

110-82-7; *p*-xylene, 106-42-3; Petrostep 420, 64104-25-2.

## Literature Cited

- Bansal, B. B.; Hornof, V.; Neale, G. *Can. J. Chem. Eng.* **1979**, *57*, 203-210.
- Cash, L.; Caylas, J. L.; Fournier, G.; MacAllister, D.; Schares, J.; Schecter, R. S.; Wade, W. H. *J. Colloid Interface Sci.* **1977**, *59*, 39-44.
- Caylas, J. L.; Schecter, R. S.; Wade, W. H. *ACS Symp. Ser.* **1975**, (8), 234-247.
- Caylas, J. L.; Schecter, R. S.; Wade, W. H. *Soc. Pet. Eng. J.* **1976**, *16*, 351-357.
- Caylas, J. L.; Schecter, R. S.; Wade, W. H. *J. Colloid Interface Sci.* **1977**, *59*, 31-38.
- Gogarty, W. B.; Tosch, W. C. *J. Pet. Technol.* **1968**, *20*, 1407-1414.
- Healy, R. N.; Reed, R. L. *Soc. Pet. Eng. J.* **1977**, *17*, 129-139.
- Hornof, V.; Neale, G.; Bourgeois, P. *Can. J. Chem. Eng.* **1981**, *59*, 554-556.
- Neale, G.; Hornof, V.; Chiewetelu, C. *Can. J. Chem.* **1981**, *59*, 1938-1943.
- Puig, J. E.; Francis, E. I.; Davis, H. T.; Miller, W. G.; Scriven, L. E. *Soc. Pet. Eng. J.* **1979**, *19*, 71-82.
- Shah, D. O.; Bansal, V. K.; Chan, K.; Hsieh, W. C. In "Improved Oil Recovery by Surfactant and Polymer Flooding"; Shah, D. O.; Schecter, R. S., Ed., Academic Press: New York, 1977; pp 293-337.
- Son, J. E.; Neale, G. H.; Hornof, V. *Can. J. Chem. Eng.* **1982**, *60*, 684-691.
- Wade, W. H.; Morgan, J. C.; Jacobson, J. K.; Schecter, R. S. *Soc. Pet. Eng. J.* **1977**, *17*, 122-128.

Received for review February 4, 1982

Revised manuscript received August 11, 1982

Accepted October 23, 1982

# Steam Cracking of Hydrocarbons. 6. Effect of Dibenzyl Sulfide and Dibenzyl Disulfide on Reaction Kinetics and Coking

Martin Bajus and Jozef Baxa

Department of Chemistry and Technology of Petroleum, Slovak Technical University, 880 37 Bratislava, Czechoslovakia

Piet A. Leclercq\* and Jacques A. Rijks

Laboratory of Instrumental Analysis, Department of Chemical Engineering, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

The influence of aromatic sulfides on the kinetics and selectivity of hydrocarbon conversion by steam cracking and on pyrolytic coke formation was investigated in stainless steel tubular reactors with relatively large inner surface. The rate of decomposition of heptane (at 700 °C, 100 kPa, and a mass ratio of steam to feed 3:1) increased by 16 to 26%, and the selectivity toward ethene decreased, if 0.1 to 1.0% mass of dibenzyl sulfide, relative to heptane, was added. Addition of 1% mass dibenzyl disulfide increased the decomposition rate of heptane by 8%. Increasing amounts of the title compounds (0.1, 0.5% mass) in the feed decreased coking up to 70% in the pyrolysis of reformer raffinate at 820 °C, without steam. The decreased coking in turn caused an increased aromatic content in the liquid pyrolysis product mixtures. Based on the analytical results, obtained by capillary gas chromatography-mass spectrometry, reaction mechanisms are suggested.

## Introduction

The production of lower olefins by pyrolysis of hydrocarbons can be enhanced in several ways. Certain additives can decrease the required temperature of pyrolysis, enhance the rate of radical conversion, increase the flexibility of the pyrolysis process, and improve the selectivity. Presently an intensive search is going on for such compounds, both of homogeneous and heterogeneous nature. Substances which favorably influence the pyrolysis process (initiators, catalysts, activators, promoters) and compounds which suppress the formation of undesirable pyrolysis products (inhibitors, retarders, deactivators, passivators) have been investigated. Application of these chemicals in production processes is, however, often limited by their effectiveness, availability, or price. Compounds which can influence the radical process of thermal decomposition include inorganic and organic derivatives of nitrogen, oxygen, sulfur, and phosphorus.

Sulfur compounds can influence the course not only of primary but also of secondary reactions, which causes considerable difficulties. Well-documented are the effects of hydrogen sulfide on the kinetics and selectivity of the

conversion of hydrocarbons (Rebick, 1981; Scacchi et al., 1970; McLean and McKenney, 1970; Large et al., 1972; Scacchi et al., 1968; Frech et al., 1976; Gousty and Martin, 1974; Hutchings et al., 1976) and on the influence of secondary reactions, proceeding on the inner surface of the pyrolysis reactor when coke is formed (Crynes and Albright, 1969; Dunkleman and Albright, 1976; Ghaly and Crynes, 1976; Albright and McConnel, 1979). Under specific pyrolysis conditions elemental sulfur, sulfur dioxide (Lang, 1967), dimethyl disulfide and methyl mercaptan (Bradshaw and Turner, 1966) have a dehydrogenation effect. Elemental sulfur (Bajus and Veselý, 1980) and thiophene (Bajus et al., 1981) significantly inhibit coke formation during pyrolysis and at the same time accelerate the conversion of hydrocarbons. The search for other sulfur compounds, which could favorably influence the pyrolysis of hydrocarbons to olefins, goes on. Aromatic sulfides and disulfides, which decompose to highly stabilized radicals, come into consideration. Such compounds are dibenzyl sulfide and dibenzyl disulfide. Their influence on the kinetics of conversion and coke formation in the pyrolysis of hydrocarbons was studied in this work.

## Materials and Methods

All experiments were performed in two flow systems with stainless steel tubular reactors with enlarged inner surface.

The influence of dibenzyl sulfide and dibenzyl disulfide (Lachema, Brno, Czechoslovakia) on the kinetics and selectivity of the conversion of heptane was studied in equipment described in detail in a previous paper (Bajus et al., 1979). The reactor is of the "tube-in-tube" type with a surface-to-volume ( $S/V$ ) ratio of  $6.65 \text{ cm}^{-1}$ . The stainless steel reactor was of the following composition (% mass): Cr, 16.8; Ni, 10.7; Mn, 1.1; C, 0.08. The starting hydrocarbon, heptane (Loba-Chemie, Vienna, Austria; 99.7%) was introduced at  $0.15\text{--}0.35 \text{ mol h}^{-1}$ . The work was carried out at  $700^\circ\text{C}$  in the presence of steam. Under the effective contribution of the inner surface, steam reacts with some reaction components, especially with high molecular weight compounds, which are the potential precursors of coke, to carbon monoxide and hydrogen. Steam also ensured the reproducibility of the measurements and enabled the equipment to be used continuously without the necessity of burning carbonaceous deposits. The mass ratio of water to heptane was in all experiments 3:1. The amount of water varied between  $2.57$  and  $5.85 \text{ mol h}^{-1}$ .

