EFFECT OF SULPHUR COMPOUNDS ON THE HEPTANE PYROLYSIS KINETICS

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The effect of 1-didecyl sulphide, diethyl disulphide, p,p'-dichlorodiphenyl disulphide, 1-butanethiol, 0,0'-di-1-butyl dithiophosphate zinc, 0,0'-diethyl dithiophosphoric acid and carbon disulphide, respectively, on the kinetics and selectivity of the thermal decomposition of heptane at 700°C and 100 kPa was studied in a stainless steel flow-through tube reactor. The sulphur substance content was 0·1—1·0 wt.%. 1-Didecyl sulphide, p,p'-dichlorodiphenyl disulphide, 1-butylthiol, 0,0'-di-1-butyl dithiophosphate zinc and carbon disulphide favour the decomposition of heptane by 5—17%. A decrease in the heptane decomposition rate was observed in the presence of diethyl disulphide (2·8%) and 0,0'-diethyl dithiophosphoric acid (13·9%). The selectivity of decomposition to ethylene is increased by diethyl disulphide, p,p'-dichlorodiphenyl disulphide, carbon disulphide and 1-didecyl sulphide and, in the range of short reaction times, also by 0,0'-diethyl dithiophosphoric acid, 0,0'-di-1-butyl dithiophosphate zinc and 1-butanethiol.

Our previous study of the behaviour of sulphur compounds during the pyrolysis of hydrocarbons has shown that elementary sulphur[1], thiophene[2], dibenzyl sulphide and dibenzyl disulphide[3], in dependence on their concentrations in the feedstock, increase the thermal decomposition rate and reduce the extent of coke formation. Hydrogen sulphide also has an inhibiting effect on the coking[4]. The formation of coke during the pyrolysis is lowered in the presence of hydrogen sulphide, ethylthiol and dimethyl disulphide, and as a consequence, the carbon monoxide and dioxide contents of the gaseous pyrolysis products are also lowered[5]. Coking in pyrolysis reactors is also efficiently suppressed by other, unspecified sulphur and phosphorus compounds[6,7]. A reduced coke formation was observed during the pyrolysis of propane and propene in reactors with sulphided inner walls, which can be obtained by means of hydrogen sulphide.

Other sulphur compounds can also be expected to affect pyrolysis of hydrocarbons to olefins. The effect of 1-didecyl sulphide, diethyl disulphide, p,p'-dichlorodiphenyl disulphide, 1-butanethiol, 0,0'-di-1-butyl dithiophosphate zinc, 0,0'-diethyl dithiophosphoric acid and carbon disulphide on the pyrolysis of heptane is therefore studied in this work.

EXPERIMENTAL

A flow-through apparatus was used[8]; its tube reactor was of stainless steel whose composition (in wt. %) was Cr 16·8, Ni 10·7, Mn 1·1, C 0·08. Heptane 99·7% (Loba-Chemie, Wien) was delivered at a rate of 0·15—0·35 mol h^{-1}. The experiments were made in the presence of steam; the water-to-heptane ratio was 3 : 1, the water rate was 2·57—5·85 mol h^{-1}. 1-Didecyl sulphide, diethyl disulphide and p,p'-dichlorodiphenyl disulphide were prepared according to refs[9,10], 0,0'-di-1-butyl dithiophosphate zinc and 0,0'-diethyl dithiophosphoric acid, according to ref.[11]. Carbon disulphide and 1-butanethiol were commercial chemicals of Lachema, Brno, and Fluka, Buchs, respectively.

RESULTS

Kinetics

A temperature of 700°C and residence times from 0·02 to 0·12 s were used. To heptane were added 1 wt.% 1-didecyl sulphide, 1 wt.% diethyl disulphide, 0·25 wt.% p,p'-dichlorodiphenyl disulphide, 1 wt.% 1-butanethiol, 1 wt.% 0,0'-di-1-butyl dithiophosphate zinc, 1 wt.% 0,0'-diethyl dithiophosphoric acid, or 0·1 wt.% carbon disulphide. The dependence of the degree of heptane conversion on the residence time is shown in Fig. 1. The results were obtained for a temperature profile with equivalent reactor volume 5—7 cm^3. The residence time and the equivalent volume were determined as previously[8]. The average values of the equivalent volumes are given in Table I and, for selected residence times, in Table II.

