# 707. *The Reaction between Paraffin Hydrocarbons and Sulphur Vapour.*

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The reactions of paraffins with sulphur vapour are approximately of the first order with respect to the hydrocarbon and nearly independent of the vapour pressure of the sulphur. Hydrogen sulphide is the only gaseous product containing sulphur which is formed in considerable amount. The influence of structure on the reaction rates of the different hydrocarbons runs parallel with that on the thermal decompositions, and is quite different from that observed in the oxidations. In the initial stages of the reaction several molecules of olefin may be formed for each molecule of hydrogen sulphide, suggesting a mechanism whereby the initial removal of hydrogen by sulphur institutes a catalysed pyrolysis of the hydrocarbon.

HYDROCARBONS are characterised by a number of properties which are of interest in relation to mechanisms of chemical change. The marked dependence of reactivity on structure in the oxidation of paraffins has been well established (Cullis, Hinshelwood, Mulcahy, and Partington, Faraday Soc. Discussion, " The Labile Molecule," 1947, **111**) but this does not hold to the same degree for their thermal decomposition (*loc. cit.*). As part of the general consideration of hydrocarbon reactivity it seemed of interest to investigate the reaction with sulphur, and in particular to determine whether there would be any resemblance between the reactions of hydrocarbons with oxygen and with sulphur respectively.

Many investigations have been devoted to the reaction of hydrocarbons with sulphur but they have been largely of a qualitative nature and little information is available concerning the mechanisms. Baker and Reid (*J. Amer. Chem. Soc.*, 1929, **51**, 1566) obtained hydrogen sulphide and small amounts of thiophens by heating *n*-heptane and *n*-butane with sulphur in sealed Pyrex-glass tubes and in steel bombs at temperatures ranging from 150° to 350°. Nellensteyn and Thoenes (*Chem. Weekblad*, 1932, **29**, 582) observed that the reaction with paraffins and paraffin oils yields carbon and that almost all the sulphur appears as hydrogen sulphide, only traces of organic compounds being formed. Taylor (*Mem. Manchester Lit. Phil. Soc.*, 1935, **79**, 99) reported that hydrocarbons of various types reacted with sulphur at 440° to produce an insoluble residue which could not be identified with known carbon–sulphur compounds because of it high sulphur content. Rasmussen, Hansford, and Sachanen (*Ind. Eng. Chem.*, 1946, **38**, 376) found that an aliphatic hydrocarbon containing at least four carbon atoms in a straight chain yielded an olefin, a diolefin, and thiophen or its homologues, together with large amounts of hydrogen sulphide. The yields were low at 600° unless the reactions were quenched after a fraction of a second. Carbon disulphide was produced, and a heavy complex tar was formed as the result of secondary reactions.

Acetylenic and ethylenic hydrocarbons react slowly at temperatures below 300° (Peel and Robinson, *J.*, 1928, 2068; Shepard, Henne, and Midgley, *J. Amer. Chem. Soc.*, 1934, **56**, 1355; Jones and Reid, *ibid.*, 1938, **60**, 2452). At higher temperatures reaction is appreciable and carbon and hydrogen sulphide are liberated with the formation of small amounts of organic sulphur compounds. The formation of polysulphides has been reported by Farmer and Shipley (*J. Polymer Sci.*, 1946, **1**, 293) for the reaction of sulphur with olefins under certain conditions; they suggest a free-radical mechanism for the process.

## EXPERIMENTAL.

*Reagents.*—The sulphur, for which we were indebted to Mr. P. A. Wright, had been purified by a series of slow crystallisations followed by repeated distillation *in vacuo*. The liquid hydrocarbons were very pure specimens, the gift of Imperial Chemical Industries Limited, Billingham, and of the Anglo-Iranian Oil Company. The gaseous hydrocarbons were obtained from commercial cylinders and were condensed and fractionated before use.

