

## COKE FORMATION DURING THE PYROLYSIS OF HYDROCARBONS IN THE PRESENCE OF SULPHUR COMPOUNDS

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The effect of 1-butanethiol, 0,0'-di-1-butyl dithiophosphate zinc, 0,0'-diethyl dithiophosphoric acid and carbon disulphide, respectively, on the formation of coke during the pyrolysis of a reformer raffinate at 820 °C and 100 kPa was studied using a stainless steel tube flow-through reactor. The sulphur compounds were added in amounts of 0.05 to 0.5 wt. %. The coke formation was followed from the beginning of the experiment. The coking rate was lower as compared with the pyrolysis of the pure reformer raffinate; 0,0'-di-1-butyl dithiophosphate zinc, 0,0'-diethyl dithiophosphoric acid and carbon disulphide have a strong inhibiting effect on the coke formation. The coking inhibition mechanism is discussed.

Some inorganic and organic nitrogen, oxygen, sulphur, and phosphorus compounds affect the radical process of thermal decomposition of hydrocarbons. Sulphur compounds are among those affecting not only the primary, but also the secondary reactions resulting in the formation of coke. This is the case with the hydrodealkylation of the BTX fraction, where elementary sulphur is added in order to reduce the extent of coking<sup>1</sup>. Dimethyl sulphide, ethanethiol and carbon disulphide inhibit the cleavage of butane<sup>2</sup>. 4-Butyl-4-thiacyclohexane lowers the decomposition rate of hexadecane<sup>3</sup>. Reactivity data are requisite for gaining insight into the mechanism of effects of sulphur compounds during the pyrolysis of organic substances. For sulphoxides, sulphones and sulphides, the reactivity is consistent with the relative stability which decreases in this order<sup>4</sup>. The kinetics of pyrolysis of allylpropargyl and isopropylpropargyl sulphides has been examined for the same purpose<sup>5</sup>.

The aim of the present work was to investigate the coke formation during the pyrolysis of hydrocarbons in the presence of 1-butanethiol, 0,0'-di-1-butyl dithiophosphate zinc, 0,0'-diethyl dithiophosphoric acid and carbon disulphide, respectively.

### EXPERIMENTAL

The coke formation was studied in a flow-through reactor as described previously<sup>6</sup>. The inner surface-to-volume ratio of the U type tube reactor was  $6.66 \text{ cm}^{-1}$ . The tube material was stainless steel containing (in wt.%) Cr 17.5, Ni 9.4, Mn 0.7, C 0.18. The effect of 1-butanethiol (Fluka),

carbon disulphide (Lachema, Brno), 0,0'-di-1-butyl dithiophosphate zinc and 0,0'-diethyl dithiophosphoric acid (prepared according to ref.<sup>7</sup>) on the coke formation was examined during the pyrolysis of a reformer raffinate obtained from gasoline from catalytic reforming after the extraction of aromatics. The composition of the reformer raffinate (in wt. %) was as follows: unbranched alkanes 18.8, branched alkanes 60.4, cycloalkanes 10.3, aromatics 6.0, other substances 4.5. The reformer raffinate was virtually free from sulphur compounds. The flow rate was 0.30 mol h<sup>-1</sup> in all experiments. The pyrolysis was carried out without any inert diluent at 820°C and 100 kPa. The amount of coke formed was determined by weighing the reactor before and after the experiment. Prior to each experiment, coke was removed by combustion with air, and metal oxides were decomposed with a mixture of 3% HCl + 3% H<sub>2</sub>SO<sub>4</sub>. Metal sulphides were isolated electrochemically by anodic dissolution of sample powder<sup>8</sup>.

## RESULTS

### Coking

The effect of sulphur compounds on the coke formation was examined at 820°C with the pure reformer raffinate and with that containing 0.1 or 0.5 wt.% 1-butanethiol, 0.5 wt.% di-1-butyl dithiophosphate zinc, 0.35 wt. % diethyl dithiophosphoric acid or 0.05 or 0.1 wt.% carbon disulphide. The results are given in Table I and the coking rates are plotted in dependence on the experiment duration in Fig. 1. For the reformer raffinate alone and in the presence of 1-butanethiol, the coking rate is highest at the

TABLE I

Amounts of coke formed (g) during the pyrolysis of a reformer raffinate at 820°C and residence time 0.25 s, in dependence on the experiment duration