Similarly as with pure heptane, the pyrolysis reaction order approaches unity also in the presence of sulphur compounds. The right-hand term of the rate equation $k . \tau$ is plotted against the residence times in Fig. 2 for the various sulphur compounds. The rate constants, determined graphically and numerically, are listed in Table I. The highest standard deviation obtained for the numerically calculated constants was 10·6%. Within this range of error the rate constants do not show any increasing or decreasing trend in dependence on the degree of conversion. Some sulphur compounds are found to favour the thermal decomposition of heptane while other hinder it. Among sulphur substances that have an accelerating effect of 5—17%, there are 1-didecyl sulphide, p,p'-dichlorodiphenyl disulphide, 1-butanethiol, 0,0'-di-1-butyl dithiophosphate zinc and carbon disulphide. A decrease in the heptane decomposition rate, of 3—14%, was observed in the presence of diethyl disulphide and 0,0'-diethyl dithiophosphoric acid.

Selectivity

In dependence on the heptane conversion degree, within the range of 11·8—36·2%, gaseous products in amounts of 10·1—33·4 wt.% are formed in the presence of sulphur compounds; their average molecular weight is 23—28·5.

Qualitative and quantitative data of the composition of the gaseous and liquid products are given in Table II. The sulphur compounds have no effect on the qualitative composition. The major product of pyrolysis of heptane is ethene; methane

TABLE I

Rate constants of heptane conversion at 700°C in the presence of sulphur compounds

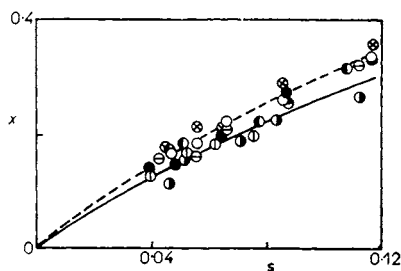| Compound added	V_R cm^3	k, s^{-1}	
		analytically	graphically
___ [a]	5·6	3·7	3·6
1-Didecyl sulphide (1 wt.%)	6·6	3·9	3·8
Diethyl disulphide (1 wt.%)	5·8	3·4	3·5
p,p'-Dichlorodiphenyl disulphide (0·25 wt.%)	6·6	4·3	4·2
1-Butanethiol (1 wt.%)	6·1	3·8	3·8
0,0'-Di-1-butyl dithiophosphate zinc (1 wt.%)	6·2	3·8	4·0
0,0'-Diethyl dithiophosphoric acid (1 wt.%)	6·3	3·1	3·1
Carbon disulphide (0·1 wt.%)	6·4	3·8	3·9

[a] Ref.[8].

FIG. 1

Dependence of the degree of heptane conversion on the residence time in the presence of 1-didecyl sulphide (○), diethyl disulphide (⊕), 1-butanethiol (●), 0,0'-di--1-butyl dithiophosphate zinc (◐), 0,0'-diethyl dithiophosphoric acid (◑), carbon disulphide (⊖) and p,p'-dichlorodiphenyl disulphide (⊗)
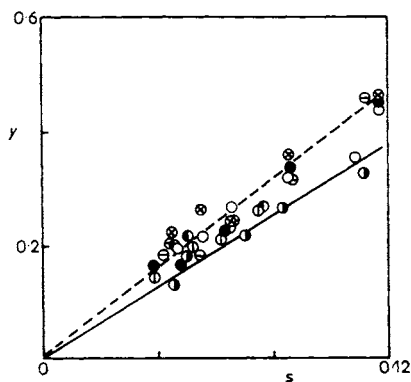

FIG. 2

First order plot for the pyrolysis of heptane in the presence of sulphur compounds. Labelling as in Fig. 1; $y = -(\varepsilon + 1)\ln(1 - x) - \varepsilon x$

TABLE II

Composition of products from the pyrolysis of heptane at 700°C, [mol per 100 mol of decomposed heptane] in the presence of sulphur compounds

