The Plasma Induced Reaction of Hydrogen Sulfide with Hydrocarbons

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Introduction

The interaction of sulfur with hydrocarbons under a range of experimental conditions has been investigated by various workers. Knight and co-workers[1] reacted excited sulfur atoms, produced by 'in situ' photolysis of COS at 250°C, with a range of paraffinic hydrocarbons and found as primary products only the correponding mercaptans. Bryce and Hinshelwood[2] studied the reaction of sulfur vapor with parafinnic hydrocarbons in the temperature range 320°C to 349°C and observed that the primary products were hydrogen sulfide and unsaturated hydrocarbons. Study of the reaction of sulfur and methane [3-7] over a catalyst at 500°C to 700°C has shown the products to be carbon disulfide and hydrogen sulfide according to the reaction

$$CH_4 + 2S_2 \rightarrow CS_2 + 2H_2S. \qquad (1)$$

Thomas and Strickland-Constable[8] studied the interaction of sulfur and hydrocarbons at temperatures 1200°K to 1500°K and in the absence of a catalyst observed no carbon disulfide formation. With a catalyst, however, the reaction proceeded yielding carbon disulfide, hydrogen sulfide, and hydrogen; reactions similar to (1) for methane, above 1200°K, being increasingly superseded by those similar to (2):

$$CH_4 + S_2 \rightarrow CS_2 + 2H_2. \qquad (2)$$

Reported now are some results of a study of the reactions of excited atomic species, generated by the dissociation of hydrogen sulfide in a plasma jet, with methane and neopentane.

This study was suggested by an earlier investigation of Vastola and co-workers[9] into the reaction between carbon and the products of water vapor microwave discharge, where it was observed that the presence of carbon downstream inhibited the recombination, to either oxygen or water, of the active atomic species. Instead, the active oxygen reacted preferentially with carbon.

Experimental Procedure

The plasma reactor is shown in Figure 1. The reactor consists of a 10 x 0.75 inch fused quartz tube. The gas to be brought to the plasma state is introduced tangentially upstream from the output coil of a 1.2 KW, 120 MHz RF induction heater. The spiraling motion imparted by the tangential input increases the dwell time of the gas in the plasma zone. The hydrocarbon gases to be reacted with the plasma dissociation products are introduced down stream from the plasma flame. By moving the hydrocarbon feed tube the distance between the plasma flame and the point of hydrocarbon introduction can be varied.

To initiate the plasma discharge argon is passed through the reactor (0.5 cu ft/hr, 1 Atm) and a graphite rod is placed in the induction field. After the heated graphite rod starts the discharge it is removed and the gas feed is switched to the desired H_2S-Ar mixture. Mass spectrometric gas analyses were made before and after the reaction.

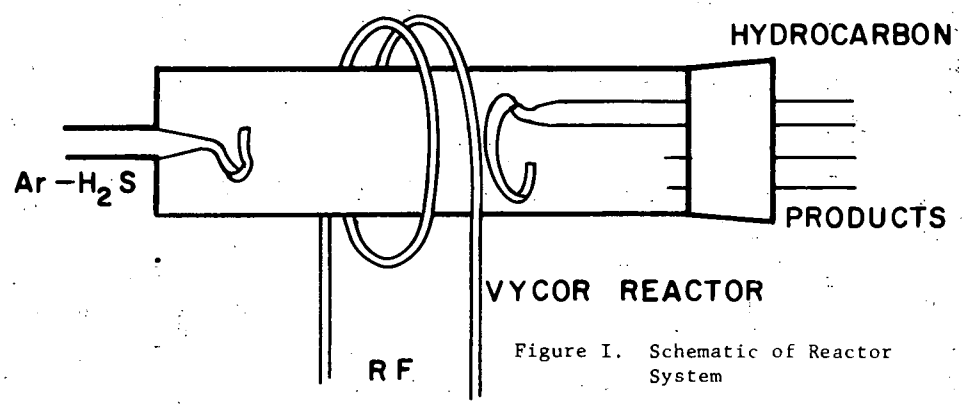

Figure I. Schematic of Reactor System

Results and Discussion

When hydrogen sulfide is introduced into an argon plasma condensing elemental sulfur produces a dense fog downstream from the plasma flame. As the amount of hydrocarbon that is introduced into this region is increased the elemental sulfur production decreases to a point where it can no longer be observed. With large excesses of hydrocarbon the color of the plasma flame changes from blue to orange due to back diffusion of the hydrocarbon.

