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## KINETICS, CATALYSIS, AND REACTION ENGINEERING

## Kinetics of Carbonyl Sulfide Hydrolysis. 1. Catalyzed and Uncatalyzed Reactions in Mixtures of Water + Propane

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Carbonyl sulfide (COS), which occurs as an impurity in commercial sources of propane, can hydrolyze in the presence of water to form hydrogen sulfide (H<sub>2</sub>S) and carbon dioxide (CO<sub>2</sub>). Whereas COS is not itself corrosive, the hydrolysis product H<sub>2</sub>S is corrosive, especially in the presence of water. In this paper, we summarize the results from studies that address the issue of COS hydrolysis in propane, thought to be a major problem in the liquefied petroleum gas industry. A series of kinetics measurements were made of COS in a propane–water system. Reaction rates were determined from chromatographic monitoring of the decrease in COS and the appearance of H<sub>2</sub>S in the vapor phase as a function of time. The hydrolysis rate was measured for 500 and 1000 ppm mixtures of COS in propane at 38, 65, and 85 °C. COS hydrolysis was not observed in propane at 16 °C. In addition, rate constants were measured for the hydrolysis reaction catalyzed by potassium hydroxide and alkanolamines. The rate of hydrolysis of COS in the aqueous propane system is several orders of magnitude lower than that in pure water.

## Introduction

Carbonyl sulfide (COS or S=C=O, CAS: 463-58-1), is present in minor amounts in petroleum and coal refinery gases and, to a greater extent, in coal gasification streams.<sup>1,2</sup> This compound occurs as an impurity in commercial sources of propane (referred to as liquefied petroleum gas, LPG) and can hydrolyze in the presence of water to form hydrogen sulfide (H<sub>2</sub>S)



Whereas COS is not itself corrosive, the hydrolysis product H<sub>2</sub>S is corrosive, especially in the presence of water. Because propane and carbonyl sulfide have relatively similar normal boiling temperatures (−42.1 °C for propane, −50.2 °C for COS), approximately 90% of petrochemical COS is found in the propane fraction of refinery gases. It is not unusual to find up to 200 ppm (mass/mass, grams of COS/10<sup>6</sup> total grams) COS in the propane refinery fraction. Carbonyl sulfide also occurs in natural gas, and reports of COS in downstream natural gas are increasing.<sup>3</sup> Natural gas is usually saturated with water at the well head, and much of the COS that is present is hydrolyzed to H<sub>2</sub>S before processing.

The corrosive nature of acidic sulfur compounds in fuel gases such as LPG is reflected in the failure of the ASTM copper strip corrosion test.<sup>4,5</sup> In this test, a

sample of moist LPG is held for 1 h at 38 °C (100 °F) in contact with a strip of polished copper. The extent of tarnish to the copper strip determines the pass/fail result. LPG lots that fail the copper strip corrosion test must be reprocessed or remixed, thus incurring additional costs for industry and the consumer. Engineering literature indicates that a COS concentration of 58 ppm (mass/mass) will cause failure of the copper strip corrosion test, with the presumed mechanism being hydrolysis of COS to H<sub>2</sub>S.<sup>6,7</sup> It has also been observed that a tank car of LPG will pass the copper strip test in the morning but fail the test in the afternoon after sitting in the sun for several hours. One researcher has reported a passing batch of LPG failing the copper strip test less than 30 min later.<sup>8</sup> Here again, the presumed mechanism is hydrolysis.

There have been many studies of the COS hydrolysis reaction over a wide pH range in aqueous solutions;<sup>9–11</sup> with amine-based catalysts in aqueous, alcoholic, and glycolic solutions;<sup>12–18</sup> and with numerous metal oxide catalytic surfaces.<sup>2</sup> The removal of COS from fuel gases by means of alkanolamine absorption has been an important industrial process for decades. There has been only one measurement of the hydrolysis of COS in a hydrocarbon medium; in this case, *n*-hexane was used as a model for LPG.<sup>7</sup> The hydrolysis rate at 25 °C was found to be more than 5 orders of magnitude lower in *n*-hexane than the value reported for pure water.<sup>9,11</sup> Although reaction rates are greatly influenced by solvent effects for mixed-solvent systems,<sup>19</sup> the solubility of alkanes in water is much too low to significantly alter the solvent properties of the aqueous phase. It was

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therefore desirable to study the hydrolysis reaction in a propane–water medium to investigate the potential of COS hydrolysis to cause LPG failure. The effects of temperature, COS and water concentrations, and base catalysis were evaluated as part of this research. In a subsequent study, the COS hydrolysis rate was measured in the presence of various water–hydrocarbon systems and found to vary significantly.<sup>20</sup>