Product	No compound added[a]		Didecyl sulphide		Diethyl disulphide		p,p'-Di-chlorodiphenyl disulphide		1-Butanethiol		O,O'-Di-1-butyl dithio-phosphate zinc		O,O'-Diethyl dithio-phosphoric acid		Carbon disulphide	
	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p	q
Hydrogen	51·1	60·4	42·1	56·1	62·9	51·5	41·1	39·5	45·7	42·4	34·6	50·1	54·6	59·6	49·2	45·2
Methane	49·5	56·9	57·7	62·5	62·9	62·3	56·3	55·7	54·4	57·3	46·8	47·2	58·7	62·1	63·3	60·1
Ethane	6·2	10·0	10·6	12·5	14·4	13·5	13·1	13·0	12·5	13·1	12·0	13·1	8·4	10·0	10·5	12·0
Ethene	116·6	137·7	131·4	144·6	144·0	140·1	130·9	138·8	127·0	127·3	118·7	122·2	122·2	130·2	123·8	141·5
Propane	0·8	1·5	1·2	1·2	1·0	1·1	0·9	0·6	0·8	0·8	1·3	1·1	1·2	1·4	1·2	1·0
Propene	31·9	38·2	30·3	32·2	31·5	35·7	33·0	42·7	35·8	36·0	38·0	34·2	32·7	37·5	35·6	32·8
Butane	0·5	0·4	0·6	0·4	0·6	0·4	0·4	0·1	0·3	0·2	0·5	0·4	0·7	0·6	0·5	0·5
1-Butene	21·3	20·2	21·2	20·4	17·2	19·5	23·9	21·3	25·0	22·6	23·0	21·0	24·6	21·4	23·9	20·2
trans-2-Butene	0·4	0·3	0·2	0·2	0·2	0·2	0·3	0·1	0·2	0·2	0·3	0·3	0·5	0·3	0·2	0·4
cis-2-Butene	0·3	0·4	0·1	0·2	0·1	0·2	0·1	0·2	0·1	0·2	0·3	0·3	0·3	0·2	0·1	0·3
1,3-Butadiene	2·6	2·6	1·9	2·4	1·4	2·1	2·3	2·8	2·0	2·6	2·6	2·4	2·0	2·7	2·1	3·1
3-Methyl-1-butene	0·1	0·2	0·1	0·2	0·1	0·2	0·3	0·3	0·1	0·2	0·2	0·1	0·1	0·2	0·2	0·3
1-Pentene	13·0	10·1	10·2	9·4	9·2	11·9	14·3	10·9	12·1	10·9	12·1	12·5	12·0	9·2	13·3	12·4
2-Methyl-1-butene	0·3	0·2	0·1	0·2	—	0·1	—	—	—	—	0·1	—	0·2	—	—	0·1
trans-2-Pentene	0·3	0·2	0·2	0·2	—	0·2	0·2	0·2	—	0·2	0·2	0·2	0·2	0·2	0·2	0·2
cis-2-Pentene	0·2	0·2	0·2	0·1	—	0·1	0·1	0·1	—	0·1	0·1	0·2	—	0·2	0·2	0·2
1-Hexene	6·0	5·5	5·5	4·8	4·3	5·4	6·1	4·8	6·3	5·0	5·9	5·3	5·8	5·1	5·6	6·8
1-Heptene	1·7	0·9	1·3	0·8	3·1	2·1	0·8	0·3	—	0·6	3·4	2·6	2·5	0·8	1·0	0·6
Carbon monoxide	26·2	12·4	18·8	20·8	9·4	17·4	11·8	11·1	24·0	27·5	22·0	18·3	16·4	30·4	18·4	25·6

[a] Ref.[8]; b-q amount added, wt.%; degree of conversion, %; V_r, cm³; MB, wt.%; b 0, 13·9, 4·8, 97·2; c 0, 26·8, 6·8, 98·8; d 1, 17·2, 6·4, 97·6; e 1, 26·8, 6·8, 97·1; f 1, 13·1, 5·3, 99·5; g 1, 20·4, 5·9, 98·8; h 0·25, 18·7, 6·1, 98·8; i 0·25, 29·5, 6·8, 98·3; j 1, 14·7, 5·3, 97·4; k 1, 27·9, 6·9, 99·5; l 1, 17·9, 6·2, 99·9; m 1, 23·0, 6·1, 96·3; n 1, 11·8, 6·2, 100·2; o 1, 27·0, 6·4, 100·2; p 0·1, 16·3, 5·7, 97·1; q 0·1, 26·3, 6·4, 101·4.

