the rate constant of the reverse reaction k_r by regressing the experimental data. The regressed rate constant (k_r in m^3/(kmol·s)) was fitted with the following Arrhenius equation:

$$k_r = (2.18 \pm 1.12) \times 10^9 \exp[-(21630 \pm 160 \text{ K})/T] \qquad (12)$$

The activation energy for COS decomposition computed from eq 12 was 180 kJ/mol.

To demonstrate the effectiveness of the COS kinetic model developed, the predictions from the kinetic model (eq 11) are compared with the experimental data in Figure 8. The calculations were performed assuming isothermal and isobaric conditions and plug flow of gases. The model predictions are in good agreement with the data over a wide range of temperatures and residence times. At higher temperatures, the predictions for COS formed in the two reactors are almost equal, which corresponds to the equilibrium condition. Since a good match was obtained between the kinetic model predictions and the experimental data for the
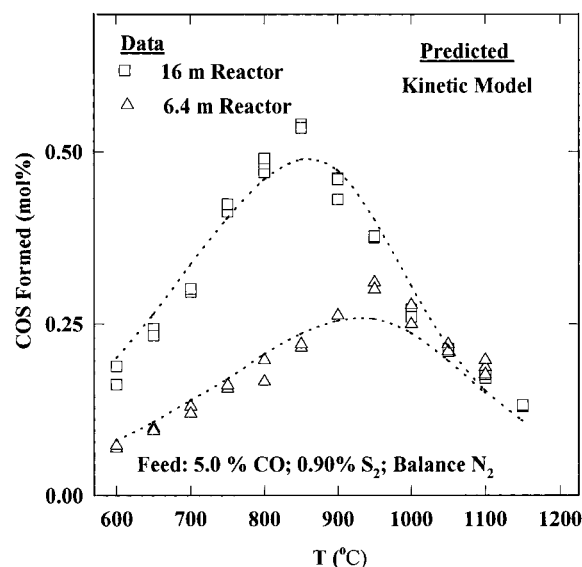

Figure 8. Predictions of COS formed in two quartz reactors using the kinetic model. (Feed: 5.0 mol % CO, 0.90 mol % S_2, balance N_2.)
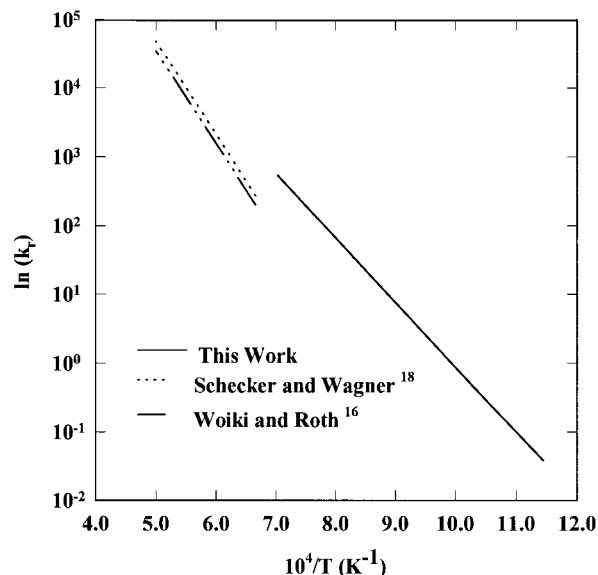

Figure 9. Comparison of rate constant for COS decomposition reaction.

complete temperature range investigated in this study, it can be concluded that the kinetic model adequately represents both the kinetic and the thermodynamic equilibrium limitation.

Although not an objective of this study, a comparison between the reaction rate constant for COS decomposition reaction reported in earlier studies[16,18] and that obtained via regression of data in this study was done. The rate constants calculated for the range of temperature used in the present experimental study is shown in Figure 9. The rate constants calculated from other studies[16,18] and this work seem to be in the same order of magnitude for a temperature of 1200 °C; however, the slopes seem to be different. There is no reliable kinetic information on a gas-phase COS decomposition reaction at lower temperatures (<1200 °C), and there is always a risk of error associated in extrapolating rate expressions beyond the temperature range recommended. Hence, to complete the kinetic model for COS reaction, we are currently conducting experimental

study on a COS decomposition reaction in the temperature range of our interest (600−1300 °C).[5]

Conclusions

A high-temperature flow reactor system to measure intrinsic kinetics of homogeneous gas-phase reactions has been developed in our laboratory. An experimental study of the intrinsic kinetics of the reaction between CO and S_2 has been completed. The reaction was found to be very rapid at temperatures exceeding 1000 °C, reaching equilibrium in 0.7 s or less. The apparent order of reaction was found to be first-order with respect to concentrations of CO and S_2. The overall second-order reaction rate can be expressed as: $k_f = (3.18 \pm 0.36) \times 10^5 \exp[-(6700 \pm 108 \text{ K})/T]$ m³/(kmol·s) for $873 \leq T \leq 1273$ K. Reliable kinetic data on a COS decomposition reaction is required to establish the intrinsic reaction rates and the reaction mechanism at conditions such as those encountered in the RF and WHB.

Acknowledgment

Nomenclature

A = cross-sectional area of tubular reactor, m²
C_{S_2} = concentration of S_2 ($=P_{S_2}/RT$), kmol/m³
C_{CO} = concentration of CO ($=P_{CO}/RT$), kmol/m³
C_{COS} = concentration of COs ($=P_{COS}/RT$), kmol/m³
C_t = total concentration of gases ($=P_t/RT$), kmol/m³
k_f = forward reaction rate constant, m³/(kmol·s)
k_r = reverse reaction rate constant, m³/(kmol·s)
K_{eq} = equilibrium constant for reaction 8 ($=[C_{COS}]^2/[C_{CO}^2 C_{S_2}]$)
P = pressure, Pa
Q = volumetric flow rate of gas, m³/s
R = universal gas constant, equal to 8314 J/(kmol·K)
r_{COS} = rate of formation of COS, kmol/(m³·s)
T = temperature, K
T_s = furnace set point temperature, °C

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