Sulphur compound added	Experiment duration, min						
	15	30	60	90	120	150	180
— <sup>a</sup>	0.35	0.56	0.72	0.72	—	—	0.83
1-Butanethiol, 0.1 wt. %	—	0.29	0.41	—	0.46	—	0.49
1-Butanethiol, 0.5 wt. %	—	0.17	0.22	—	0.22	—	—
0,0'-Di-1-butyl dithiophosphate zinc, 0.5 wt. %	0.03	—	—	—	—	—	0.03
0,0'-Diethyl dithiophosphoric acid, 0.35 wt. %	0.11	—	—	—	0.10	—	—
Carbon disulphide, 0.05 wt. %	—	0.11	0.10	—	0.08	—	—
Carbon disulphide, 0.1 wt. %	—	0.16	0.14	—	0.10	—	0.07

<sup>a</sup> Ref.<sup>6</sup>.

beginning of the experiment and it attains a steady-state value in a time. In the presence of any of the sulphur compounds the coking rate is lower than in their absence. The coking rate decreases with increasing concentration of butylthiol. Dibutyl dithiophosphate zinc, diethyl dithiophosphoric acid and carbon disulphide exert a strong inhibiting effect.

The shape of the coking kinetics dependences indicates that at the beginning of the experiment, when the pyrolysis sets in, the inner surface of the reactor has a decisive effect on the extent of the secondary reactions leading to the formation of coke. Clearly, this formation is catalyzed by the metal surface. The steady state is attained in a time when the surface becomes coated by the carbon deposit. The presence of 0,0'-dialkyl dithiophosphoric acid and its zinc salt, 1-butanethiol and carbon disulphide invariably reduces the extent of coking.

### Coke Composition

The secondary reactions during the pyrolysis of the hydrocarbon matter give rise to pyrocarbon which deposits as coke on the inner surface of the reactor. Under the pyrolysis conditions, interactions occur between the metal surface of the reactor and the pyrocarbon, resulting in the formation of metal carbides. Metal sulphides are formed if sulphur substances are present in the reaction system. The presence of carbides and sulphides was confirmed by chemical analysis of the stainless steel material of the pyrolysis tube reactor which had been in use for 10 years under conditions given in ref.<sup>9</sup>. The results are given in Table II.

The long-term use of the pyrolysis reactor resulted in carbonization and sulphidization; the carbon and sulphur contents increased 8 and 6 times, respectively. The amounts of other elements did not change. Metal oxides were absent, although

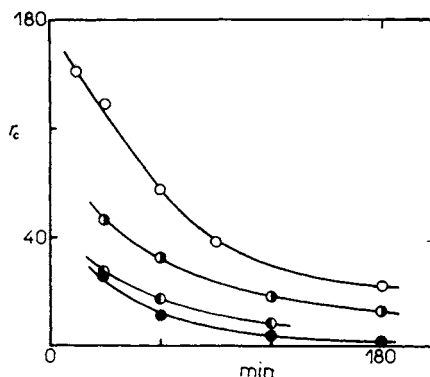


FIG. 1

Coking rate  $r_c$  ( $\text{mg cm}^{-2} \text{h}^{-1}$ ) in dependence on the experiment duration (min) for the pyrolysis of a reformer raffinate in the absence of sulphur compounds (O) and in the presence of 0.1 wt.% 1-butanethiol (◐), 0.5 wt.% 1-butanethiol (◑) and 0.1 wt.% carbon disulphide (●)

the pyrolysis had taken place in the presence of steam and oxygen had been used for burning the coke deposited. From this it can be inferred that ultimately the pyrolysis proceeds under reduction conditions. The oxidation residue knocked out of the reactor after the coke combustion, however, contained metal oxides in a quantity of 17.6% with respect to oxygen.

The situation is different if the pyrolysis reactor has been run for a relatively short time, such as four months. No essential changes were revealed by chemical analysis of the reactor material, although hard conditions of pyrolysis without any inert diluent had been used. The results of the chemical and spectral analysis of the reactor material are given in Table III.

Now, it is of interest to seek how the material of the reactor walls affects the composition of the coke formed. The carbonaceous deposit (coke) coating the reactor surface during the experiment was therefore analyzed (Table IV). The prevailing substances are graphite, metal carbides and metal sulphides. Carbides make up 90.8 wt. %, sulphides 7.8 wt. %. Carbides of chromium are predominantly formed, carbides of iron and manganese are present to a lesser extent. The amount and composition of metal sulphides are markedly affected by the quality of the raw material pyrolyzed, particularly the quality and quantity of the sulphur compounds present. Sulphides of iron and manganese predominate for the pyrolysis of hydrogenation-treated feedstocks in the presence elementary sulphur. The amount of sulphides increases from 17 wt.% to 36 wt.% if the reactor has been passivated by hydrogen sulphide before the pyrolysis sets in; chromium and iron sulphides (36.4 and 22.5%, respectively) are formed.