## Experimental Section

**Chemicals.** The propane used in this study had a specified purity of 99.7% (mass/mass) or better; purity was confirmed by gas chromatography with flame ionization detection. Our commercially obtained COS had a specified purity of 99.0% (mass/mass); however, hydrogen sulfide was found as an impurity by gas chromatographic analysis. To remove this impurity, the COS was passed first through a column with 3A molecular sieve to remove any water that might have contributed to the formation of H<sub>2</sub>S and then through a column packed with 4A molecular sieve to remove the H<sub>2</sub>S. The molecular sieves had been activated at 330 °C under vacuum overnight. After the purification, H<sub>2</sub>S was not detected by injection of even large volumes of COS into a gas chromatograph equipped with a sulfur chemiluminescence detector with a detection limit of 1 ppb (mass/mass, grams of sulfur/10<sup>9</sup> total grams) total sulfur. Potassium hydroxide (KOH), monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), triethanolamine (TEA), *N,N*-dimethylformamide (DMF), and methanol (MeOH) were research grade or better and were used as received from commercial suppliers, with the exception of DMF, which was dried over 5A molecular sieve. Distilled, deionized water was used for all experiments and was not buffered. For one series of measurements, a comparison was made of the rate constants obtained for a sample of untreated water versus those obtained with water that had been degassed by bubbling helium through the sample for several hours prior to use. No distinction could be made between the two rate constants obtained; all other experiments were done with water in contact with atmospheric gases.

**Sample Preparation.** For each measurement of the hydrolysis reaction rate, mixtures of COS and propane were prepared gravimetrically with additions of the components into a clean, evacuated sample cylinder. Sample cylinders were constructed of carbon steel, and all valves, fittings, and tubing were 316 stainless steel. Mixtures contained nominally 100 ± 0.001 g of propane plus the quantity of COS (± 0.001 g) necessary to make the desired concentration. Concentrations ranged from 50 to 1000 ppm (mass/mass) COS.

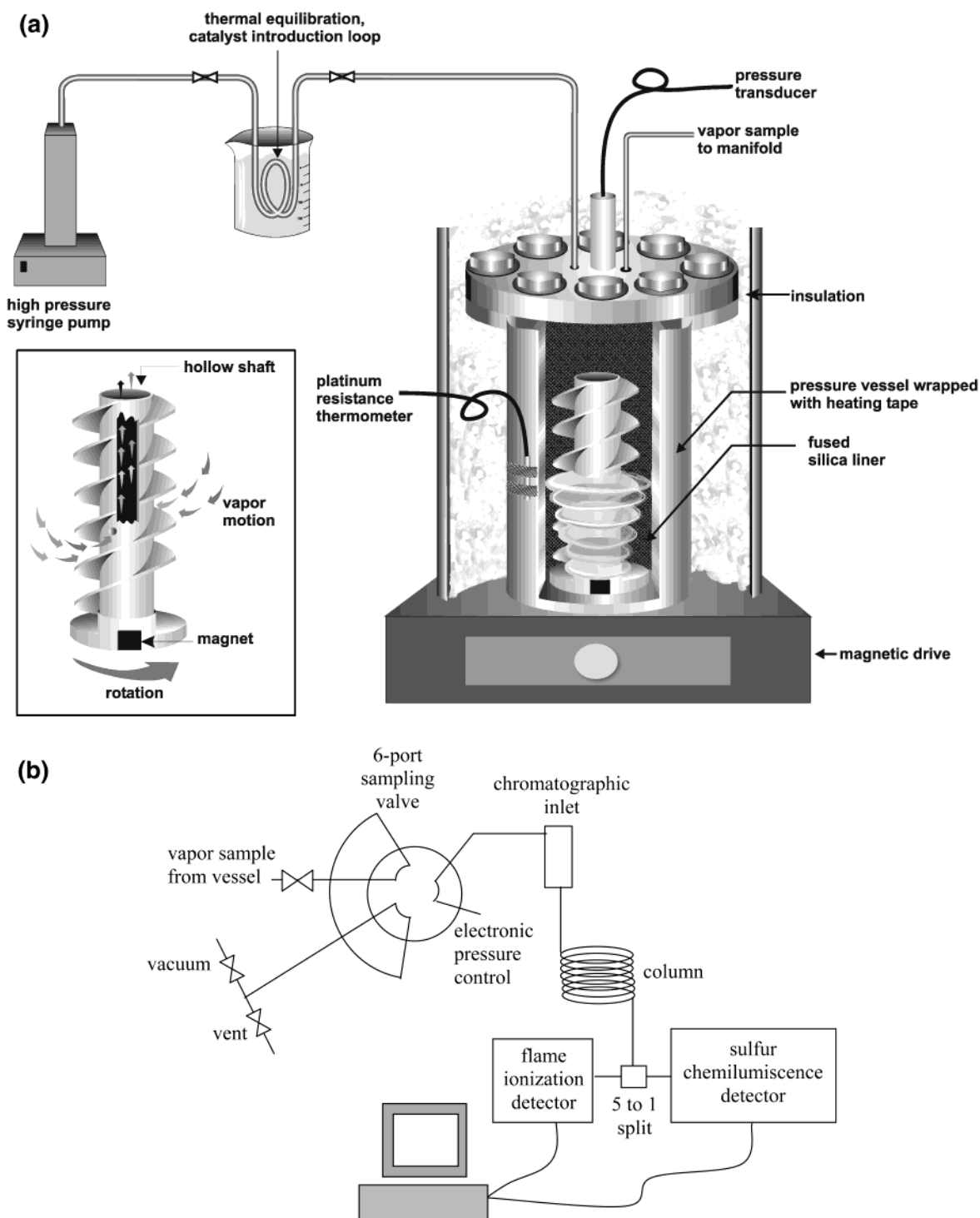
**Apparatus.** The apparatus designed and constructed for the measurement of the hydrolysis consisted of a 600-mL thin-walled pressure vessel made of 316 stainless steel (Figure 1a). The vessel had a bolted closure secured with spring washers and sealed with a 25% glass-filled PTFE gasket. A fused silica liner was incorporated into the vessel to provide an inert environment for the sample. A magnetically coupled mixing rotor for vapor–liquid entrainment was placed inside the fused silica liner to create dynamic equilibration of