*Apparatus.*—The principal components of the apparatus were a 300-ml. Pyrex-glass reaction vessel heated in an electric furnace, an evacuating system, and storage vessels for the hydrocarbons. The progress of the reaction was followed by measurement of the pressure increase in the system with a glass Bourdon gauge and by analyses for the principal volatile reaction products. The reaction vessel and gauge are shown in Fig. 1. In order to permit the removal of the reaction vessel from the furnace for cleaning after each experiment the capillary side-arm of the vessel and the jacket of the gauge were connected to the rest of the apparatus by cone and socket joints. The side-arm could be closed by means of a tap to isolate the reaction vessel from the rest of the system. Sulphur was weighed into the vessel through a second side-arm which was sealed off before the vessel was placed in the furnace. The capillary side-arm and the lower portion of the jacket of the gauge were wound with resistance wire and heated electrically to prevent the condensation of sulphur in these portions of the system.

The movement of the pointer of the gauge was followed by means of a small fixed telescope with a graduated scale in the eye-piece. A manometer was connected to the outer jacket of the gauge, and as the pressure in the reaction vessel increased air was let into the jacket to return the pointer to a zero reading. The pressure shown on the manometer was thus the pressure in the reaction vessel.

The temperature of the reaction vessel was measured with a calibrated mercury thermometer and was controlled to ±0·5° by means of an electronic temperature controller. The apparatus was evacuated by a mercury diffusion pump backed by a rotary oil-pump.

At the temperatures used in this investigation, 320—349°, the sulphur was in the vapour state for all experiments in which the saturation concentration was not deliberately exceeded. A constant initial sulphur-vapour pressure was established before admission of the hydrocarbon. To obtain samples of the reaction mixture for analysis the temperature of the vessel was reduced rapidly before sampling to a value at which the sulphur-vapour pressure was negligible.

*Analytical Methods.*—Mercaptans were determined by extraction of the gaseous sample with " AnalaR " benzene and interaction of an aliquot of the solution with an excess of standard silver nitrate (Bell and Agruss, *Ind. Eng. Chem., Anal. Edn.*, 1941, **13**, 297), the residual amount of which was titrated with standard ammonium thiocyanate solution. Hydrogen sulphide was removed before the analysis by washing the benzene solution with acidified cadmium chloride (Sachanen, " The Chemical Constituents of Petroleum," Reinhold, New York, 1945, p. 353).

Carbon disulphide was estimated colorimetrically by means of its reaction with copper and diethylamine to form a coloured complex (Callan, Russell-Henderson, and Strafford, *J. Soc. Chem. Ind.*, 1932, **51**, 193T). Thiophens were tested for with isatin solution (Weissburger and Proskauer, " Organic Solvents," Clarendon Press, 1935, p. 105), and acetylenes with the standard copper–ammonium reagent (Treadwell and Hall, " Analytical Chemistry, Vol. II, Quantitative Analysis," Wiley and Sons, New York, 1935, p. 701) after removal of hydrogen sulphide from the gaseous sample.

Hydrogen sulphide was determined quantitatively by extraction of the reaction mixture with dilute alkali and interaction of the hydrogen sulphide liberated on acidification with standard silver nitrate solution. The very small amount of mercaptans present was neglected in this analysis.

To determine unsaturated hydrocarbons the gas sample was allowed to react with a standard bromine solution (*ibid.*, p. 745). The residual bromine was determined, as iodine, with standard sodium thiosulphate, allowance being made for the amount of bromine required to react with the hydrogen sulphide present.

From the results of the analyses of the contents of the sampling pipettes the partial pressures of hydrogen sulphide and unsaturated hydrocarbons in the reaction vessel under the conditions of the reactions were calculated.

FIG. 1.

*Reaction vessel and gauge.*

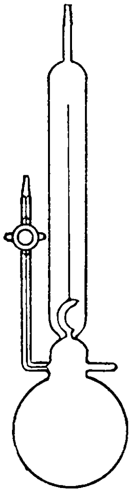
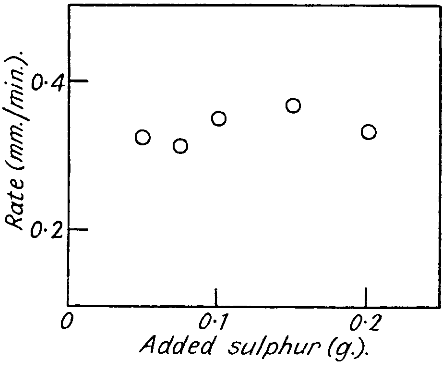


FIG. 2.