The formation of coke was studied in the flow equipment described previously (Bajus and Veselý, 1980). The tubular reactor is of the U type, with  $S/V = 6.66 \text{ cm}^{-1}$ . The construction material is stainless steel (% mass): Cr, 17.5; Ni, 9.4; Mn, 0.7; C, 0.18. The influence of dibenzyl sulfide and dibenzyl disulfide on the formation of coke was studied in the pyrolysis of a reformer raffinate, obtained from the catalytic reforming of naphtha after extraction of aromatics. This raffinate (distillation range  $27\text{--}156^\circ\text{C}$ ) had the following composition (% mass): unbranched alkanes, 18.8%; branched alkanes, 60.4; cycloalkanes, 10.3; aromatics, 6.0; remaining products, 4.5. Its flow was  $0.30 \text{ mol h}^{-1}$  in all experiments. The pyrolysis was carried out without steam at  $820^\circ\text{C}$  and  $100 \text{ kPa}$ . The amount of coke formed was determined by weighing the reactor before and after the experiment. In order to achieve reproducible results, the preparation of the reactor before each experiment is of prime importance. Burning out the coke from the preceding experiment with air and decomposition of metal oxides by the action of a solution of acids ( $3\% \text{ HCl} + 3\% \text{ H}_2\text{SO}_4$ ) preceded each run. In this way a reproducibility was obtained, corresponding with standard deviations from 5 to 12%.

The equivalent volume  $V_R$  of the reactors was determined from the temperature profile of the nonisothermal reactor according to Hougen and Watson (1947). The residence times were determined as described previously (Bajus et al., 1979).

The composition of the gaseous and liquid product mixtures was determined by packed column gas chromatography as described previously (Bajus et al., 1979; Bajus and Veselý, 1980).

The liquid products were further examined by high-resolution gas chromatography. A  $30 \text{ m} \times 0.25 \text{ mm}$  i.d. glass capillary column, coated with SE-30 stationary phase, was operated with helium carrier gas. Samples were injected via a splitter. Separations were carried out under temperature programming. For the detection of sulfur compounds, the capillary column was mounted in a gas chromatograph (Type F17, Perkin-Elmer, Beaconsfield, Buckinghamshire, England) equipped with parallel flame ionization (FID) and flame photometric detectors (FPD). For identification purposes, the column end was directly inserted into the ion source of a quadrupole mass spec-

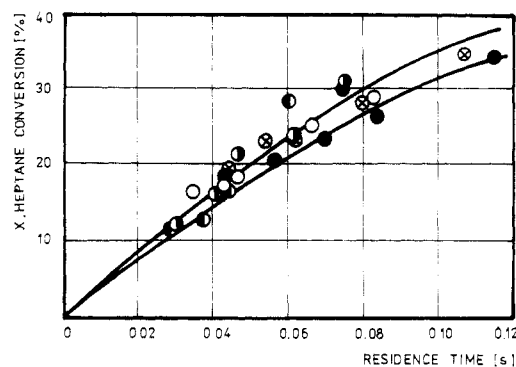


Figure 1. Conversion of heptane as a function of residence time at different additive contents (% mass) of dibenzyl sulfide: (○) 0.1; (◐) 0.5; (●) 1.0 (TP II); and (⊗) 1.0 (TP I); and dibenzyl disulfide: (●) 1.0 (TP I).

Table I. Rate Constants of the Heptane Conversion Conversion at  $700^\circ\text{C}$

content % mass	T.P.	$V_R, \text{ cm}^3$	$k_{\text{anal}}, \text{ s}^{-1}$	$k_{\text{graph}}, \text{ s}^{-1}$
Dibenzyl Sulfide				
0	II	4.8 <sup>a</sup>	4.0 <sup>a</sup>	3.8 <sup>a</sup>
0.1	II	4.8	4.5	4.4
0.5	II	4.7	4.7	4.8
1.0	II	4.5	4.5	4.6
1.0	I	6.3	4.5	4.5
Dibenzyl Disulfide				
0	I	5.6 <sup>b</sup>	3.7 <sup>b</sup>	3.6 <sup>b</sup>
1.0	I	6.6	4.0	3.9

<sup>a</sup> From Bajus and Veselý (1980). <sup>b</sup> From Bajus et al. (1979).

trometer (Type 4000, Finnigan, Sunnyvale, CA) (Cramers et al., 1981). Quantitative analyses were performed using the same column in a gas chromatograph (Type 3900, Dani, Rome, Italy) equipped with an FID and using a chromatography data system (Type 4000, Spectra Physics, Santa Clara, CA).

## Results

**Kinetics of Thermal Decomposition.** The decomposition of heptane was investigated at  $700^\circ\text{C}$  at residence times of  $0.02\text{--}0.12 \text{ s}$  in the presence of 0.1, 0.5, and 1% mass of dibenzyl sulfide and 1% mass of dibenzyl disulfide. The dependence of the conversion of heptane on the residence time for three different concentrations of dibenzyl sulfide and 1% of dibenzyl disulfide is illustrated in Figure 1. The results were obtained in two temperature profiles (Bajus and Veselý, 1980). Temperature profile I is the broader one and approximates the reactor dimensions; the equivalent volume of the reactor  $V_R$  is in the range of 5 to  $7 \text{ cm}^3$ . Temperature profile II is narrower and the corresponding calculated equivalent volume of the reactor is in the range of 4 to  $5 \text{ cm}^3$ . The average values of the equivalent volumes are given in Table I for the selected residence times in Tables II and III.

To determine the reaction order of the decomposition of heptane, the method applied by Kershenbaum and Martin (1967) was used. As for the conversion of heptane itself (Bajus and Veselý, 1979), the values of the reaction order in the presence of dibenzyl sulfide and dibenzyl disulfide are about 1. Figure 2 illustrates the determination of the reaction order for the decomposition of heptane in the presence of 1% (mass) of dibenzyl sulfide at constant temperature and pressure profile, applying the relation

$$\log(-\Delta F) = n \log \bar{X} + \log(\text{constant})$$

Table II. Product Distribution in the Reaction Mixture from Steam Cracking of Heptane at 700 °C (mol/100 mol of Heptane Decomposed)

product	dibenzyl sulfide content, % mass							
	0 <sup>a</sup>	0 <sup>a</sup>	0.1	0.1	0.5	0.5	1.0	1.0
	conversion, %							
	14.2	28.1	16.5	28.9	12.9	31.1	11.8	29.9
	V <sub>R</sub> , cm <sup>3</sup>							
	4.2	4.9	4.9	4.9	4.4	4.6	4.1	4.6
product	M.B., % mass							
	100.0	98.9	97.9	96.7	99.8	102.0	101.2	101.2
hydrogen	33.4	42.1	24.5	29.5	30.1	25.6	35.6	42.9
methane	53.3	51.6	41.4	57.8	41.7	37.3	47.4	55.1
ethane	11.8	12.9	10.8	10.1	7.8	20.0	9.3	12.8
ethene	145.7	147.5	145.8	158.6	149.9	147.4	129.7	135.6
propane	1.3	1.2	1.1	1.4	0.9	1.2	1.6	1.5
propene	37.9	41.0	41.5	43.6	37.3	40.0	36.6	45.8
butane	0.7	0.6	0.5	0.7	0.4	0.6	0.5	0.4
1-butene	19.9	15.8	21.4	15.7	22.1	20.0	23.8	21.8
<i>trans</i> -2-butene	0.3	0.4	0.5	0.4	0.7	0.5	0.4	0.6
<i>cis</i> -2-butene	0.3	0.3	0.3	0.3	0.2	0.4	0.4	0.5
1,3-butadiene	2.1	2.4	2.1	2.4	2.3	3.5	2.4	3.5
3-methyl-1-butene	0.3	0.2	0.7	0.2	0.4	0.2	0.4	0.2
1-pentene	9.5	8.6	12.8	8.9	11.5	10.9	12.8	7.3
2-methyl-1-butene	0.1	0.2	0.7	0.2	0.6	0.3	0.3	0.3
<i>trans</i> -2-pentene	0.3	0.4	0.5	0.4	0.8	0.5	0.5	0.4
<i>cis</i> -2-pentene	0.3	0.3	0.2	0.4	0.5	0.4	0.1	0.4
1-hexene	5.3	4.8	5.0	5.0	6.8	5.4	9.1	5.1
1-heptene	0.3	0.1	-	0.2	-	-	-	-
carbon monoxide	14.8	22.0	2.1	2.8	8.2	5.3	10.9	10.9

<sup>a</sup> The product distribution obtained in the absence of dibenzyl sulfide is taken from Bajus and Veselý (1980).

