THE REACTION OF SULPHUR WITH HYDROCARBONS

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The kinetics of the reactions of sulphur with methane and with some higher hydrocarbons to form carbon disulphide have been investigated at high temperatures. Al_2O_3 was used as catalyst for methane but was quite inactive for higher hydrocarbons, for which, however, V_2O_5 was found suitable. All the reactions show the unusual feature of a rate increasing throughout the course of the reaction until a rather abrupt stop is reached on completion. This was attributed to the formation of unsaturated hydrocarbons as intermediate compounds. With CH_4 the intermediate would most probably be ethylene, and this compound was shown to react with S_2 to form CS_2 at about the same rate as CH_4 itself. With higher hydrocarbons substantial amounts of liquid unsaturateds were shown to be present in the initial stages of the reactions.

The interaction of sulphur and methane has been studied by a number of earlier workers [1-5] and was found to proceed at temperatures of 500° C to 700° C on alumina and silica gel catalysts according to the equation

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

The rate of the catalytic reaction was found to be proportional to the partial pressures of CH_4 and S_2, both with respect to initial conditions, and throughout the course of reaction. A much smaller rate of homogeneous reaction in the gas phase was also observed.

Regarded as a process for the manufacture of carbon disulphide, this reaction suffers from the disadvantage that 50 % of the sulphur reverts to H_2S. Owen, Sykes and Thomas [6] have pointed out, however, that although hydrogen sulphide is thermodynamically stable at low temperatures it begins to be substantially dissociated at temperatures above 1000° C, according to the equation

$$2H_2S \rightarrow 2H_2 + S_2. \qquad (2)$$

The reaction of CH_4 with S_2 according to the equation

$$CH_4 + S_2 \rightarrow CS_2 + 2H_2 \qquad (3)$$

will therefore supersede reaction (1) to a progressively greater extent as the temperature rises.

The use of higher hydrocarbons in place of CH_4 will also reduce H_2S production. Hydrocarbons of high molecular weight can be represented closely by the formula $(CH_2)_n$, and they will react as follows

$$(CH_2)_n + \tfrac{3}{2}n\,S_2 \rightarrow n\,CS_2 + n\,H_2S, \qquad (4)$$

or

$$(CH_2)_n + n\,S_2 \rightarrow n\,CS_2 + n\,H_2. \qquad (5)$$

The object of the present investigation was to study the reaction of sulphur with CH_4 and higher hydrocarbons in the high temperature range favourable to the dissociation of H_2S. In order to illustrate the extent of this dissociation the thermodynamic data of Kelly [7] and Cross [8] were used to calculate the equilibrium composition of the product from various typical mixtures.

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With CH_4 the possible reactions can be represented stoichiometrically by

$$CH_4 = C + 2H_2, \tag{6}$$

$$C + S_2 = CS_2, \tag{7}$$

$$2H_2 + S_2 = 2H_2S, \tag{8}$$

with corresponding equations for the higher hydrocarbons. It was found that at the temperatures considered eqn. (6) could be treated as going to completion, and the percentage of CH_4 as effectively zero.

It is evident from eqn. (7) and (8) that when the ratio of S_2 to CH_4 is low, free carbon will be present at equilibrium, but that when the initial S_2/CH_4 ratio exceeds a certain critical value, referred to as α, free carbon will no longer be present. It can also be shown that the equilibrium yield of CS_2 is a maximum when the initial S_2/CH_4 ratio is equal to α, and for this reason the calculations below include mixtures of this composition. Values of K_p for eqn. (7) and (8) are given in table 1.

TABLE 1.

Partial pressures, p, in atm

$$K_p\,(7) = \frac{p_{CS_2}}{p_{S_2}} \qquad K_p\,(8) = \frac{p^2_{H_2S}}{p^2_{H_2} \times p_{S_2}}$$

temp. ° K	1000	1100	1200	1300	1400	1500
K_p (7)	11·4	10·0	8·77	7·96	7·33	6·79
K_p (8) × 10^{-2}	200	35·5	5·75	1·32	0·40	0·113

The calculated equilibrium compositions of the reaction mixtures to be expected from four different initial systems at atmospheric pressure are given in table 2. It will be seen that for αn of S_2 reacting at 1500° K with $(CH_2)_n$, the amount of sulphur as CS_2 in the product is 4½ times the amount as H_2S.

TABLE 2.—EQUILIBRIUM COMPOSITIONS

initial system	temp. ° K	α	partial pressures, atm			
			CS_2	H_2S	S_2	H_2
$CH_4 + \alpha S_2$	1100	2·01	·32	·58	·03	·06
	1300	1·82	·32	·45	·04	·19
	1500	1·57	·31	·27	·05	·37
$CH_4 + 3S_2$	1100		·25	·48	·26	·01
	1300		·24	·42	·27	·07
	1500		·23	·28	·32	·17
$(CH_2)_n + \alpha n S_2$	1100	1·56	·48	·44	·05	·04
	1300	1·50	·47	·35	·06	·12
	1500	1·37	·47	·21	·07	·25
$(CH_2)_n + 3n S_2$	1100		·28	·28	·43	·01
	1300		·28	·25	·44	·03
	1500		·27	·19	·45	·08

EXPERIMENTAL

A flow method was used. The reaction vessel consisted of a mullite tube (Thermal Syndicate Ltd.) of internal diameter 1·3 cm, having conical ground ends, to which Pyrex glass cones were satisfactorily cemented by means of a product known as anti-scuffing paste, made by the Ragosine Oil Co. The mullite tube was heated in a platinum-wound furnace. The temperature was measured by a thermocouple which was in contact with the outside of the tube.