*The dependence of rate on the amount of sulphur for the reaction of* 112 *mm. of hexane at* 320°.



## RESULTS.

The reaction in general exhibits a short induction period after which the rate rises quickly to a maximum value. For the normal paraffins the length of the induction period increases and the autocatalytic nature of the reaction–time curves decreases with decreasing number of carbon atoms.

*Dependence of Rate on the Initial Sulphur Concentration.*—Rates were measured for the reaction of various amounts of sulphur with a fixed initial amount of hexane (112 mm.) at 320°. The results for the experiments in which the quantity of sulphur did not exceed the saturation value for the vessel (0·200 g.) are given in Fig. 2. In this range of sulphur concentration there was no significant dependence of rate of the initial amount of sulphur.

When the amount of sulphur was increased beyond the saturation concentration, so that liquid sulphur was present in the vessel, there was a considerable increase in rate. The liquid apparently has a marked accelerating effect on the reaction. The molecular structure of molten sulphur is not known with certainty but is generally considered to involve long chains of atoms. The free valencies occurring as " end-groups " in such a system might account for the greater reactivity of the liquid sulphur.

In all subsequent experiments a fixed amount (0·100 g.) of sulphur was used.

*Dependence of Rate on Initial Hydrocarbon Pressure.*—The effect on the rate of variation in the initial hydrocarbon pressure from 15 to 225 mm. is shown in Fig. 3 where the logarithm of the rate (0·100 g. of sulphur at 320°) is plotted against the logarithm of the initial hexane pressure. The reaction is of the first order with respect to the hydrocarbon except at high initial hydrocarbon pressures when the order becomes greater than one.

*Effect of Packing the Reaction Vessel.*—A fifteen-fold increase in the surface : volume ratio was effected by the packing of the vessel with short lengths of Pyrex-glass tubing. The reaction–time curves of 112 mm. of hexane and 0·100 g. of sulphur at 320° for packed and unpacked vessels are compared in Fig. 4. Increase in the surface area causes a distinct increase in the initial rate of the reaction but after a short time the effect disappears. The main course of the reaction therefore appears to be unaltered by the packing of the vessel.

FIG. 3.

*Relation between rate and initial hexane pressure at* 320°.

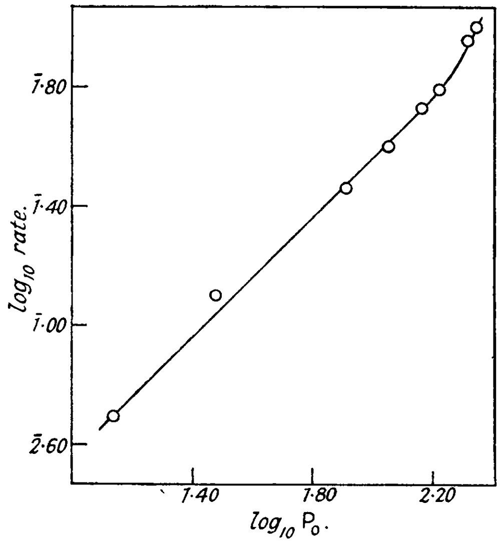


FIG. 4.

*The effect of packing the reaction vessel, and of the addition of hydrogen sulphide, on the reaction of* 112 *mm. of hexane with sulphur at* 320°.

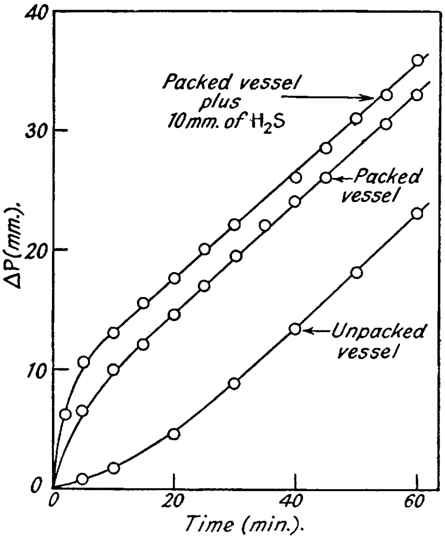
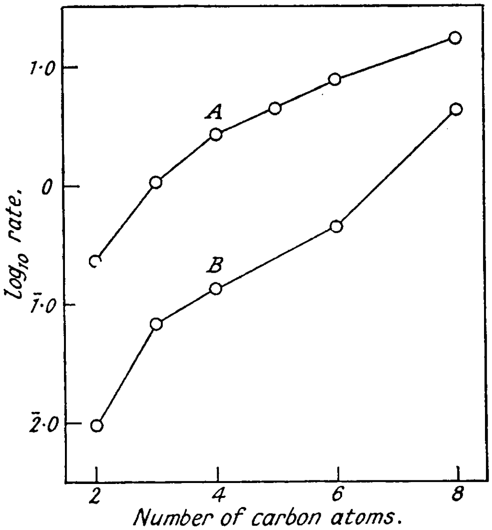