the phases (Figure 1a, inset).<sup>21,22</sup> The mixing rotor was constructed of Delrin<sup>23</sup> for its light weight and inertness. It was equipped with a PTFE-coated strontium carbonate–iron oxide magnet coupled to an external magnetic stirring motor positioned below the reaction vessel. The apparatus was equipped with a digital strain gauge and readout to provide monitoring of the internal pressure (±7 kPa) of the system. A vortex tube was used for heat balancing for the 16 °C measurements.<sup>24</sup> For all other temperatures, the vessel was wrapped in heating tape and insulated with glass wool. A platinum resistance probe and microprocessor-based temperature controller provided both temperature control and measurement to within ±0.5 °C.

The reaction vessel was evacuated to 0.13 Pa, and the prepared mixture was quantitatively transferred by thermal distillation into the chilled vessel. The vessel contents were mixed and heated to the desired temperature, and the mixture was allowed to reach equilibrium. Equilibrium typically required 1 day and was determined by observation of the vessel temperature and pressure and by monitoring of the chemical composition of the vessel contents as described below. These observations provided verification of the leak-tight integrity of the apparatus, as well as verification that the hydrolysis reaction had not started by the inadvertent introduction of fugitive water.

The reaction vessel was attached to a manifold that allowed sampling of the vapor phase and addition of the water needed to initiate the hydrolysis reaction. Unless otherwise specified, 100 mL of water was injected into the reaction vessel with a high-pressure syringe pump capable of dispensing ±0.02 mL at a pressure of up to 41.4 MPa (6000 psig). The pump was typically operated at 6.9 MPa (1000 psig) to eliminate the potential of backflow into the pump. The injected water was first passed through a heat exchanger coil submerged in a water bath to preheat the water to the reaction vessel temperature. For the catalyzed reactions, a weighed amount of catalyst was added to the heat exchanger coil. The coil was then back-filled with water and reattached to the syringe pump. No residual catalyst could be detected in the coil after the 100-mL volume had been injected into the reaction vessel. The experimental pressure of the reaction mixture was the saturation pressure of the COS–propane–water system at each experimental temperature. For systems consisting of 1000 ppm (mass/mass) COS in propane and 100 mL of water, the experimental pressure was approximately 3.5, 3.0, and 1.7 MPa for system temperatures of 85, 65, and 38 °C, respectively.

**Analytical Method.** The COS–propane–water system exists as a pressurized vapor–liquid–liquid equilibrium. Although a chemical analysis applied to each of the three phases (as a function of time) is conceptually attractive, numerous factors make this approach impractical. We therefore designed our measurements to utilize the vapor concentrations of COS and H<sub>2</sub>S as a probe for the reaction. Entrainment of the vapor into the liquid propane and aqueous phases is critical to the measurement of a multiphase kinetics reaction, because it promotes mass transfer and a rapid approach to chemical equilibrium. For the COS–H<sub>2</sub>O system, mass transport is fast relative to hydrolysis,<sup>25,26</sup> which, coupled



**Figure 1.** Experimental apparatus consists of (a) reaction vessel (entraining rotor is shown in the inset), and (b) chromatographic system.

with the use of the vapor–liquid entraining rotor, makes vapor monitoring a practical approach.<sup>21,22</sup> To illustrate the advantage of the entraining rotor, at the beginning of the hydrolysis measurement, the introduction of water invariably produced a perturbation in the system (pressure and phase equilibrium). When the rotor was used, up to 1 h was required to recover from the perturbation. With a commercial stir bar, recovery took nearly 24 h.