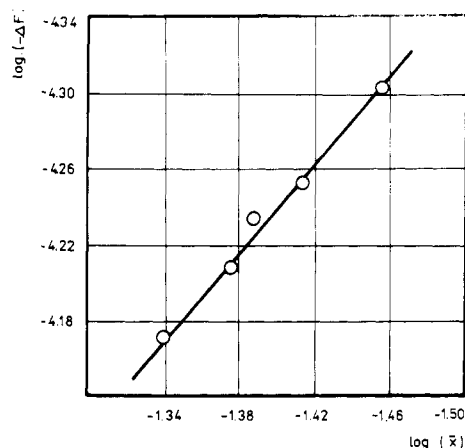


Figure 2. Relation between rate of heptane consumption and average molar fraction of heptane in the presence of 1.0% (mass) of dibenzyl sulfide.

The order thus determined has the value 1.07. The right-hand term of the rate equation ( $k \cdot \tau$ ) as a function of residence time for the corresponding amounts of dibenzyl sulfide and dibenzyl disulfide is plotted in Figure 3. The values of the rate constants determined graphically and calculated numerically are given in Table I. This table also contains the rate constants of conversion of heptane without sulfur compounds, determined under the same experimental conditions (Bajus et al., 1979; Bajus and Veselý, 1980). For the numerically calculated values of the rate constants the maximum standard deviation is 9.6% ( $m = 5$ ). The degree of conversion has no significant influence on the rate constants.

It can be concluded that dibenzyl sulfide and dibenzyl disulfide accelerate the thermal decomposition of heptane; in the case of dibenzyl sulfide by 16–26%, with dibenzyl disulfide by 8%. Under comparable conditions, the rate of decomposition of heptane in the presence of 0.1–0.5%

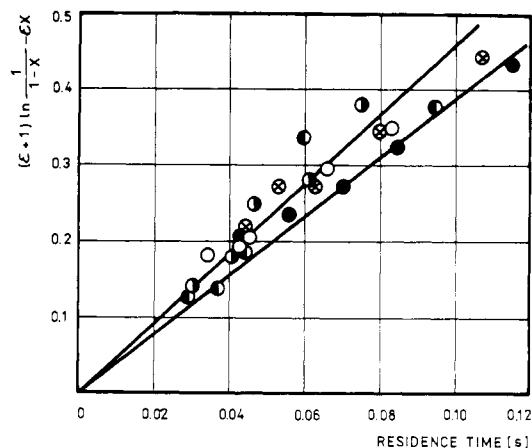


Figure 3. Graphic representation of the first-order rate equation at different contents (% mass) of dibenzyl sulfide: (○) 0.1%; (●) 0.5%; (●) 1.0 (TP II); and (⊗) 1.0 (TP I); and dibenzyl disulfide: (●) 1.0 (TP I).

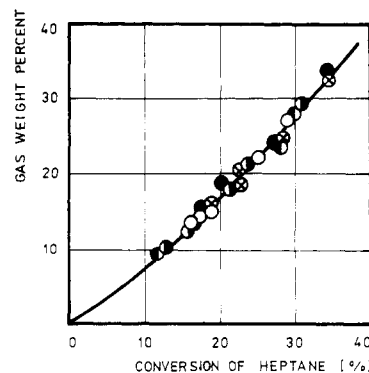
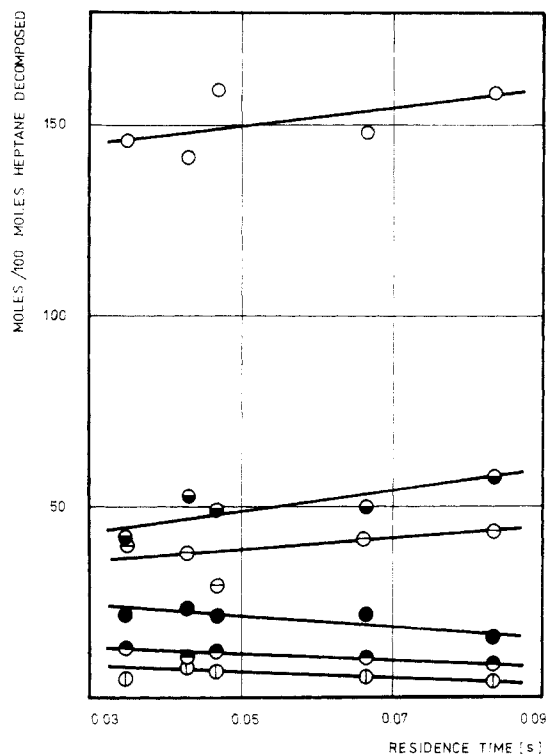
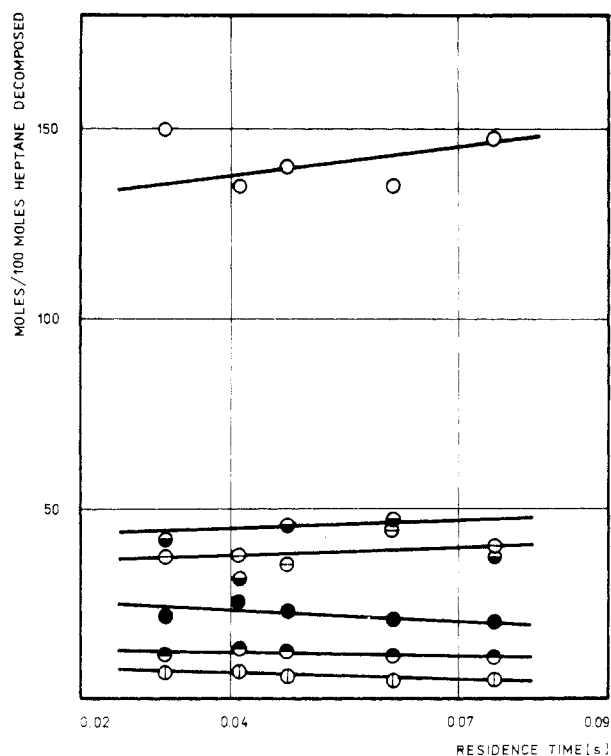


Figure 4. Gas production as a function of the conversion of heptane at different contents (% mass) of dibenzyl sulfide: (○) 0.1%; (●) 0.5%; (●) 1.0 (TP II); and (⊗) 1.0 (TP I); and dibenzyl disulfide: (●) 1.0 (TP I).