FIG. 5.

*Reaction rate as a function of the number of carbon atoms.*



*Curve* A, *pyrolysis at* 550°. *Curve* B, *sulphur reaction at* 320°.

The large increase in initial rate indicates a surface catalysis of the reaction. The subsequent return to the normal rate may be due to poisoning of the surface by the products so that the reaction later becomes essentially homogeneous. The possibility that this poisoning may be due to hydrogen sulphide was investigated by addition of 10 mm. of this gas to the reaction vessel before admission of the hexane. The reaction–time curve for this experiment (Fig. 4) shows, however, that the addition has no significant effect. Similarly the addition of hydrogen sulphide was shown to have no effect on the reaction in the unpacked vessel.

*Effect of Hydrocarbon Structure on Rate.*—(a) *Straight-chain hydrocarbons.* The paraffins investigated in this series were ethane, propane, *n*-butane, *n*-hexane, and *n*-octane. Reaction rates for the last three (112 mm. of the hydrocarbon and 0·100 g. of sulphur) were measured at 320°, for hexane and butane at 320° and 349°, and for propane and ethane at 349°. Those for the two latter were calculated for 320° in terms of the ratio to hexane and butane, so that all five hydrocarbons could be compared at one temperature. The results for these experiments are given in Table I.

TABLE I.

*Reaction rates for* 112 *mm. of various normal paraffins with* 0·100 *g. of sulphur at* 320°.

| No. of C atoms | 2 | 3 | 4 | 6 | 8 |
|---|---|---|---|---|---|
| Rate (mm./min.) | 0·0095 | 0·066 | 0·14 | 0·45 | 4·25 |

The approximately four-hundredfold increase in the rate of the reaction with sulphur which occurs as the series is ascended from ethane to octane contrasts markedly with the two-hundred-thousandfold increase which occurs in the same series for the reaction with oxygen (Cullis *et al.*, *loc. cit.*). This difference suggests that the mechanisms of the two reactions bear little resemblance. On the other hand, distinct similarities in the effect of structure are apparent when the rates for the sulphur reaction are compared with the rates for the thermal decomposition of the normal paraffins. This comparison is given in Fig. 5 in which the logarithms of the two reaction rates are plotted against the number of carbon atoms in the hydrocarbon. The results for the thermal decompositions were obtained in this laboratory by Dr. F. J. Stubbs (unpublished results) and Dr. R. G. Partington (Cullis *et al.*, *loc. cit.*).

(b) *Branched hydrocarbons.* The effect of the degree of branching was determined by measurement of the rates for reaction of 112 mm. (at 320°) of each of the isomers *n*-hexane, 2- and 3-methylpentane, and 2 : 3-dimethylbutane, and of *cyclo*hexane. The results (Table II) show that there is a slight increase in the rate as the degree of branching increases from *n*-hexane to 2 : 3-dimethylbutane. The reaction–time curves for these four hydrocarbons were similar in shape. *cyclo*Hexane, however, exhibits a distinct induction period followed by a rapid acceleration of rate to a value eight times that for normal hexane and roughly equal to that for octane under similar conditions.

TABLE II.