To analyze the reaction vessel contents, a sample of the vapor phase was expanded by flowing into a six-

port gas chromatographic sampling valve (Figure 1b). All of the lines from the reaction vessel to the sampling valve were heat traced (to 95 °C) to prevent condensation of the gaseous sample. The sample residing in the six-port valve at atmospheric pressure was then injected into a septum-purged split–splitless gas chromatograph inlet. The inlet was maintained at 250 °C, and the pressure was controlled isobarically with electronic pressure programming at 69 kPag (10 psig). The sample was separated on an analytical chromatographic column (30-m open tubular column of styrene/divinyl benzene

**Table 1. Summary of Hydrolysis Rate Constants**

| COS in propane<br>[ppm (mass/mass)] | temp<br>(°C) | H <sub>2</sub> O<br>(mL) | catalyst    | N <sup>a</sup> | <i>K</i><br>(s <sup>-1</sup> ) | ±2σ                     | uncertainty<br>( <i>k</i> = 2) (%) | <i>t</i> <sub>1/2</sub><br>(h) |
|-------------------------------------|--------------|--------------------------|-------------|----------------|--------------------------------|-------------------------|------------------------------------|--------------------------------|
| 1000                                | 85           | 100                      | —           | 3              | 2.84 × 10 <sup>-5</sup>        | 2.25 × 10 <sup>-6</sup> | 7.90                               | 6.77                           |
| 1000                                | 65           | 100                      | —           | 2              | 5.94 × 10 <sup>-6</sup>        | 2.33 × 10 <sup>-7</sup> | 3.92                               | 32.4                           |
| 1000                                | 38           | 100                      | —           | 2              | 5.29 × 10 <sup>-7</sup>        | 6.22 × 10 <sup>-8</sup> | 11.80                              | 364                            |
| 500                                 | 85           | 100                      | —           | 2              | 2.28 × 10 <sup>-5</sup>        | 7.03 × 10 <sup>-7</sup> | 3.09                               | 8.45                           |
| 500                                 | 65           | 100                      | —           | 3              | 3.89 × 10 <sup>-6</sup>        | 3.54 × 10 <sup>-7</sup> | 9.11                               | 49.5                           |
| 500                                 | 38           | 100                      | —           | 1              | 6.53 × 10 <sup>-7</sup>        | 1.31 × 10 <sup>-7</sup> | 20.1                               | 295                            |
| 50                                  | 65           | 100                      | —           | 1              | 3.63 × 10 <sup>-6</sup>        | 1.05 × 10 <sup>-6</sup> | 28.9                               | 53.1                           |
| 500                                 | 85           | 10                       | —           | 2              | 2.94 × 10 <sup>-6</sup>        | 4.09 × 10 <sup>-7</sup> | 13.9                               | 65.4                           |
| 250                                 | 85           | 10                       | —           | 2              | 2.87 × 10 <sup>-6</sup>        | 5.27 × 10 <sup>-7</sup> | 20.0                               | 67.1                           |
| 125                                 | 85           | 10                       | —           | 2              | 2.94 × 10 <sup>-6</sup>        | 2.42 × 10 <sup>-7</sup> | 8.24                               | 65.5                           |
| 1000                                | 85           | 100                      | 1.0 M KOH   | 2              | 3.24 × 10 <sup>-4</sup>        | 2.52 × 10 <sup>-5</sup> | 7.79                               | 0.595                          |
| 1000                                | 85           | 100                      | 0.15 M KOH  | 1              | 1.51 × 10 <sup>-4</sup>        | 1.12 × 10 <sup>-5</sup> | 7.44                               | 1.28                           |
| 1000                                | 85           | 100                      | 0.15 M MEA  | 1              | 3.83 × 10 <sup>-5</sup>        | 2.76 × 10 <sup>-6</sup> | 7.21                               | 5.03                           |
| 1000                                | 85           | 100                      | 0.15 M DEA  | 1              | 6.10 × 10 <sup>-5</sup>        | 2.22 × 10 <sup>-6</sup> | 3.64                               | 3.15                           |
| 1000                                | 85           | 100                      | 0.15 M TEA  | 1              | 1.31 × 10 <sup>-5</sup>        | 3.28 × 10 <sup>-7</sup> | 2.50                               | 14.7                           |
| 1000                                | 85           | 100                      | 0.15 M DIPA | 1              | 4.63 × 10 <sup>-5</sup>        | 5.61 × 10 <sup>-6</sup> | 12.1                               | 4.16                           |
| 1000                                | 85           | 100                      | 0.15 M DMF  | 1              | 2.71 × 10 <sup>-5</sup>        | 6.10 × 10 <sup>-7</sup> | 2.25                               | 7.10                           |
| 1000                                | 85           | 100                      | 0.15 M MeOH | 1              | 2.61 × 10 <sup>-5</sup>        | 1.88 × 10 <sup>-6</sup> | 7.20                               | 7.39                           |