Table 1 gives the reactant and product concentrations for reactions of dissociated hydrogen sulfide with methane and neopentane. With the exception of run number 3 the only gaseous products detected were hydrogen sulfide, unreacted hydrocarbon, carbon disulfide, and hydrogen.

Table 1
Reactant and Product Analyses

Run No.	Reactants	Reactant Mixture Composition Mole %			Products Composition Mole %					
		HC	H_2S	Ar	HC	H_2S	H_2	CS_2	C_2H_2	Ar
1	H_2S, CH_4	6.4	17.6	76.5	2.2	4.5	18.5	3.8	0	70.1
2	"	6.4	17.6	76.5	4.3	6.7	13.4	1.6	0	71.1
3	"	25.5	9.9	64.7	13.0	1.3	21.9	3.5	3.0	57.8
4	H_2S, C_5H_{12}	15.3	14.9	70.2	11.0	0.7	18.1	3.9	0	69.7
5	"	15.3	14.9	70.2	13.4	4.8	12.9	2.8	0	70.0

The following stoichiometry would be expected for the reaction of methane:

$$2H_2S + CH_4 \rightarrow CS_2 + 4H_2. \qquad (3)$$

In run number 3 the acetylene was produced by the back diffusion of methane into the plasma region.

The stoichiometry for the neopentane reaction would be

$$10H_2S + C_5H_{12} \rightarrow 5CS_2 + 16H_2S. \qquad (4)$$

The reactions of neopentane were performed with a large excess of hydrocarbon with the hope of detecting sulfur insertion compounds or reaction intermediates. However, hydrogen and carbon disulfide were the only gaseous species produced. This indicates that once the neopentane reacts with one sulfur atom its resistance to further reaction is lowered.

Table 2 shows the variation of reactant decomposition with changes of hydrogen sulfide to hydrocarbon flow ratio and plasma-hydrocarbon injection distance. From Table 2 it can be seen that the extent of hydrogen sulfide decomposition is a function of the amount of hydrocarbon present downstream from the plasma flame and the distance from the flame that the hydrocarbon is introduced, the highest decomposition, 95 per cent, occurring in run number 4 with an approximately ten fold excess of neopentane introduced 1/4 inch from the flame. The figures for the decomposition of hydrogen sulfide tend to be misleading, the hydrocarbon addition does not change the degree of dissociation of the hydrogen sulfide but rather it reacts with the atomic sulfur minimizing formation of hydrogen sulfide by the recombination of the

Table 2
Experimental Variables and Reaction Conversion Efficiencies

Run No.	Reactants	Flow rate (total) c.f.h.*	H_2S/HC	HC inlet distance from plasma inches	Reactant decomposition H_2S %	Reactant decomposition HC %	Conversion of decomposed reactants to: CS_2 H_2S %	CS_2 HC %	H_2 H_2S + HC %
1	H_2S, CH_4	0.14	2.75	1/4	72	63	65	~100	~100
2	"	0.14	2.75	1	59	28	33	~100	~100
3	"	0.33	0.39	1/4	85	43	93	36	81
4	H_2S, C_5H_{12}	0.25	1.03	1/4	95	28	55	19	46
5	"	0.25	1.03	1	68	12	56	30	61

*cu ft/hr.

atomic hydrogen and sulfur. The data on extent of conversion to hydrogen and carbon disulfide in Table 2 show that in runs 1 and 2 essentially all of the carbon from the decomposed methane is converted into carbon disulfide and the hydrogen into molecular hydrogen. In run number 3 the acetylene produced accounts for the missing carbon and hydrogen. In runs number 4 and 5 a large fraction of the neopentane that was decomposed was converted into a solid product.

Table 2 also shows the percentage of the sulfur, resulting from the decomposition of the hydrogen sulfide, that is converted into carbon disulfide; the remainder of the sulfur appears as elemental sulfur (runs 1-3) or can be incorporated with the carbon-hydrogen polymeric solid that is produced in the runs using neopentane.

These results indicate that hydrogen sulfide can be completely dissociated by an electric discharge and the excited atomic hydrogen and sulfur generated can be reacted with hydrocarbons to produce molecular hydrogen and carbon disulfide. Under conditions which minimize back diffusion of the hydrocarbon into the electric discharge substantially complete conversion of the hydrogen sulfide and hydrocarbon to hydrogen and carbon disulfide can be effected.

References

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