*Effect of branching on the rates of reaction of isomeric hexanes with aulphur at* 320°.

| Hydrocarbon. | Rate relative to 2 : 3-dimethylbutane. |
|---|---|
| *n*-Hexane | 0·5 |
| 2-Methylpentane | 0·6 |
| 3-Methylpentane | 0·7 |
| 2 : 3-Dimethylbutane | 1·0 |
| *cyclo*Hexane | 4·0 |

The slight increase in rate with increased branching of the hydrocarbon contrasts markedly with the structural influences reported by Cullis *et al.* (*loc. cit.*) who found that the rate of oxidation decreased by a factor of 1580 on going from *n*-hexane to 2 : 3-dimethylbutane. The results (Table II) are, however, similar to those reported by Partington (*loc. cit.*) who found that increased chain branching causes a slight increase in the rate of thermal decomposition of the paraffins.

It appears, therefore, that so far as the influence of hydrocarbon structure on reaction rate is concerned the reaction of both straight- and branched-chain hydrocarbons resemble the thermal decomposition of these compounds much more than they resemble the reaction with oxygen.

*Analysis for Reaction Products.*—Quantitative analyses at various stages in the reaction of hexane and sulphur at 320° showed that carbon disulphide and mercaptans were formed in very small amounts only. The test for thiophens was negative. A qualitative test for acetylenes showed that these hydrocarbons are formed to a small extent.

The appearance of a dark-coloured involatile tar was observed as soon as any significant pressure change occurred in the system. It was not possible to make a quantitative estimate of the amount because of the small mass of the reactants and because the tar could be removed from the reaction vessel only by boiling nitric and sulphuric acid. Its chemical composition was therefore not investigated.

The principal volatile products of the reactions were hydrogen sulphide and unsaturated hydrocarbons. The calculated pressures of these compounds at various stages in the reaction of hexane and sulphur at 349° are given in Table III. In columns 7, 8, and 9 the pressures of hydrogen sulphide and of unsaturated hydrocarbons (calculated as " double bonds ") and the pressure increase are divided by the initial hexane pressure to reduce these values to the same scale. The ratios of the pressure of unsaturated hydrocarbons to the pressure of hydrogen sulphide are given in column 10. The values in the last four columns of Table III are plotted as a function of time in Fig. 6.

FIG. 6.

*Analytical results for various stages in the reaction of 22 mm. of hexane with sulphur at 349°, expressed as ratios (mm./mm.) of $H_2S$/initial hexane, pressure increase/initial hexane, " double bonds "/initial hexane, and " double bonds "/$H_2S$.*

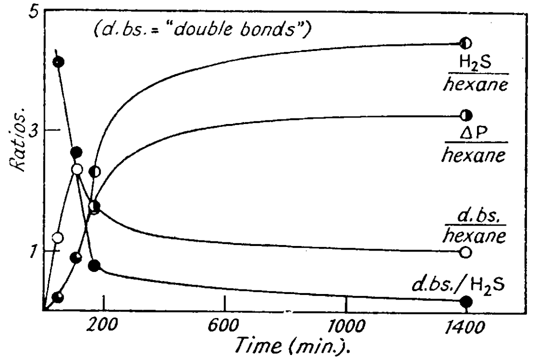
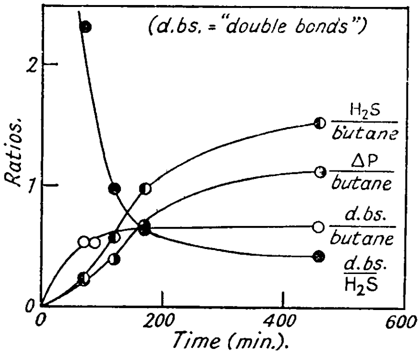


FIG. 7.

*Analytical results for various stages in the reaction of 60 mm. of butane with sulphur at 349°, expressed as ratios (mm./mm.) of $H_2S$/initial butane, pressure increase/initial butane, " double bonds "/initial butane, and " double bonds "/$H_2S$.*



The corresponding results for the reaction of butane with sulphur at 349° are given in Table IV, and are shown graphically in Fig. 7. The results for similar analyses in the reactions of propane and ethane are given in Tables V and VI.

TABLE III.