CH_4 and N_2 from commercial cylinders were passed through Carbosorb and $CaCl_2$ and then through calibrated capillary flow meters to measure the feed rates. Sulphur was vaporized into a carrier stream of N_2, the proportion being determined by the bath temperature. All tubes through which sulphur containing gases had to pass were electrically lagged. In calculating the proportion of S_2 gas to be expected in the reaction vessel account had to be taken of the proportions of S_2, S_6 and S_8 to be expected in the sulphur vapour in the saturator, using the data given by Kelly. Satisfactory checks were made by condensing the sulphur from a given stream.

The sulphur stream was joined to the hydrocarbon stream before entry to the reaction vessel. The hydrocarbon stream consisted of CH_4 with or without additional N_2, or of higher hydrocarbons vaporized into a N_2 stream.

On leaving the reactor the gases passed through a $1\frac{1}{2}$-in. diam. U-tube heated at 130° C to condense unchanged sulphur, which was determined by weighing. The gases could then be passed through a trap cooled to − 78° C by solid CO_2 and methanol, in which CS_2 and higher hydrocarbons condensed. This trap could be by-passed and a gas-phase sample collected containing all the reaction products (except sulphur).

Two different analytical procedures were used. For high yields of CS_2 the liquid sample at − 78° C was collected and analysed for CS_2, and, in the reaction of higher hydrocarbons with sulphur, unsaturateds could also be determined: the cold trap was then by-passed and a gas sample collected for the determination of the products other than CS_2. With smaller amounts of CS_2, the cold trap was by-passed, and a gas-phase sample alone collected and analysed for CS_2 and other products.

The liquid samples were diluted with benzene, shaken with aqueous $CdCl_2$ to remove H_2S, and with Hg to remove any traces of sulphur which may have been carried over from the sulphur U-tube. CS_2 was then determined by conversion to xanthic acid, which was titrated with N/10 iodine, according to the method of Bell and Argus.[9] Unsaturated hydrocarbons could also be determined by shaking another sample of the diluted condensate with N/1000 Br_2 water, and back-titrating with sodium thiosulphate.

The gas sample could contain CS_2, H_2S, H_2, N_2, and hydrocarbons. Analysis was made by measuring the pressure change at constant volume as each component was absorbed in a suitable reagent. The gases were confined over Hg, the attack of H_2S being insufficient to affect the accuracy of the analysis. H_2S was first removed with aqueous $CdCl_2$, and then CS_2 with alcoholic potash. In estimating the pressure changes, allowance was made for the vapour pressure of the solvent in which the reagent was dissolved. The gases were then dried over $CaCl_2$ and the hydrogen eliminated by passing through a palladium tube heated to 400° C over which a current of air was blown. The amount of N_2 was taken as equal to the amount fed to the reaction vessel during the time over which the sample was being collected. Hydrocarbons were estimated by difference.

Satisfactory test analyses of known mixtures of H_2S, CS_2, H_2, CH_4 and N_2 were made.

RESULTS

METHANE

In view of the high temperatures which were to be used, and of the resulting high reaction rates, a small reactor volume was necessary: throughout the work 3 g of catalyst were used, which occupied 6 cm^3 of reactor volume in the central section of the mullite tube over which the temperature was reasonably uniform. All experiments were at atmospheric pressure, the difference between this pressure and the sum of the initial partial pressures of the reactants being made up with N_2. All partial pressures are quoted in mm of Hg (except in tables 1 and 2).

In a first series of experiments, different catalysts were tried at 1400° K. Silca gel, which was shown by previous workers to be extremely active at lower temperatures, was found to be unsuitable at the higher temperatures, the catalyst sintering and rapidly losing activity. Vanadium pentoxide, chromium oxide and nickel oxide, all co-precipitated with aluminium oxide, were found to be active, but aluminium oxide alone was found to be even more so, and was adopted for the further work on CH_4. The catalyst actually used was supplied by Messrs. Peter Spence under the name of Activated Alumina: it consists initially of γ-$Al_2O_3 . H_2O$, and is probably largely transformed at the temperatures used to α-Al_2O_3, corundum. In the absence of a catalyst no CS_2 could be detected and although no special study was made of this point, it should be noted that this result is not in agreement with those of Nabor and Smith [1] and Fisher and Smith [4] who observed a small homogeneous reaction even at much lower temperatures.