<sup>a</sup> *N* = number of measurement replicates.

copolymer) that was maintained isothermally at 60 °C. A 5:1 postcolumn split directed the “5” stream into a flame ionization detector and the “1” stream into a sulfur chemiluminescence detector (SCD). The onset of the hydrolysis reaction was noted by the gradual decrease of COS and the concurrent increase of H<sub>2</sub>S. The SCD is an equimolar detector providing a peak area signal that gives equivalent responses for COS and H<sub>2</sub>S. Peak areas are thus directly proportional to the molar concentrations of COS and H<sub>2</sub>S in the sampled vapor, and response factors were unnecessary for quantitation.

**Rate Determination.** The general rate law for eq 1 is

$$-\frac{\partial[\text{COS}]}{\partial t} = k[\text{COS}][\text{H}_2\text{O}][\text{catalyst}] \quad (2)$$

Under the condition of excess water and catalyst (or no catalyst), pseudo-first-order kinetics are observed, and eq 2 reduces to

$$-\frac{\partial[\text{COS}]}{\partial t} \approx k'[\text{COS}] \quad (3)$$

where *K* is the pseudo-first-order rate constant. Therefore, a plot of ln [COS], or in this case ln(COS peak area), against time yields a line with a slope equal to *K*.

## Results

The desire in this work was to simulate conditions typically found in industrial LPG operations. We initially sought to conduct measurements with small quantities of water, ambient temperatures, and low concentrations of COS. Several hydrolysis measurements were made with microliter quantities of water added to the COS–propane mixture. A mixture containing 50 μL of water [500 ppm (mass/mass)] and 1000 ppm (mass/mass) COS in propane was maintained at 16 °C (60 °F) for 81 days with no H<sub>2</sub>S being detected. A second mixture, containing 150 μL of water [1500 ppm (mass/mass)] and 1800 ppm (mass/mass) COS in propane was maintained at 65 °C for 2–3 weeks, and again, no H<sub>2</sub>S was detected. We concluded from these experiments that

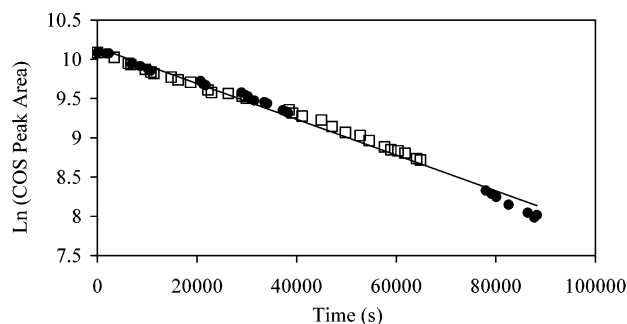
a separate aqueous phase would be required to make the reaction proceed and that the reaction itself most probably occurs in the aqueous phase.<sup>27</sup> Hydrogen bonding polarizes the C=O bond, making it more susceptible to hydrolysis. An environment with an abundance of water will produce a field in which hydrolysis is favorable.<sup>28</sup>

In subsequent experiments, 100 mL of water was added to the vessel to ensure that a large liquid water phase was present. Even with the large excess of water, the measurement of two 1000 ppm (mass/mass) COS mixtures at 16 °C resulted in no observable reaction after 5 days. For many industrial operations, LPG that has not produced any H<sub>2</sub>S after 5 days would not be considered problematic. In less common cases, a batch of LPG can be stored for several months. In those cases, the low-temperature reaction could be important.

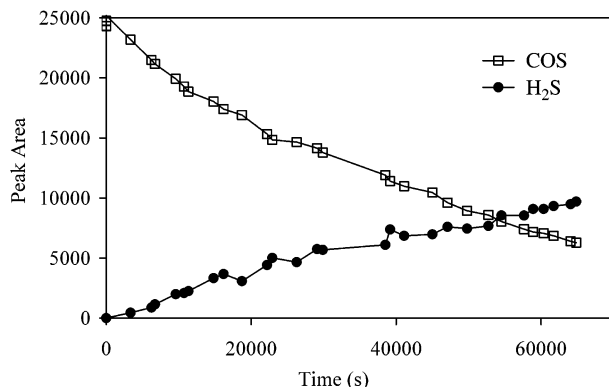
Hydrolysis reaction rates were measured over the temperature range of 38–85 °C in a three-phase system consisting of water, liquefied propane, and the resulting vapor. Rates, half-lives, and uncertainties for all COS mixtures are summarized in Table 1. All rate constants reported include a combined standard uncertainty based on two standard deviations (coverage factor, *k* = 2) about the slope of the measurement result.<sup>29</sup> The average standard uncertainty for these measurements was 9.82%. Each measurement of the hydrolysis rate included an average of 30 peak area–time pairs. When the rate was measured in duplicate or triplicate (denoted by *N* in Table 1), each of the ln(COS peak area) versus time plots was overlaid, and the rate constant was derived from the slope of the combined data. The standard deviation in the slope of each separate measurement was less than the uncertainty about the slope of the combined data. As an example of the measured data, a plot of ln(COS peak area) against time for the 500 ppm (mass/mass) measurements at 85 °C is provided in Figure 2. The pseudo-first-order behavior is apparent from the linearity of the plot and from essentially the same slope being obtained for the first and second half-lives.