*Analytical results for the reaction of hexane with 0·100 g. of sulphur at 349°.*

| Initial hexane (mm.). | $p_{\text{Total}}$ (mm.). | $\Delta P$. (mm.). | Time (min.). | $H_2S$ (mm.). | " Double bonds " (mm.). | $H_2S$/Hexane | " Double bonds "/Hexane | $\Delta P$/Hexane | " Double bonds "/$H_2S$ |
|---|---|---|---|---|---|---|---|---|---|
| 20·5 | 67·0 | 5·0 | 50 | 5·8 | 24·4 | 0·28 | 1·19 | 0·24 | 4·17 |
| 22·0 | 86·0 | 20·0 | 110 | 19·7 | 51·5 | 0·90 | 2·34 | 0·91 | 2·62 |
| 23·5 | 103·5 | 40·0 | 170 | 53·5 | 40·6 | 2·28 | 1·73 | 1·70 | 0·76 |
| 23·5 | 123·0 | 78·0 | 1400 | 104·0 | 24·1 | 4·42 | 1·05 | 3·33 | 0·24 |

TABLE IV.

*Analytical results for the reaction of butane with 0·100 g. of sulphur at 349°.*

| Initial butane (mm.). | $p_{\text{Total}}$ (mm.). | $\Delta P$ (mm.). | Time (min.). | $H_2S$ (mm.). | " Double bonds " (mm.). | $H_2S$/Butane | " Double bonds "/Butane | $\Delta P$/Butane | " Double bonds "/$H_2S$ |
|---|---|---|---|---|---|---|---|---|---|
| 60·0 | 79·0 | 12·0 | 70 | 13·5 | 31·3 | 0·23 | 0·52 | 0·20 | 2·32 |
| 60·0 | 75·5 | 23·5 | 120 | 33·3 | 32·0 | 0·55 | 0·53 | 0·39 | 0·97 |
| 59·5 | 132·0 | 40·0 | 170 | 56·0 | 36·0 | 0·94 | 0·61 | 0·67 | 0·64 |
| 60·8 | 145·5 | 67·5 | 460 | 92·5 | 40·8 | 1·52 | 0·67 | 1·11 | 0·44 |

TABLE V.

*Analytical results for the reaction of propane with 0·100 g. of sulphur at 349°.*

| Initial propane (mm.). | $p_{\text{Total}}$ (mm.). | $\Delta P$ (mm.). | Time (min.). | $H_2S$ (mm.). | " Double bonds " (mm.). | $H_2S$/Propane | " Double bonds "/Propane | $\Delta P$/Propane | " Double bonds "/$H_2S$ |
|---|---|---|---|---|---|---|---|---|---|
| 112 | 137 | 13·0 | 70 | 11·6 | 19·8 | 0·10 | 0·18 | 0·12 | 1·70 |
| 112 | 170 | 23·0 | 120 | 31·4 | 20·4 | 0·28 | 0·19 | 0·21 | 0·65 |
| 111 | 180 | 52·5 | 315 | 74·5 | 26·6 | 0·67 | 0·24 | 0·47 | 0·36 |

TABLE VI.

*Analytical results for the reaction of ethane with* 0·100 *g. of sulphur at* 349°.

| Initial ethane (mm.). | $P_{\text{Total}}$ (mm.). | $\Delta P$ (mm.). | Time (min.). | $H_2S$ (mm.). | " Double bonds " (mm.). | $\frac{H_2S}{\text{Ethane}}$. | $\frac{\text{" Double bonds "}}{\text{Ethane}}$. | $\frac{\Delta P}{\text{Ethane}}$. | $\frac{\text{" Double bonds "}}{H_2S}$. |
|---|---|---|---|---|---|---|---|---|---|
| 112 | 128 | 8·0 | 120 | 8·2 | 10·5 | 0·07 | 0·09 | 0·07 | 1·23 |
| 109 | 141 | 17·0 | 240 | 19·9 | 8·5 | 0·18 | 0·08 | 0·15 | 0·43 |
| 114 | 141 | 16·5 | 360 | 16·7 | 6·0 | 0·15 | 0·05 | 0·15 | 0·36 |

A comparison of the analytical results for hexane, butane, propane, and ethane shows that there are distinct similarities in the variation of the proportions of hydrogen sulphide and unsaturated hydrocarbons at the various stages. The pressure of hydrogen sulphide corresponds closely to the pressure increase in the early stages but exceeds it in the later stages. For all four hydrocarbons the initial rate of production of " double bonds " is greater than the initial rate of production of hydrogen sulphide. For hexane the pressure of " double bonds " rises to a maximum value as the reaction reaches its maximum rate. For the other paraffins this quantity rises quickly in the early stages of the reaction and then maintains a constant value. The initial ratio of double bonds to hydrogen sulphide is approximately 5 for hexane, 4 for butane, 3 for propane, and 2 for ethane. In each case the value of this ratio falls quickly to a value less than unity, the rate at which it diminishes decreasing from hexane to ethane.