TABLE II  
Chemical composition of the pyrolysis reactor material (wt.%)

Element	Unused reactor	Reactor used for 10 years
C	0.074	0.573
Mn	1.07	1.01
Si	0.41	0.40
P	0.028	0.027
S	0.015	0.095
Cr	16.78	15.86
Ni	9.71	10.31
Mo	0.27	0.29
Ti	0.75	0.75

## DISCUSSION

1-Butanethiol, 0,0'-di-1-butyl dithiophosphate zinc, 0,0'-diethyl dithiophosphoric acid and carbon disulphide act against the coke formation during the pyrolysis of the refined petrol product similarly as elementary sulphur<sup>6</sup>, thiophene<sup>10</sup>, dibenzyl sulphide and dibenzyl disulphide<sup>11</sup>. This can be explained so that the same sulphur-

TABLE III  
Composition of the pyrolysis reactor material (wt.%)

Element	Unused reactor	Reactor used for 4 months
Chemical analysis		
C	0.141	0.136
Mn	0.65	0.64
Si	0.36	0.36
P	0.034	0.033
S	0.028	0.027
Cr	18.30	18.50
Ni	9.85	10.01
Mo	0.28	0.32
Semiquantitative spectral analysis		
V	0.2	0.2
W	0.15	0.15
Ti	0.25	0.25
Cu	0.3	0.3
Al	0.2	0.2

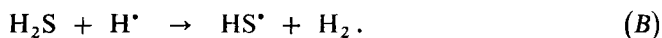
TABLE IV  
Composition of the carbonaceous deposit in the pyrolysis reactor

Element	Amount, wt.%
Fe	7.1
Cr	18.3
Ni	1.8
Mn	4.9
C	66.0
S	0.3

-containing decomposition or intermediate product is formed, and this product suppresses the coke formation irrespective of the properties of the initial sulphur compound added. This product, which always forms during the thermal decomposition of sulphur compounds, can be hydrogen sulphide. Thiyl radicals  $\cdot\text{SH}$ , as reaction intermediates, play a decisive part in the formation of hydrogen sulphide. These radicals are most readily formed by scission of alkylthiols according to reaction

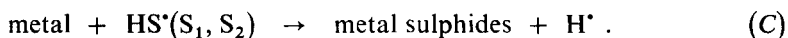


1-Butanethiol decomposes at  $697-762^\circ\text{C}$  by this radical mechanism following the 1st order reaction patterns<sup>12</sup>. Alkylthiols occur as profiling reaction products also during the thermal decomposition of dialkyl dithiophosphates<sup>13,14</sup>. The pyrolysis products of zinc 0,0'-bis(2-ethylhexyl) dithiophosphate were studied by gas chromatography and octanethiol isomers and octenes were identified<sup>15</sup>; no dialkyl sulphides or disulphides were observed. Thiol radicals can also emerge, in the pyrolysis conditions<sup>16</sup>, from the decomposition of hydrogen sulphide in the presence of hydrogen radicals:



Reactions during which elementary sulphur is formed in the atomic state  $\text{S}_1$  or in the molecular state  $\text{S}_2$  with paramagnetic properties are assumed to occur<sup>16</sup> under specific conditions at  $2700-3800\text{ K}$  and at low concentrations of hydrogen sulphide in the reaction mixture (25–200 ppm).

The  $\text{HS}\cdot$  radicals or  $\text{S}_1$  and  $\text{S}_2$  sulphur can enter either gas phase reactions or reactions with the metal surface of the reactor giving metal sulphides,



According to present day knowledge, secondary reactions take place, as a result of which pyrocarbon is formed, either in the gaseous phase or on the inner surface of the reactor. Thiyl radicals in the gas phase also can capture active hydrocarbon radicals, thereby preventing formation of coke precursors. This mechanism is borne out by the fact that stable sulphur compounds such as thiophene, 2- and 3-methylthiophene, 2- and 3-ethylthiophene, 2- and 3-vinylthiophene and benzothiophene are formed during the pyrolysis in the presence of 0,0'-diethyl dithiophosphoric acid<sup>11</sup>.

The main effect of thiol radicals and sulphur ( $\text{S}_1, \text{S}_2$ ) is directed towards the reaction with the metal surface giving rise to a layer of metal sulphides. The latter inhibit the secondary reactions as a result of which the arising pyrocarbon forms a coke deposit on the inner surface of the reactor. From the high efficiency of 0,0'-diethyl dithiophosphoric acid and 0,0'-di-1-butyl dithiophosphate zinc in suppressing the coke formation as compared with the other sulphur compounds it can be inferred that the

formation of thiophosphoryl reaction intermediates can also play a part; reacting with the metal surface, these intermediates can give phosphides which also have a passivating effect.

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