For all initial concentrations of COS, appreciable hydrolysis occurred only for the measurements at 65 and 85 °C. At these temperatures, the reaction proceeds





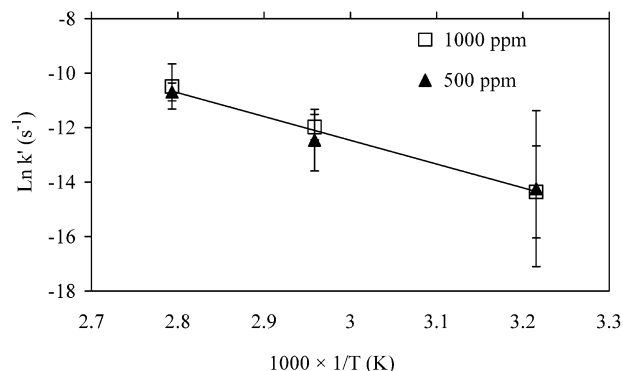
**Figure 2.** Kinetics data for two 500 ppm (mass/mass) COS-propane mixtures at 85 °C.



**Figure 3.** GC-SCD analysis of reaction vapor shows depletion of COS and increase of H<sub>2</sub>S for 500 ppm (mass/mass) COS-propane mixture at 85 °C.

to completion, with the total loss of COS and concurrent emergence of H<sub>2</sub>S (Figure 3). In this context, completion refers to our inability to detect COS in the vapor phase with an instrument having a detection limit of 1 ppb (mass/mass) total sulfur. Rate constants were calculated from data covering the first two half-lives of the reaction. At 85 °C, the hydrolysis reaction for the 1000 and 500 ppm (mass/mass) mixtures was essentially complete after 2.5 days. At 65 °C, the reaction required about 2 weeks to completely deplete the COS. Very slow progress of the hydrolysis was observed at 38 °C, and the reaction was monitored for only 7 days, or about half of the first half-life. The larger relative uncertainties in the measured rate constants at 38 °C are likely a result of attempting to observe small changes in large peak areas.

The temperature dependence of the hydrolysis from 38 to 85 °C is shown in Figure 4. The data yield an Arrhenius expression equal to  $k' = 9.18 \times 10^5 \text{ s}^{-1} \exp[-8700/T(\text{K})]$  with an activation energy of  $72 \pm 4 \text{ kJ/mol}$ . The slight discrepancy between the pseudo-first-order rate constants obtained with mixtures starting at 1000 ppm (mass/mass) and those starting at 500 ppm (mass/mass) fall within the experimental uncertainty of the data. This discrepancy is relatively minor for kinetic studies, however. It must be understood that, when the concentration of the 1000 ppm (mass/mass) mixture reaches 500 ppm (mass/mass), the pH and ionic strength are undoubtedly different from the initial conditions of the 500 ppm (mass/mass) mixture. Clearly, buffering the media would moderate this effect and perhaps improve the agreement, but doing so would not



**Figure 4.** Temperature dependence of the COS hydrolysis reaction from 38 to 85 °C.

simulate the conditions that are encountered in industry; therefore, no buffer was added to the mixtures.

Finally, the hydrolysis rate of a 50 ppm (mass/mass) COS in propane mixture was measured at 65 °C and yielded a rate constant of  $3.63 \times 10^{-6} \text{ s}^{-1}$  with a standard uncertainty ( $k = 2$ ) of 28.9%. Although this measured rate constant is comparable to the 500 and 1000 ppm (mass/mass) data at 65 °C, the low concentration of COS limited our sampling frequency so that the COS concentration would not be significantly depleted. The standard uncertainty is much higher for this rate constant than for the other measurements, because of the small number of data points obtained. Regardless, the similarity of this rate constant to those of the higher-concentration mixtures supports the pseudo-first-order nature of the hydrolysis reaction.