## DISCUSSION.

The most significant single feature of the analytical results is the observation that in the initial stages of the reaction the number of double bonds formed is several times the number which would correspond to the hydrogen sulphide formed in a simple dehydrogenation of the paraffin. This suggests that the mechanism involves a type of catalysed pyrolysis of the hydrocarbon to yield unsaturated reaction products. The similarity of the effect of hydrocarbon structure on the rates of the reaction with sulphur to that on the thermal decompositions lends support to this supposition.

In considering a mechanism for the reaction of hydrocarbons with sulphur it will be assumed that the sulphur participates in a chain-initiating step as sulphur atoms. In the equilibrium $S_8 \rightleftharpoons 8S$ the concentration of atomic sulphur at the temperatures used in this investigation would certainly be low (Preuner and Schupp, *Z. physikal. Chem.*, 1909, **68**, 129) but with atomic sulphur as the reacting species the reaction rate would be dependent on the sulphur-vapour pressure to the one-eighth power, a result which would agree quite well with experiment. Moreover, reaction steps involving atomic sulphur would be less complex than those in which higher molecular forms of sulphur were involved. In the discussion of the subsequent steps the example of butane will be taken as typical.

The initial reaction is assumed to be :

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_3 + S \longrightarrow CH_3\cdot CH_2\cdot CH\cdot CH_3 + HS \quad . \; . \; . \; . \quad (1)$$

The removal of a secondary rather than a primary hydrogen atom is in accordance with what is known about the relative strengths of the C–H bonds (Steacie, " Atomic and Free Radical Reactions," Reinhold, New York, 1946). The HS radical is assumed to attack a second paraffin molecule :

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_3 + HS \longrightarrow CH_3\cdot CH_2\cdot CH\cdot CH_3 + H_2S \quad . \; . \; . \; . \quad (2)$$

The alkyl radicals formed in (1) and (2) can now begin to decompose by mechanisms which are generally accepted as occurring in normal pyrolysis (*loc. cit.*; Rice and Rice, " The Aliphatic Free Radicals," Baltimore, 1935) :

$$CH_3\cdot CH_2\cdot CH\cdot CH_3 \longrightarrow CH_3 + CH_3\cdot CH{:}CH_2 \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$CH_3\cdot CH_2\cdot CH\cdot CH_3 \longrightarrow CH_3\cdot CH_2 + CH_2{:}CH_2 \quad . \; . \; . \; . \; . \; . \quad (4)$$

$$CH_3\cdot CH_2 \longrightarrow CH_2{:}CH_2 + H \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

The mechanism has yielded an average of about three olefin molecules to one molecule of hydrogen sulphide. This gives an initial ratio of double bonds to hydrogen sulphide which agrees roughly with the value observed experimentally for the reaction of butane (Table IV).

The H atom is assumed to react with sulphur as follows :

$$H + S_x \longrightarrow HS + S_{x-1} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

yielding another radical which may attack more paraffin as in reaction (2).

The methyl radicals are assumed to disappear according to the reaction :

$$\mathrm{CH_3 + S}_x \longrightarrow \text{tar} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

A value of 7 or 8 for $x$ would yield a tar high in sulphur content.

The apparently autocatalytic nature of the reaction may be accounted for by the increasing number of hydrocarbon molecules which permit reactions of the type :

$$\mathrm{CH_3{\cdot}CH{:}CH_2 + S \longrightarrow CH_3{\cdot}CH{:}CH + HS} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

and yield additional chain-propagating HS radicals. The unsaturated radical might be stabilised as an acetylene by the loss of another hydrogen atom or might combine with another hydrocarbon radical in a three-body collision :

$$\mathrm{CH_3{\cdot}CH{:}CH + CH_3 \longrightarrow CH_3{\cdot}CH{:}CH{\cdot}CH_3} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

A reaction of this last type is not essential to the mechanism, and it is assumed that most of the methyl radicals disappear according to reaction (7). Reactions (3) and (7) jointly may be considered to be chain-terminating since they lead to stable products.