propene, 1-butene, 1-pentene, 1-hexene, hydrogen and carbon monoxide are also present. The effect of the residence time on the selectivity of the pyrolysis in the presence of the sulphur compounds is shown in Figs 3—9. As the residence time is extended, the formation of ethene, propene and methane increases whereas that of butene, pentene and hexene decreases in the presence of didecyl sulphide, 1-butanethiol, diethyl dithiophosphoric acid and dichlorodiphenyl disulphide. The situation is similar in the presence of dibutyl dithiophosphate zinc except that the selectivity to ethene remains constant. The characteristics are different in the presence of diethyl disulphide and carbon disulphide. With the former, surprisingly, the amount of ethene does not change with residence time while the methane level decreases and the selectivity to butene, pentene and hexen increases. With carbon disulphide, the yield of ethene increases while the yields of methane, propene and C_4—C_6 1-alkenes decrease.

As compared with the pyrolysis of pure heptane, the decomposition to ethene in the presence of diethyl disulphide, dichlorodiphenyl disulphide, carbon disulphide, or didecyl sulphide is more selective within the entire residence time period, and for short residence times this applies also to diethyl dithiophosphoric acid, dibutyl
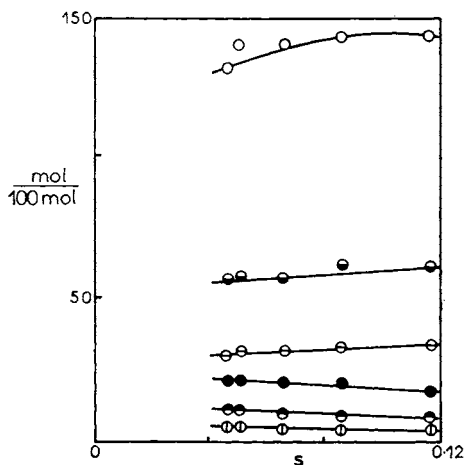

FIG. 3

Effect of the residence time on the formation of products during the pyrolysis of heptane at 700°C in the presence of 1 wt.% 1-didecyl sulphide. Products: ○ ethene, ◓ methane, ◔ propene, ● 1-butene, ◒ 1-pentene, ◍ 1-hexene
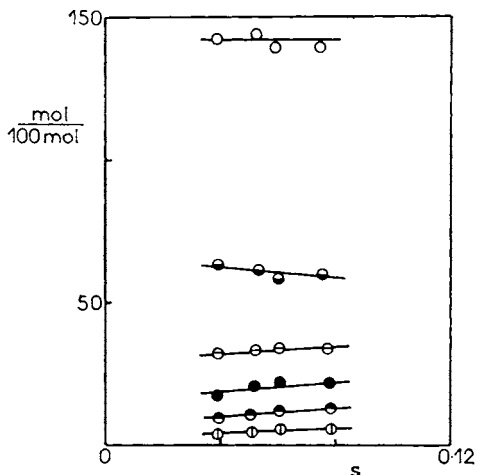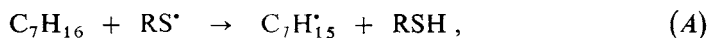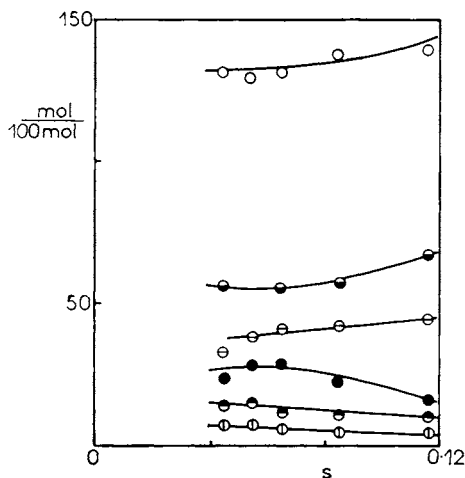
FIG. 4

Effect of the residence time on the formation of products during the pyrolysis of heptane at 700°C in the presence of 1 wt.% diethyl disulphide. Product labelling as in Fig. 3

dithiophosphate zinc and butanethiol, whereas at longer residence times the selectivity to ethene does not attain the value observed in their absence.