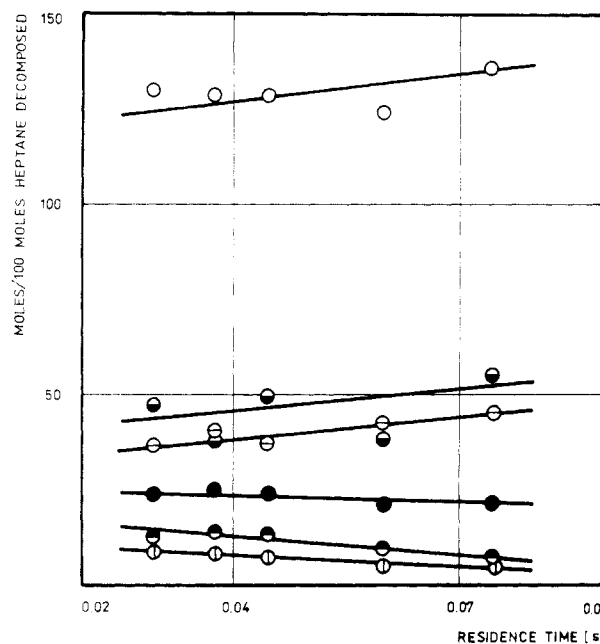
**Figure 5.** Product distribution vs. residence time for the conversion of heptane with 0.1% (mass) of dibenzyl sulfide at TP II: (○) ethene; (◐) methane; (◑) propene; (●) 1-butene; (◐) 1-pentene; (◑) 1-hexene.



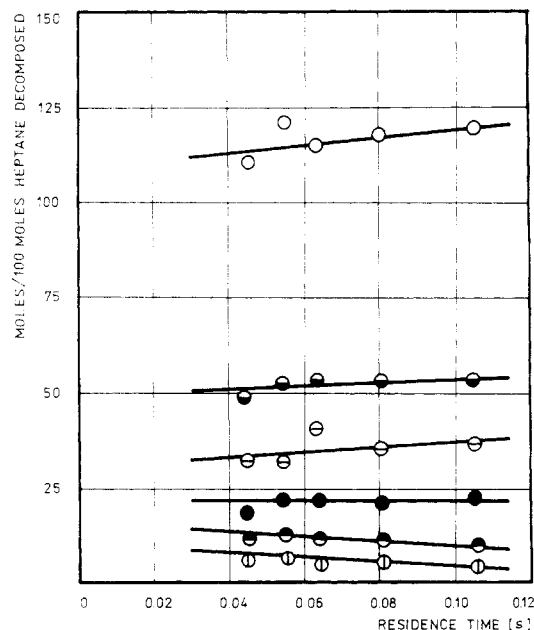
**Figure 6.** Product distribution vs. residence time for the conversion of heptane with 0.5% (mass) of dibenzyl sulfide at TP II: (○) ethene; (◐) methane; (◑) propene; (●) 1-butene; (◐) 1-pentene; (◑) 1-hexene.

mass of thiophene increased by 14% (Bajus et al., 1981), and in the presence of 0.02% mass of elemental sulfur by as much as 28% (Bajus and Veselý, 1980).

**Selectivity of Thermal Decomposition.** In the decomposition of heptane in the presence of dibenzyl sulfide and dibenzyl disulfide, 10–35% of the products formed are gaseous, dependent on the degree of conversion (Figure 4). Collected at  $-18^{\circ}\text{C}$ , the gaseous products included



**Figure 7.** Product distribution vs. residence time for the conversion of heptane with 1% (mass) of dibenzyl sulfide at TP II: (○) ethene; (◐) methane; (◑) propene; (●) 1-butene; (◐) 1-pentene; (◑) 1-hexene.



**Figure 8.** Product distribution vs. residence time for the conversion of heptane with 1% (mass) of dibenzyl sulfide at TP I: (○) ethene; (◐) methane; (◑) propene; (●) 1-butene; (◐) 1-pentene; (◑) 1-hexene.

primarily hydrogen, carbon monoxide, decomposition products up to and including  $\text{C}_4$  hydrocarbons, and minor quantities of 1-pentene, 1-hexene, 1-heptene, and heptane. The differences in gas yields for the various concentrations of sulfur additives are negligible in both temperature profiles. The yields were determined with a standard deviation of less than 4.2% ( $m = 7-10$ ). The average molecular mass of the gaseous products is in the range of 24.5–28.1.

The qualitative and quantitative composition of the bulk of gaseous and liquid products is given in Tables II and III. The presence of dibenzyl sulfide and dibenzyl disulfide has no influence on the qualitative composition. Among the reaction products ethene has a dominant position. Main products are, furthermore, methane, propene, 1-butene, 1-pentene, 1-hexene, hydrogen, and carbon monoxide. The influence of the residence time on the selec-

Table III. Product Distribution in the Reaction Mixture from Steam Cracking of Heptane at 700 °C (mol/100 mol of Heptane Decomposed)

product	additive content, % mass					
	none		dibenzyl sulfide		dibenzyl disulfide	
	0 <sup>a</sup>	0 <sup>a</sup>	1.0	1.0	1.0	1.0
	conversion, %					
	13.9	26.8	19.2	34.7	17.8	34.6
	V <sub>R</sub> , cm <sup>3</sup>					
	4.8	6.8	6.1	6.5	6.0	6.9
product	M.B., % mass					
	97.2	98.8	96.7	98.8	97.4	99.2
hydrogen	51.1	60.4	42.8	85.1	46.4	36.3
methane	49.5	66.9	48.1	52.2	53.9	63.7
ethane	6.2	10.0	12.0	12.9	14.7	13.5
ethene	116.6	137.7	109.9	118.3	138.2	138.8
propane	0.8	1.5	1.2	1.4	0.7	0.9
propene	31.9	38.2	30.6	34.7	39.7	41.3
butane	0.5	0.4	0.5	0.3	-	0.2
1-butene	21.3	20.2	18.7	20.6	25.1	20.8
trans-2-butene	0.4	0.3	0.1	0.2	0.3	0.4
cis-2-butene	0.3	0.4	0.1	0.2	0.1	0.3
1,3-butadiene	2.6	2.6	1.9	3.1	1.1	3.4
3-methyl-1-butene	0.1	0.2	0.1	0.1	0.2	0.2
pentane	0.3	0.2	-	-	-	-
1-pentene	13.0	10.1	10.1	8.8	9.1	8.4
2-methyl-1-butene	0.3	0.2	-	-	-	-
trans-2-pentene	0.3	0.2	-	0.2	-	0.1
cis-2-pentene	0.2	0.2	-	0.2	0.1	0.1
1-hexene	6.0	5.5	4.6	4.1	5.2	3.2
1-heptene	1.7	0.9	3.0	1.4	0.3	0.3
carbon monoxide	26.2	12.4	12.2	52.2	29.7	15.3

<sup>a</sup> The product distribution obtained in the absence of sulfur compounds is taken from Bajus et al. (1979).

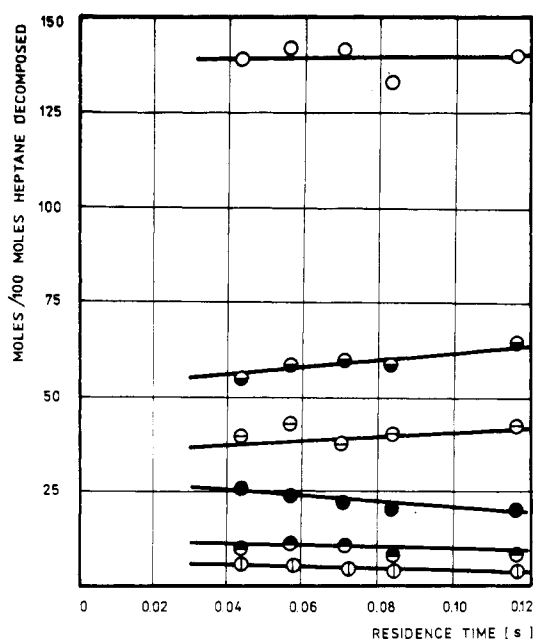


Figure 9. Product distribution vs. residence time for the conversion of heptane with 1% (mass) of dibenzyl disulfide at TP I: (○) ethene; (◐) methane; (◑) propene; (●) 1-butene; (◐) 1-pentene; (◑) 1-hexene.