**Rate Dependence on Water Concentration.** In addition to the 100 mL of water experiments and the low-water-concentration experiments discussed above, the COS hydrolysis reaction in propane at 85 °C was measured in duplicate for COS concentrations of 125, 250, and 500 ppm, wherein each measurement was initiated by the injection of only 10 mL of water. The rate constant was identical for all six measurements, yielding an average of  $k' = 2.92 \times 10^{-6} \text{ s}^{-1}$  with an average standard uncertainty ( $k = 2$ ) of 14.3%, as shown in Table 1. Although we did not see a change in  $k'$  with decreasing COS concentration,  $k'$  was an order of magnitude lower with 10 mL of water than with 100 mL of water.

**Base-Catalyzed Hydrolysis.** The pronounced catalytic effect of base is evident from the measurements made at 85 °C on mixtures of 1000 ppm (mass/mass) COS in propane (Table 1). In these experiments, H<sub>2</sub>S that formed in the aqueous phase immediately reacted with the base, and vapor-phase H<sub>2</sub>S was usually not detected chromatographically. The 0.15 M KOH solution resulted in a pseudo-first-order rate constant over 5 times higher than  $k'$  for pure water. Increasing the KOH concentration to 1.0 M increased  $k'$  by more than an order of magnitude above that of pure water. Reaction rates for the hydrolysis reaction in alkanolamine solutions were also measured. As shown in Table 1,  $k'$  increases in the order TEA < H<sub>2</sub>O < MEA < DIPA < DEA (where H<sub>2</sub>O represents the uncatalyzed reaction), with the 0.15 M DEA solution doubling the uncatalyzed reaction rate. Although the alkanolamines are less catalytic toward the hydrolysis than KOH, with the

exception of TEA, the compounds studied showed a 35–115% increase in hydrolysis rate.

## Discussion

Previously, Derdall and Hyne found<sup>7</sup> that, at 25 °C, the rate of hydrolysis of COS in a hexane–water system is  $1 \times 10^{-10} \text{ s}^{-1}$ , or more than 5 orders of magnitude lower than the rate reported for pure water ( $2.2 \times 10^{-5} \text{ s}^{-1}$ ).<sup>9,11</sup> Although our study only covered the temperature range 38–85 °C, extrapolation of the Arrhenius equation for propane–water to 25 °C yields  $k \approx 1.9 \times 10^{-7} \text{ s}^{-1}$ , a value intermediate between those for hexane–water and pure water. The pure-water rate constant at 85 °C can be estimated from extrapolation of Thompson's hydrolysis data from 16 to 48 °C to yield  $k \approx 1.4 \times 10^{-2} \text{ s}^{-1}$ .<sup>9</sup> Although both extrapolations are only approximate, it is clear that the presence of a hydrocarbon in contact with the aqueous phase causes the rate of the hydrolysis reaction to decrease by several orders of magnitude. This is a rather remarkable result considering that the solubility of alkanes in water is much too low to significantly alter the solvent properties of the aqueous phase. In related work, we found that the COS hydrolysis rate is affected by the size of the alkane present and that  $k$  is well correlated with the diffusion coefficient for alkane diffusion in water.<sup>20</sup>

When only microliter quantities of water were added to the reaction mixtures, the water molecules outnumbered the COS molecules by factors of only 2 to 1 and 50 to 1, and no reaction was observed. When 10 mL of water was present,  $k$  was an order of magnitude lower than the hydrolysis rate constant measured for the 100 mL of water experiments. Although 10 mL of water represents a 330-fold molar excess of water to COS, the reaction rate is obviously limited under these conditions. The linearity of the  $\ln(\text{COS peak area})$  versus time plots shows that the hydrolysis follows first-order kinetics in COS concentration, yet the observed rate dependence on water concentration clearly shows that the 10 mL of water experiments do not adhere to the pseudo-first-order approximation overall. The experiments with 100 mL of water represented a 3300-fold molar excess of water to COS. Under the conditions of the experiment, when 100 mL of water is present, the volume of the water phase is roughly equal to the volume of the condensed propane phase. It is unlikely that more than an equal volume of water would be found in commercial LPG. Therefore, we did not increase the quantity of water above 100 mL.

**Measurements of Base-Catalyzed Systems.** In a base-catalyzed system, COS hydrolysis is a two-step reaction that proceeds through a monothiocarbamate ( $\text{HCO}_2\text{S}^-$ ) intermediate.<sup>11,14</sup>



Experimental plots of  $\ln(\text{COS peak area})$  vs time yielded a straight line for the base-catalyzed hydrolysis with an average standard deviation ( $k = 2$ ) about the slope of only 6.78% for the six basic systems measured. From the linearity of the first-order approximation, it appears

that the pseudo-first-order rate approximation is valid for these measurements made in large excess of water and base. Nevertheless, the KOH-catalyzed results clearly show that the reaction is not first-order overall because increasing the KOH concentration from 0.15 to 1.0 M doubles the observed reaction rate. This is a common observation in catalyzed hydrolysis reactions.