DISCUSSION

The pyrolysis of hydrocarbons involves chain radical reactions. The primary scission of heptane occurs preferentially at carbon–carbon bonds, their dissociation energies being $300 - 350 \text{ kJ mol}^{-1}$ as compared to those of the hydrogen–carbon bonds, $380 - 430 \text{ kJ mol}^{-1}$. Sulphur compounds have an initiating or retarding influence. The dissociation energies of C—S and S—S bonds are largely lower than those of hydrocarbon bonds[12] (Table III). Thermal decomposition of sulphur compounds gives rise to thiyl radicals in which sulphur atoms carry a substituent and possess an unpaired electron; a carbon atoms is usually bonded to sulphur. Under the pyrolysis conditions the thiyl radicals $(RS^\bullet)$ can enter the following reactions:
abstraction,

$$C_7H_{16} + RS^\bullet \rightarrow C_7H_{15}^\bullet + RSH, \qquad (A)$$

combination,

$$RS^\bullet + {}^\bullet R' \rightleftarrows RSR', \qquad (B)$$

Fig. 5

Effect of the residence time on the formation of products during the pyrolysis of heptane at 700°C in the presence of 0·25 wt.% *p,p'*-dichlorodiphenyl disulphide. Product labelling as in Fig. 3
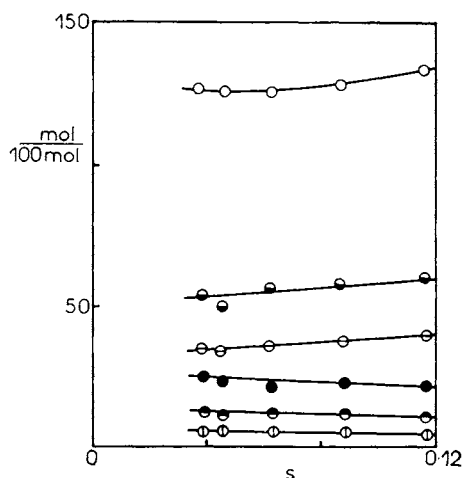
Fig. 6

Effect of the residence time on the formation of products during the pyrolysis of heptane at 700°C in the presence of 1 wt.% 1-butanethiol. Product labelling as in Fig. 3

addition,

$$\pi\text{-system} + \text{RS}^{\bullet} \ \rightleftarrows \ \text{radical adduct} - \text{RS} . \qquad (C)$$
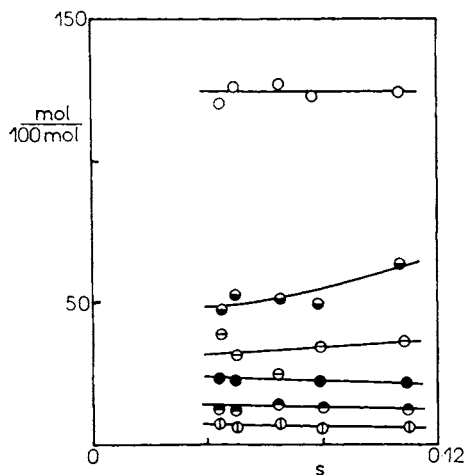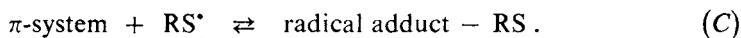

FIG. 7

Effect of the residence time on the formation of products during the pyrolysis of heptane at 700°C in the presence of 1 wt.% 0,0'-di--1-butyl dithiophosphate zinc. Product labelling as in Fig. 3
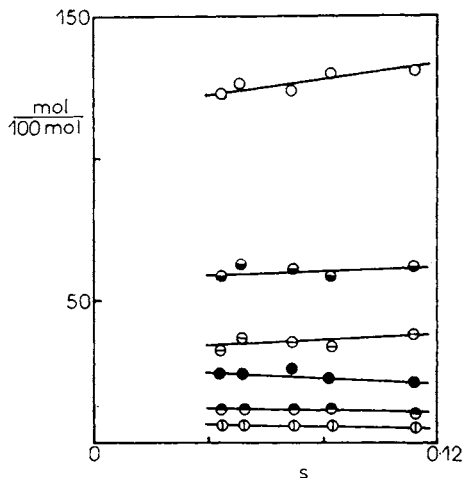