tivity of the conversion of heptane in the presence of dibenzyl sulfide is illustrated in Figures 5–7, under conditions of temperature profile II. Figures 8 and 9 show the influence of dibenzyl sulfide and dibenzyl disulfide, respectively, under conditions of temperature profile I. With increasing residence time, the formation of ethene, propene, and methane tends to increase, while the formation of 1-butene, 1-pentene, and 1-hexene decreases. With hydrogen and carbon monoxide, the influence of the res-

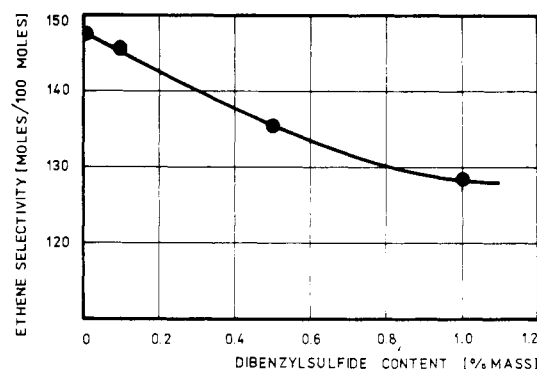


Figure 10. Relation between selectivity of the conversion of heptane to ethene and the dibenzyl sulfide content in the feed.

idence time is less equivocal, which is obviously related to the proceeding of secondary reactions. At 1% concentration of dibenzyl sulfide, the selectivity of the conversion to ethene is better under the conditions of temperature profile II (Figure 7) than with temperature profile I (Figure 8). Using the same temperature profile (TP I) and a 1% concentration of sulfur compounds, the decomposition of heptane to ethene proceeds most selectively in the presence of dibenzyl disulfide. The influence of the presence of dibenzyl sulfide at average conversion (in an interval of 16.0–17.5%) on the formation of ethene is illustrated in Figure 10. With increasing concentrations of dibenzyl sulfide, the selectivity of the conversion of heptane to ethene is decreased.

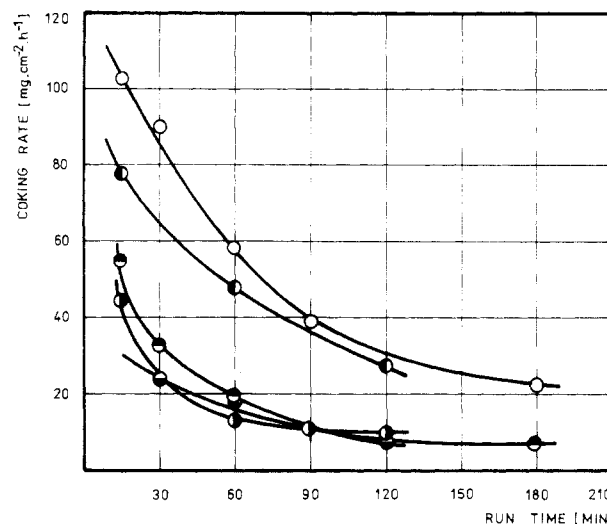
**Coking.** The formation of coke was studied at 820 °C and a residence time of 0.25 s with reformer raffinate as such, and after the addition of 0.1 and 0.5% (mass) of dibenzyl sulfide and dibenzyl disulfide, respectively. The results are condensed in Table IV. The rate of coking, as a function of the duration of the experiment, is depicted

**Table IV.** Deposition of Coke (in g) in the Pyrolysis of Reformer Raffinate at 820 °C and Residence Time 0.25 s

expt duration, min	additive content, % mass				
	none	dibenzyl sulfide		dibenzyl disulfide	
	0	0.1	0.5	0.1	0.5
15	0.35	0.22	0.14	0.17	0.15
30	0.56	0.46	-	0.20	-
60	0.72	0.59	0.16	0.24	0.22
90	0.72	-	0.20	-	-
120	-	0.68	0.24	-	-
150	-	-	-	-	0.22
180	0.83	-	-	0.24	-

in Figure 11. The highest rate of coking was observed during the pyrolysis of reformer raffinate without sulfur compounds. With increasing concentrations of dibenzyl sulfide and dibenzyl disulfide, the rate of coking is lowered in the entire time interval under observation. From the course of the kinetic relations it is evident that at the outset coking proceeds at a higher rate. After a certain time a steady state is reached. This points to the decisive influence of the inner surface of the reactor on the course of secondary reactions which lead to the formation of coke. The clean stainless steel surface at the beginning of the pyrolysis of the reformer raffinate significantly promotes the formation of coke. After a certain time, when its catalytic effect is eliminated by carbonaceous deposits, a steady state is reached. The results show that the catalytic effect of the surface of the metal reactor on the formation of coke can be greatly reduced by addition of dibenzyl sulfide and dibenzyl disulfide. This is manifested by the manifold decrease in coke formation, in the presence of these compounds.

**Analysis of the Liquid Pyrolysis Products of Reformer Raffinate, Doped with Various Sulfur Compounds.** The liquid pyrolysis product mixtures, obtained in near steady-state conditions with respect to coking (i.e., after more than 2 h pyrolysis in the carefully cleaned re-

**Figure 11.** Rate of formation of coke during the pyrolysis of reformer raffinate at different additive contents (% mass): (●) 0.1 and (○) 0.5 dibenzyl sulfide; (■) 0.1 and (□) 0.5 dibenzyl disulfide; (○) without the inhibitor.

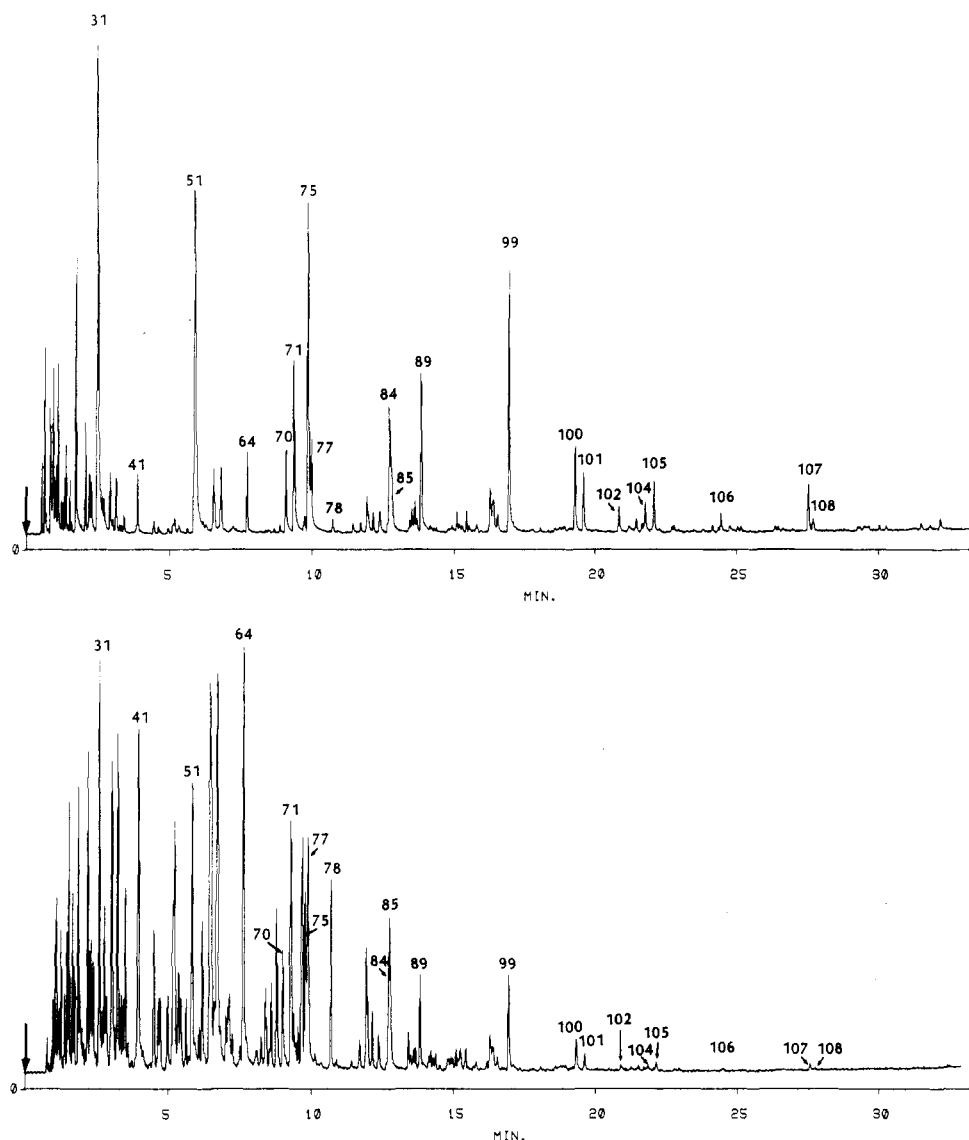
actor), were analyzed by combined capillary gas chromatography-mass spectrometry (GC/MS). The mass spectra, in conjunction with retention data, led to the identification or characterization of more than 100 hydrocarbons.