Researchers have found correlations between the COS hydrolysis rate and  $\text{p}K_b$  of basic catalysts;<sup>12–14</sup> however, the few catalysts measured in this study did not yield a linearly correlated data set. Furthermore, MEA and DEA are expected to partially decompose at 85 °C, and the presence of basic decomposition products would further complicate the rate measurement.<sup>30,31</sup> At 85 °C, DEA exhibited the highest catalytic activity of the alkanolamines tested. Reaction rates for the catalyzed propane–water systems are still several orders of magnitude lower than those for alkanolamine-catalyzed reactions in aqueous, alcoholic, or glycolic solutions.<sup>12–18</sup>

Interestingly, TEA caused a 2-fold decrease in reaction rate. Ernst et al.<sup>13</sup> also saw a large decrease in the COS hydrolysis rate constant in the presence of TEA compared with other tertiary amines. It was suggested that the hydroxyl groups on TEA might hydrogen bond to COS or  $\text{H}_2\text{O}$  in a way that lowers the accessibility of the lone pair of electrons on the nitrogen atom. Because we do not obtain the same rate constant in TEA as we do for the uncatalyzed reaction, it is likely that TEA interacts with COS in a way that prevents the COS from reacting. Littel found that the reverse of reaction 4 is more than 4 times faster than the forward reaction for  $\text{COS} + \text{TEA}$  in water–glycol mixtures.<sup>14</sup> This would cause a decrease in the observed reaction rate for TEA-catalyzed hydrolysis.

The hydrolysis reaction was also measured in the presence of MeOH and DMF, two pH-neutral compounds used as “catalysts”. As expected, the reaction rates in the mixed solvent media are similar to that in pure water, although somewhat lower. Previously, COS hydrolysis was found to be more than an order of magnitude slower in concentrated ethanol solutions than in pure water.<sup>9</sup> With a concentration of only 0.15 M, or 2.6 mol %, both MeOH and DMF will slightly lower the dielectric constant of the mixture relative to that of pure water, with a slightly larger reduction for MeOH. The decrease in  $k$  for these two solvent systems is most likely the result of the reduced dielectric constant. It is well-known that changes in solvent media will cause changes in reaction rate.

**Consequences for the LPG Industry.** Although COS hydrolysis is thought to be a major problem for the LPG industry, our measurements indicate that, under the temperatures most commonly encountered in industrial operations (16–38 °C) and in the absence of large quantities of water or basic catalysts, COS hydrolysis is probably too slow to observe. Consistent with our rate measurements, in related work, we found that propane containing as much as 1000 ppm (mass/mass) COS will pass the copper strip corrosion test.<sup>32</sup> The measured rate constant obtained from the present work predicts that a 1000 ppm (mass/mass) COS in propane sample tested by the ASTM method<sup>4</sup> at 38 °C will have lost only 0.19 mol % of the original COS concentration in the 1-h test period. The resulting  $\text{H}_2\text{S}$  concentration

would be only 0.5 ppm (mass/mass), an order of magnitude lower than what is required for an unambiguous copper strip test failure.<sup>32</sup> Note, however, that this scenario is applicable for a batch of LPG that does not contain any H<sub>2</sub>S prior to the copper strip test. It is possibly more realistic that the LPG will contain some quantity of H<sub>2</sub>S, and the additional amount produced during the corrosion test might then cause the batch of LPG to fail the corrosion test.

## Conclusions

The hydrolysis of COS in water–propane systems was studied from 16 to 85 °C to investigate the potential of COS to cause LPG batches to be rejected. Pseudo-first-order rate constants were measured by gas chromatographic analysis of the pressurized vapor–liquid–liquid equilibrium under neutral and basic conditions. No hydrolysis was detected at 16 °C. Over the temperature range where the hydrolysis was measurable (38–85 °C), the rate was found to be several orders of magnitude lower in the presence of propane than in pure water. The hydrolysis rate was found to be strongly dependent on the quantity of water available for reaction, with no reaction occurring when the water-to-COS ratio was 50:1 or lower and an order of magnitude increase in reaction rate when the concentration of water was increased from 330 to 3330 mol of water per mole of COS. In addition to these neutral systems, the hydrolysis was studied for systems catalyzed by KOH and alkanolamines. Except for TEA, which decreased the reaction rate by 50%, the 0.15 M basic solutions tested increased the hydrolysis rate by 35–430%. Although the observed base-catalyzed reaction showed linear pseudo-first-order behavior, the large increase in rate for a 1.0 M KOH-catalyzed reaction confirmed that the kinetics of hydrolysis is dependent on base concentration. In the absence of catalytic compounds, large quantities of water, and/or temperatures higher than those encountered in field operations, the COS hydrolysis reaction alone in propane is unlikely to be problematic for the LPG industry.

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