FIG. 8

Effects of the residence time on the formation of products during the pyrolysis of heptane at 700°C in the presence of 1 wt.% 0,0'--diethyl dithiophosphoric acid. Product labelling as in Fig. 3
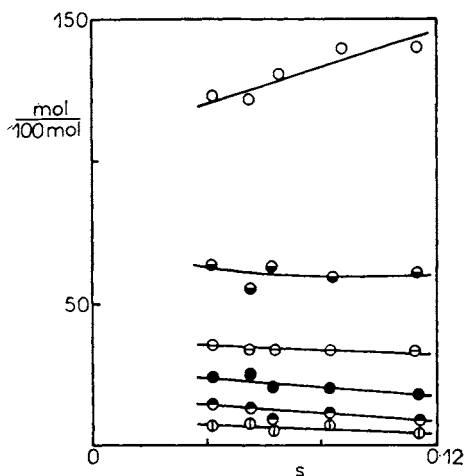
FIG. 9

Effect of the residence time on the formation of products during the pyrolysis of heptane at 700°C in the presence of 0·1 wt.% carbon disulphide. Product labelling as in Fig. 3
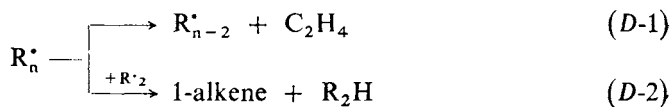
Taking into account the results of our previous work[3], where the effect of dibenzyl sulphide and dibenzyl disulphide was investigated, it can be concluded that the next aromatic disulphide studied, p,p'-dichlorodiphenyl disulphide, exerts a similar initiating effect; this is probably due to the fact that owing to the relatively low dissociation energy of the S—S bond $(230 \, \text{kJ} \, \text{mol}^{-1})$, p-chlorophenyl thiyl radicals are readily generated. The rate constant increase is 19%, which is more than double as compared with dibenzyl disulphide, the selectivity of conversion to ethene being the same.

For diethyl disulphide the dissociation energy of the C—S bond is $225 \cdot 7 \, \text{kJ} \, \text{mol}^{-1}$, and so this compound might be expected to be a good initiator, giving ethyl dithiyl radicals during its thermal decomposition. Disappointedly, however, diethyl disulphide does not accelerate the thermal decomposition of heptane; it actually has rather a retarding effect. The selectivity to ethene, on the other hand, is high, with a uniform course in dependence on the residence time. In contrast to the other sulphur compounds, diethyl disulphide brings about an increase in the amounts of 1-butene, 1-pentene and 1-hexene, which implies that as the pyrolysis conditions become harder, the C_4—C_6 α-radicals are decomposed to ethene according to reaction $(D\text{-}1)$ at a constant rate, whereas the rate of decomposition associated with the abstraction of a hydrogen radical and formation of 1-alkenes $(D\text{-}2)$ increases.

TABLE III

Dissociation energies of bonds in sulphur compounds[12]

Compound	Dissociation energy $\text{kJ} \, \text{mol}^{-1}$
R—S$\dashv$S—R'	309·3
R—S$\dashv$CH$_2$CH$_3$	309·3
C$_6$H$_5$—S$\dashv$S—C$_6$H$_5$	230
R—S—S$\dashv$CH$_2$CH$_3$	225·7
R—S—S$\dashv$C$_6$H$_5$	290·5
R—S$\dashv$H	384·6
(CH$_3$)$_3$C$\dashv$SH	288·4
HS$\dashv$H	384·6
C$\Dashv$S	723·2
SC$\Dashv$S	432·2

$$R_n^\bullet \quad \begin{cases} \longrightarrow R_{n-2}^\bullet + C_2H_4 & (D\text{-}1) \\ \xrightarrow{+R_2^\bullet} 1\text{-alkene} + R_2H & (D\text{-}2) \end{cases}$$

($R_n^\bullet$ is 1-hexyl, 1-pentyl or 1-butyl radical and $R_2^\bullet$ is C_2H_5—S—S$^\bullet$ or $C_2H_5S^\bullet$ radical).

It is noteworthy that ethyl thiyl and ethyl dithiyl radicals exhibit marked splitting and, particularly, dehydrogenating properties only after the thermal initiation of heptane to radicals.