The results, obtained from reformer raffinate without additive, and admixed with 1% of dibenzyl sulfide, 1% of dibenzyl disulfide, 1% of thiophene (Bajus et al., 1981), and 0.1% of elementary sulfur (Bajus and Vesely, 1980), respectively, are condensed in Table V. These data are average values of duplicate experiments. The standard deviation corresponds with a precision of about 5%. Typical gas chromatograms are shown in Figure 12. From these results it is evident that the presence of sulfur-containing compounds in the feed causes increased conversion of alkanes and increased formation of aromatic com-

**Table V.** Concentration (% Mass) of Selected Compounds in the Liquid Product Mixture from Pyrolysis of Reformer Raffinate Admixed with Sulfur Containing Additives<sup>a</sup>

peak no. (Figure 12)	product	additive content, % mass				
		thiophene	dibenzyl sulfide	dibenzyl disulfide	sulfur	none
		1.0	1.0	1.0	0.1	0
		residence time, s				
		0.25	0.16	0.10	0.14	0.10
41	heptane	0.66	0.77	3.18	0.29	4.70
64	octane	0.76	0.71	3.74	0.46	5.17
78	nonane	0.20	0.02	0.52	0.08	0.67
31	benzene	36.7	26.6	14.8	23.5	7.76
51	toluene	15.9	14.3	10.7	13.0	4.71
70	ethylbenzene	0.71	1.19	1.61	1.23	0.83
75	styrene	9.21	6.49	4.56	8.46	1.24
71	<i>m</i> - and <i>p</i> -xylene	3.33	3.67	4.45	3.84	2.95
77	<i>o</i> -xylene	0.91	0.92	1.01	0.99	0.57
85	trimethylbenzene	0.88	1.10	1.57	1.08	0.93
84	indan	1.72	1.54	1.49	1.96	0.62
89	indene	3.44	2.57	1.79	3.49	0.57
99	naphthalene	5.28	4.20	1.91	4.92	0.52
100	2-methylnaphthalene	0.80	0.82	0.45	0.84	0.15
101	1-methylnaphthalene	0.59	0.56	0.30	0.59	0.10
102	biphenyl	0.23	0.25	0.11	0.25	0.05
104	dihydroacenaphthylene	0.30	0.31	0.13	0.34	0.05
105	biphenylene and/or acenaphthylene	0.43	0.45	0.15	0.51	0.05
106	fluorene	0.20	0.19	0.04	0.18	0.02
107	phenanthrene or anthracene	0.21	0.22	0.05	0.21	0.04
108	anthracene or phenanthrene	0.06	0.04	0.02	0.02	0.01
	remaining products	17.48	33.08	47.42	33.76	58.30

<sup>a</sup> Pyrolysis temperature: 800 °C.



**Figure 12.** Chromatograms of the liquid pyrolysis products from reformer raffinate admixed with 1% of dibenzyl sulfide (upper) and without additive (lower). Compounds are listed in Table V.

pounds. Since the liquid fraction constitutes only 2.5–26.8% mass of the total pyrolysis products, the (polynuclear) aromatics represent only trace quantities. Several sulfur compounds were detected with the FPD but could not be identified by GC/MS because of their low concentration and insufficient separation (Agrawal et al., 1972).

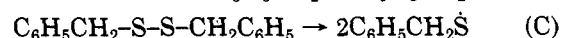
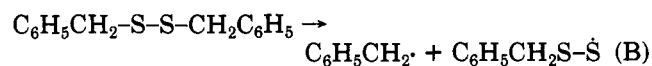
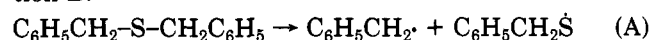
Therefore, the pyrolysis of the reformer raffinate was repeated, under otherwise identical reaction conditions, with increased amounts of additives: 15% of thiophene; 17% of hydrogen sulfide, and saturated solutions of elemental sulfur ( $\leq 1\%$ ), dibenzyl sulfide, dibenzyl disulfide, and diethyl dithiophosphoric acid (up to 5% mass). The FPD chromatograms were qualitatively similar. GC/MS now permitted identification of thiophene, 2- and 3-methylthiophene, 2- and 3-ethylthiophene, 2- and 3-vinylthiophene, and benzothiophene as the main sulfur-containing products in all instances. The gaseous samples contained primarily hydrogen sulfide and thiophene.

### Discussion

The thermal decomposition of hydrocarbons proceeds via a series of primary and secondary reactions. A decisive role is played by the initiation, propagation, and termination of radicals. From the comparison of the kinetics and the selectivity of decomposition of heptane, and from

the rate of coking of reformer raffinate, it can be seen that dibenzyl sulfide and dibenzyl disulfide influence the conversion of radicals in the homogeneous phase and on the surface of the reactor. Concerning aromatic sulfides and disulfides, it is known that their decomposition takes place preferentially by the cleavage of  $-C-S-$  bonds as a consequence of a relatively low dissociation energy:  $C_6H_5CH_2-SC_2H_5$ , 221.5 kJ mol $^{-1}$  (Mackle, 1963);  $C_6H_5CH_2-S-CH_3$ , 213.2 kJ mol $^{-1}$  (Magaril, 1970), 248.3 kJ mol $^{-1}$  (Colussi and Benson, 1977);  $C_6H_5CH_2-SH$ , 221.5 kJ mol $^{-1}$  (Magaril, 1970);  $C_6H_5S-CH_3$ , 250.8 kJ mol $^{-1}$  (Back and Sehon, 1960); 282.1 kJ mol $^{-1}$  (Colussi and Benson, 1977).

Upon decomposition, phenylthio and benzyl radicals are formed with stabilization energies of 40.1 and 57.2 kJ mol $^{-1}$ , respectively (Colussi and Benson, 1977). Benzyl radicals can be formed during decomposition of dibenzyl sulfide according to reaction A, and, for dibenzyl disulfide, reaction B.