In the steady state the concentrations of radicals are given by

$$\begin{aligned}
\mathrm{d[C_4H_9]}/\mathrm{d}t &= k_1\mathrm{[C_4H_{10}][S]} + k_2\mathrm{[C_4H_{10}][HS]} - k_3\mathrm{[C_4H_9]} - k_4\mathrm{[C_4H_9]} = 0 \\
\mathrm{d[HS]}/\mathrm{d}t &= k_1\mathrm{[C_4H_{10}][S]} - k_2\mathrm{[C_4H_{10}][HS]} + k_6\mathrm{[H][S}_x] + k_8\mathrm{[C_3H_6][S]} = 0 \\
\mathrm{d[H]}/\mathrm{d}t &= k_5\mathrm{[C_2H_5]} - k_6\mathrm{[H][S}_x] = 0 \\
\mathrm{d[CH_3{\cdot}CH_2]}/\mathrm{d}t &= k_4\mathrm{[C_4H_9]} - k_5\mathrm{[C_2H_5]} = 0.
\end{aligned}$$

The rate of the reaction as measured under the conditions of the experiment is practically equal to the rate of production of hydrogen sulphide. Therefore

$$\text{Rate} = \mathrm{d[H_2S]}/\mathrm{d}t = k_2\mathrm{[C_4H_{10}][HS]}$$

whence

$$\frac{\mathrm{d[H_2S]}}{\mathrm{d}t} = \frac{k_1\mathrm{[C_4H_{10}][S]}\left(1 + \dfrac{k_4}{k_3 + k_4}\right) + k_8\mathrm{[C_3H_6][S]}}{\left(1 - \dfrac{k_4}{k_3 + k_4}\right)}$$

or

$$\text{Rate} = C_1\mathrm{[C_4H_{10}][S]} + C_2\mathrm{[C_3H_6][S]}$$

The mechanism thus yields an expression for the rate which is of the first order with respect to the initial hydrocarbon presssure in agreement with experimental observation for most of the range investigated. It also requires the first order with respect to the sulphur-atom concentration. This latter is proportional to $[\mathrm{S_8}]^{\frac{1}{8}}$ and hence the rate becomes very nearly independent of the sulphur-vapour pressure.

The second term of the rate expression allows for the effectively autocatalytic nature of the reaction. Hydrogen sulphide is formed as an end product of the reaction and is not involved in any of the intermediate steps.

The primary reaction for all the hydrocarbons is assumed to be the removal of a hydrogen atom with the formation of alkyl and HS radicals. There is evidence (Steacie, " Atomic and Free Radical Reactions," Reinhold, New York, 1946) that the rupture of the weakest C–H bond occurs with increasing ease as a homologous series of paraffins is ascended. Since the formation of the alkyl radicals is assumed to be the rate-controlling step, the mechanism accounts for the observation that the reaction rate increases with the length of the straight-chain hydrocarbon. It also allows for the observed slight increase in rate with increased chain branching since the C–H bond strengths decrease from primary to tertiary groups in the hydrocarbons (Steacie, *op. cit.*; Walsh, *Trans. Faraday Soc.*, 1946, **42**, 269). That the structure of the hydrocarbon influences similarly the rate of the reaction with sulphur and the thermal decomposition may be attributed to similarities in the ease of initial rupture of the hydrocarbon chain in the two reactions.

The mechanism accounts for the correspondence between the pressure increase and the hydrogen sulphide pressure in the early stages of the reaction, and for the observation that initially the number of double bonds formed is several times the number of molecules of hydrogen sulphide produced. The extent of the catalysed pyrolysis yielding unsaturated hydrocarbons will clearly be greater the longer the parent hydrocarbons.

The above suggestions about the mechanism of attack of hydrocarbons by sulphur in the gaseous state apply to processes occurring during the early stages of the reaction. Beyond the initial stages the reactions doubtless become increasingly complex owing to the degradation of primary products and to polymerisation processes which yield tars and other products of lower unsaturation.

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