Although alkyl sulphides possess higher dissociation energies of the C—S bond ($309 \cdot 3$ kJ mol^{-1}) than the corresponding disulphides, didecyl sulphide has an initiating effect on the decomposition of heptane according to reaction (A); in the presence of this compound the decomposition proceeds $5 \cdot 6\%$ faster than in its absence. Butanethiol has a similar effect. The $5 \cdot 6\%$ pyrolysis rate increase is associated with the approximately equal dissociation energy of the C—S bond ($228 \cdot 4$ kJ mol^{-1}) in thiols as compared with alkanic sulphides. While the heptane pyrolysis rates in the presence of 1-didecyl sulphide and 1-butanethiol are equal, the selectivity to ethene is lower in the latter case.

0,0'-Diethyl dithiophosphoric acid and 0,0'-di-1-butyl dithiophosphate zinc are combined compounds containing both organic (alkoxy) and inorganic (sulphur, phosphorus, zinc) parts. Typical scission products resulting from their decomposition at temperatures of 200°C and more are alkenes, thiols, sulphides, disulphides and hydrogen sulphide, all of them gaseous under the conditions used. Liquid and solid products are also formed. The solid residue has rather the character of an inorganic substance, the liquid products contain mainly alkyl mono- through tetrathiophosphates[13,14]. With such a gamut of decomposition products, no unique effect on the pyrolysis of heptane in the presence of dialkyl dithiophosphates can be expected. This applies to 0,0'-di-ethyl dithiophosphoric acid and 0,0'-di-1-butyl dithiophosphate zinc, the former having a retarding and the latter, an initiating effect. The two dialkyl dithiophosphates are comparable as far as the selectivity to ethene is concerned.

Carbon disulphide is a simple compound where sulphur is bonded to carbon by a double bond. The dissociation energy of the C=S bond, $432 \cdot 2$ kJ mol^{-1}, is beyond the upper limit for the C—H bonds in hydrocarbons; still, the pyrolysis of heptane is $8 \cdot 3\%$ favoured by carbon disulphide.

LIST OF SYMBOLS

k rate constant, s^{-1}
x degree of heptane conversion
V_R equivalent volume of reactor, cm^3
MB   mass balance of the hydrocarbon fraction
v number of mol of products per mol of reacted heptane
ε relative volume change during the reaction
τ residence time, s

REFERENCES

1. Bajus M., Veselý V.: This Journal *45*, 238 (1980).
2. Bajus M., Veselý V., Baxa J., Leclercq P. A., Rijks J. A.: Ind. Eng. Chem., Prod. Res. Develop. *20*, 741 (1981).
3. Bajus M., Baxa J., Leclercq P. A., Rijks J. A.: Ind. Eng. Chem., Prod. Res. Develop. *22*, 335 (1983).
4. Trim D. L., Turner Ch. J.: J. Chem. Technol. Biotechnol. *31*, 285 (1981).
5. Santiago J. A., Francesconi J. D., Moretti N. L.: Oil Gas J., Sept. *26*, 78 (1983).
6. Boone K.: Oil Gas J., Sept. *26*, 84 (1983).
7. Figueiredo J. L., Orfao J. J. M., Holmen A., Lindvoag O. A., Trimm D. L.: *3rd Int. Conf. Chem. Eng. Chempor '81*, Póvoa de Varzim, April 20—24, 1981.
8. Bajus M., Veselý V., Leclercq P. A., Rijks J. A.: Ind. Eng. Chem., Prod. Res. Develop. *18*, 30 (1979).
9. Reid Emmet E.: *Organic Chemistry of Bivalent Sulphur*, Vol. 2. Chemical Publ. Co., New York 1960.
10. Marko M., Krasnec L.: *Základy preparatívnej organickej chémie*. Published by SNTL, Bratislava 1962.
11. Bajus M.: *Thesis*. Slovak Institute of Technology, Bratislava 1965.
12. Benson S. W.: Chem. Rev. *78*, 23 (1978).
13. Bajus M., Veselý V.: *Zborník prác Chemickoteckotechnologickej fakulty SVŠT (1975—1976)*, p. 123. Alfa, Bratislava 1978.
14. Kozák P., Rábl V.: Ropa Uhlie *25*, 647 (1983).

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