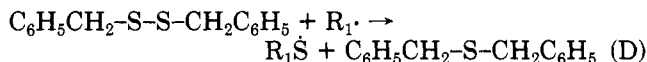
Dissociation energies of  $-S-S-$  and  $-S-H$  bonds are substantially higher: p.e., 290–305 kJ mol $^{-1}$  for dialkyl di-

Table VI. Product Distribution in the Reaction Mixture from Steam Cracking of Heptane at 700 °C (mol/100 mol of Heptane Decomposed)

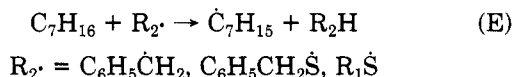
product	additive content, % mass							
	dibenzyl sulfide				sulfur <sup>a</sup>			
	0	0.1	0.5	1.0	0	0.02	0.05	0.1
	conversion, %							
	17.5	16.5	16.1	16.7	12.1	14.6	13.5	13.3
	V <sub>R</sub> , cm <sup>3</sup>							
	5.0	4.9	4.9	4.5	4.8	4.3	4.6	4.7
product	M.B., % mass							
	100.5	97.9	102.0	100.9	100.8	99.4	99.6	99.8
methane	47.8	41.4	31.5	37.8	53.1	44.6	39.5	41.3
ethane	13.0	10.8	10.9	8.5	13.4	13.4	10.9	9.3
ethene	147.3	145.8	135.3	128.3	148.0	136.2	128.8	130.4
propene	39.5	41.5	37.8	37.1	38.7	38.8	42.8	40.6
1-butene	20.6	21.4	25.1	24.1	19.7	22.4	21.4	22.7
1,3-butadiene	1.9	2.1	3.3	3.1	1.8	2.3	2.4	2.7
1-pentene	10.3	12.8	13.7	13.8	8.9	10.8	12.1	10.6
1-hexene	5.7	5.0	7.6	7.8	3.9	5.3	5.7	5.9
total hydrocarbon	289.7	287.6	261.8	255.6	293.5	283.0	272.5	273.2

<sup>a</sup> The product distribution obtained in the presence of sulfur is taken from Bajus and Veselý (1980).

sulfides (Kooymans, 1967; Magaril, 1970) and 372 kJ mol<sup>-1</sup> for methyl mercaptan (Kooymans, 1967). Nevertheless, cleavage of the -S-S- bond in dibenzyl disulfide, with formation of two benzylthiyl radicals according to reaction C, is likely to occur. A benzylthiyl radical can also be formed by reaction A, and a benzylthiyl radical according to reaction B. The further fate of the primary products of unimolecular decomposition of aromatic sulfides and disulfides depends on the reaction conditions. Under very low pressure pyrolysis (VLPP), the splitting of aromatic sulfides is highly selective (Colussi and Benson, 1977). On the other hand, under conditions of pyrolytic chromatography, the decomposition of dibenzyl disulfide at temperatures of 180–300 °C yields hydrogen sulfide, ethyl mercaptan, dimethyl sulfide, methyl phenyl sulfide, ethyl phenyl sulfide, methyl phenyl mercaptan, and ethyl phenyl mercaptan (Kundryavtseva et al., 1977). At 600 °C, sulfur compounds other than hydrogen sulfide are not formed. Among the reaction products only benzene and toluene are present. In the pyrolysis of reformer raffinate at 820 °C, dibenzyl sulfide and dibenzyl disulfide also decompose mainly to hydrogen sulfide, but thiophene, methyl-, ethyl-, vinyl- and benzothiophenes are formed as well. In the presence of radicals, generated by thermal decomposition of hydrocarbons (R<sub>1</sub>·), reactions can occur with aromatic sulfides or disulfides, under formation of a range of thiyl radicals. For example, according to reaction D



A characteristic property of benzyl, benzylthiyl, and alkylthiyl radicals is that they may enter reactions where they can cause abstraction of hydrogen. Under pyrolysis conditions, thiyl radicals can also split off hydrogen from a heptane molecule, reaction E, thereby initiating the propagation of reactants in the homogeneous phase.

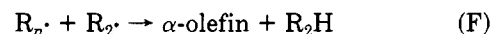


This is apparent from the increase of the rate of decomposition of heptane in the presence of dibenzyl sulfide and dibenzyl disulfide. Variation of the dibenzyl sulfide concentration does not affect the overall cracking rate of heptane significantly, however.

The decrease in selectivity of the heptane decomposition into ethene, ethane, and methane, with increasing dibenzyl sulfide concentrations, could be concluded from the data in Table II. This effect is more apparent if the influence of the dibenzyl sulfide content is compared at more-or-less constant conversion factors (Table VI). The analogous influence of increasing elemental sulfur concentrations (Bajus and Veselý, 1980) is included in Table VI for comparison.

Table VI also shows that increasing amounts of the respective sulfur-containing additives cause higher yields of  $\alpha$ -olefins C<sub>4</sub>–C<sub>6</sub> and butadiene. It should be noted, however, that the presence of these sulfur-containing additives increases the cracking rate of heptane, irrespective of their concentrations (up to 1% mass).

From the mechanistic point of view, increasing concentrations of thiyl radicals have no influence on the course of the hydrogen transfer reaction E, but they do influence the course of decomposition reactions F and G. In the presence of a greater number of thiyl radicals in the decomposition of hexyl, pentyl, butyl, and butenyl radicals, the cleavage of C–H bonds according to reaction F is favored over the cleavage of C–C bonds according to reaction G.



R<sub>n</sub>· = 1-hexyl-, 1-pentyl-, 1-butyl radical

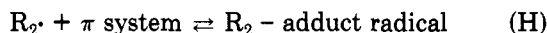


The energy needed for splitting off a hydrogen atom from the hydrocarbon radical in reaction F is about 167 kJ mol<sup>-1</sup>, while the dissociation energy of the C–H bond in heptane cleaving according to reaction E is in the range of 372–422 kJ mol<sup>-1</sup>. The decrease in the decomposition of radicals according to reaction G, in comparison with the decomposition reaction F, is manifested also in the decrease of the total amount of moles of hydrocarbon product per mole of decomposed heptane. The increase of the dibenzyl sulfide content causes a decrease in the number of consecutive radical decomposition steps per mole of decomposed reactant. With elemental sulfur it can be assumed that reactions E, F, and G involve molecular sulfur S<sub>2</sub>, atomic sulfur S<sub>1</sub>, and ·SH radicals, respectively.

The decrease of selectivity to methane, ethane, and ethene was also observed by Rebick (1981) in the pyrolysis

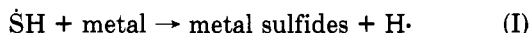


of hexadecane in the presence of hydrogen sulfide. Unlike our results, it was found that with increasing concentrations of  $H_2S$ , butane and higher alkanes are formed, and the overall rate of decomposition increases. The probable cause is the different influence of dibenzyl sulfide and elemental sulfur on one hand, and hydrogen sulfide on the other, on the course of hydrogen transfer reactions which predominate in the radical mechanisms, both from the point of view of reaction rate and selectivity. It can be assumed that, with increasing concentrations of sulfur additives in the feed, an increase occurs in the formation of benzyl and thiyl radicals in the reaction zone, giving rise to conditions for further characteristic reactions with compounds having  $\pi$  bonds (reaction H)



Because, among the olefinic reaction products, ethene is found to be the main product, it is very probable that the diminished yield is caused by a greater participation of dibenzyl sulfide in reaction H. This would result in the formation of an adduct radical from ethene and from benzyl and benzylthiyl radicals. These adduct radicals can either decompose by the reverse reaction to the original components or, in consecutive reactions, react with organosulfur compounds, which is proven by the presence of thiophene, methyl-, ethyl-, vinyl- and benzenethiophenes.

Thermal decomposition of sulfur compounds is, as a rule, always accompanied with the formation of hydrogen sulfide. This has also been verified in the pyrolysis of aromatic sulfides (Colussi and Benson, 1977) and disulfides (Kundryavstseva et al., 1977). On this basis it is legitimate to assume that, in the reaction zone, an increased concentration of radicals  $\dot{S}H$  exists, either as intermediate reaction products in the formation of hydrogen sulfide, or as being formed in the decomposition reaction of hydrogen sulfide. On the other hand, the formation of S atoms cannot be excluded (Foss, 1950; Price and Oae, 1962).  $\dot{S}H$  radicals or S atoms can react not only with heptane according to reaction E, but can also enter a reaction with the metal surface of the reactor under formation of metal sulfides according to reaction I



The presence of metal sulfides was proven by the analysis of the carbonaceous deposits from the reactor. Metal sulfides, which are formed according to reaction I, inhibit the course of secondary reactions on the inner surface of the reactor. The thin layer of metal sulfides thus decreases the catalytic effect of the metal surface in the formation of coke during the pyrolysis of reformer raffinate. As a consequence of the inhibition by sulfur additives, (condensed) aromatic compounds are expected to be present in higher concentrations in the product mixture. This has been confirmed experimentally.

## Conclusions

This study demonstrates that dibenzyl sulfide and dibenzyl disulfide, introduced into the reaction system together with the starting hydrocarbon, influence the rate of decomposition, the selectivity, and the formation of coke in the pyrolysis of hydrocarbons. Compared to the decomposition of pure heptane, the rate of decomposition in the presence of dibenzyl disulfide increases by 8%, and in the presence of dibenzyl sulfide by as much as 26%. Increasing concentrations of dibenzyl sulfide in the feed decrease the selectivity of the thermal decomposition of heptane to ethene. In this paper, it was assumed that the influence on the rate and selectivity of the conversion of

heptane is caused by benzyl and benzylthio radicals, which are formed by thermal decomposition of dibenzyl sulfide and dibenzyl disulfide. Alternatively,  $\dot{S}H$  radicals and S atoms can be formed, reacting with the inner surface of the reactor to metal sulfides. By the formation of a protective layer of metal sulfides, the inner surface is passivated, and the formation of coke is inhibited in the pyrolysis of reformer raffinate. The presence of sulfur-containing additives in the feed causes evident decreases in coking. Consequently, compounds, known or suspected to be precursors in the coke formation processes (condensed aromatics as naphthalene and its homologues), are found in increased concentrations among the pyrolysis products of sulfur-containing raffinate.

## Nomenclature

$S$  = inner surface of the reactor,  $cm^2$

$V$  = reactor volume,  $cm^3$

$\Delta F$  = rate of heptane consumption,  $mol\ h^{-1}$

$\bar{X}$  = average mole fraction of heptane

$m$  = number of measurements

$n$  = order of the reaction

$k$  = first-order rate constant,  $s^{-1}$

$x$  = conversion of heptane

$V_R$  = equivalent reactor volume,  $cm^3$

$r_c$  = coking rate,  $mg\ cm^{-2}\ h^{-1}$

M.B. = material balance of the hydrocarbon part

T.P. = temperature profile

## Greek Letters

$\nu$  = moles of product formed per mole of heptane decomposed

$\epsilon$  = relative volume change in the reactor

$\tau$  = residence time, s

**Registry No.** Heptane, 142-82-5; ethene, 74-85-1; dibenzyl sulfide, 538-74-9; dibenzyl disulfide, 150-60-7.

## Literature Cited

- Agrawal, B. B.; Tesarik, K.; Janak, J. J. *Chromatogr.* **1972**, *65*, 207.  
 Albright, L. F.; McConnell, Ch. F. *Adv. Chem. Ser.* **1979**, No. 183, 205.  
 Back, M. H.; Sehon, A. H. *Can. J. Chem.* **1960**, *38*, 1076.  
 Bajus, M.; Vesely, V.; Leclercq, P. A.; Rijks, J. A. *Ind. Eng. Chem. Prod. Res. Dev.* **1979**, *18*, 30.  
 Bajus, M.; Vesely, V. *Collect. Czech. Chem. Commun.* **1980**, *45*, 238.  
 Bajus, M.; Vesely, V.; Baxa, J.; Leclercq, P. A.; Rijks, J. A. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 741.  
 Bradshaw, Ch. P.; Turner, L. U.K. Patent 129 006, 1966.  
 Colussi, A. J.; Benson, S. W. *Int. J. Chem. Kinet.* **1977**, *9*, 295.  
 Cramers, C. A.; Scherpenzeel, G. J.; Leclercq, P. A. *J. Chromatogr.* **1981**, *203*, 207.  
 Crynes, B. L.; Albright, L. F. *Ind. Eng. Chem. Process Des. Dev.* **1969**, *8*, 25.  
 Dunklema, J. J.; Albright, L. F. *ACS Symp. Ser.* **1976**, No. 32, 241.  
 Frech, K. J.; Hoppstock, F. H.; Hutchings, D. A. *ACS Symp. Ser.* **1976**, No. 32, 197.  
 Foss, O.; *Acta Chem. Scand.* **1950**, *4*, 404.  
 Ghaley, M. A.; Crynes, B. L. *ACS Symp. Ser.* **1976**, No. 32, 218.  
 Gousty, Y.; Martin, R. *React. Kinet. Catal. Lett.* **1974**, *1*, 189.  
 Hogen, O. A.; Watson, K. M. "Chemical Process Principles"; Wiley: New York, 1947, Vol. III, p 884.  
 Hutchings, D. A.; Frech, K. J.; Hoppstock, F. H. *ACS Symp. Ser.* **1976**, No. 32, 178.  
 Kershenbaum, L. S.; Martin, J. J. *AIChE J.* **1967**, *13*, 148.  
 Kooyman, E. C. In "Organosulfur Chemistry"; Janssen, M. J., Ed., Interscience: New York, 1967, p 2.  
 Kundryavstseva, N. A.; Lulova, N. Y.; Furaev, A. A.; Borshchevskii, S. B. *Khim. Tekhnol. Topl. Masel* **1977**, *3*, 59.  
 Lang, A. Fr. Patent 1 487 433, 1967.  
 Large, J. F.; Martin, R.; Niclaude, M. *C.R. Acad. Sci., Paris* **1972**, *274C*, 322.  
 Mackle, H. *Tetrahedron* **1963**, *19*, 1159.  
 Magaril, R. Z. "Mechanizm i kinetika gomogenykh termicheskikh uglevodorodov"; Editor Khimija: Moscow, 1970; p 20.  
 McLean, P. R.; McKenney, D. J. *Can. J. Chem.* **1970**, *48*, 1782.  
 Price, C. C.; Oae, S. "Sulfur Bonding"; Ronald Press: New York, 1962, p 44.  
 Rebeck, Ch. *Ind. Eng. Chem. Fundam.* **1981**, *20*, 54.  
 Scacchi, G.; Baronnet, F.; Martin, R.; Niclaude, M. *J. Chem. Phys.* **1968**, *65*, 1671.  
 Scacchi, G.; Dzierzynski, M.; Martin, R.; Niclaude, M. *Int. J. Chem. Kin.* **1970**, *2*, 115.

Received for review June 28, 1982

Accepted December 21, 1982