Using this catalyst an exploratory series of runs was then carried out using various temperatures, flow rates and S_2/CH_4 ratios. The initial partial pressure of CH_4 was held constant at 127 mm. The results are shown in table 3; the percentages are of total product after subtraction of N_2; the flow rates are of total gas including N_2. The last column gives the percentages to be expected at equilibrium, according to the data of Cross and of Kelly.

TABLE 3.—APPROACH TO EQUILIBRIUM: CH_4 AND S_2

$p^\circ_{CH_4}$: 127 mm

temp. °K	$\frac{p^\circ_{S_2}}{p^\circ_{CH_4}}$	species	% of N_2-free product					% at equilib.
			flow rate : cm³ at s.t.p. per min					
			300	200	100	75	50	
1200	2	CS_2	6·5	11·0	—	24·7	31·0	32·0
		H_2S	11·0	18·0	—	41·8	53·5	53·0
		H_2	—	1·5	—	10·3	10·0	11·0
		S_2	—	—	—	6·7	5·0	4·5
1300	2	CS_2	8·2	14·2	24·0	28·4	32·5	32·0
		H_2S	15·5	25·4	37·5	44·1	45·3	45·0
		H_2	—	—	—	—	18·8	19·4
		S_2	—	—	—	—	3·6	4·5
1300	3	CS_2	12·2	17·4	20·2	24·6	23·9	24·0
		H_2S	23·0	29·0	36·0	39·2	38·0	41·0
1400	1	CS_2	—	14·5	—	17·0	—	18·0
		H_2S	—	30·3	—	35·2	—	39·0
1400	2	CS_2	10·4	20·7	28·2	—	30·7	32·0
		H_2S	13·4	20·0	26·0	—	25·0	27·0

The results serve principally to show the rates of approach to equilibrium under the various conditions, and the degree of agreement between observed and calculated equilibrium values. The calculated equilibrium figures agree with the experimental results obtained at a flow rate of 50 cm³/min to a satisfactory degree of accuracy in almost all cases. They can therefore be regarded both as confirming the data of Cross and of Kelly which were themselves based on a rather limited amount of experimental data, and at the same time confirming the accuracy of the methods of analysis used here.

A systematic investigation of the kinetics was then undertaken. In a series of runs at 1250° K the feed rate was maintained constant at 300 cm³/min of total gas including N_2, measured at s.t.p., and the initial partial pressure of CH_4 was also constant at 100 mm Hg; the initial partial pressure of S_2 was varied between 100 and 250 mm. The moles of CS_2 produced per minute in each run are plotted against the initial partial pressure of S_2 in fig. 1 and the points are seen to fall on a line that is very nearly straight, and also passes through the origin. Only about 13 % of the S_2 reacted in each run; consequently the straight-line plot indicates that the initial rate of reaction is of the first order with respect to the partial pressure of sulphur.

A similar series of runs at 1250° K was carried out, but in which the initial partial pressure of S_2 was fixed, and that of CH_4 varied. The results are plotted as the lower curve in fig. 2. It will be seen that the rate of reaction is constant, and independent of the initial partial pressure of CH_4. Two different individual samples of the catalyst were used, as shown; and satisfactory agreement is seen to have been achieved. The above results show the reaction to be of the first order with respect to the initial partial pressure of S_2, and zero order with respect to that of CH_4.

In the next series the initial partial pressure of S_2 was 245 mm and of CH_4 135 mm throughout: total feed flow rate was varied between 273 and 43 cm³ at s.t.p. per min. The temperature, 1200° K, was lower than in the preceding series, since, as will be seen, interest attached particularly to the results where the percentage conversion was small. The results are shown in fig. 3 where the percentage composition of the product gases (excluding N_2) is plotted against *t*, the residence time. The residence time is equal to the volume of empty reaction space (6 cm³) divided by the volumetric flow-rate measured in cm³/min at the reaction temperature. The composite plot so obtained is considered to represent the course of reaction with time such as would be observed in a static system.

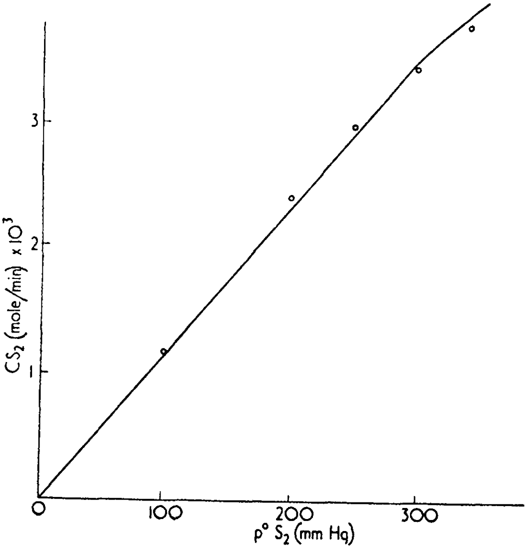

FIG. 1.—Moles of CS_2 formed per minute, × 10^3, against initial partial pressure of S_2 in mm; $p^{\circ}_{CH_4}$ 100 mm; temp. 1250° K; flow rate 300 cm³/min.

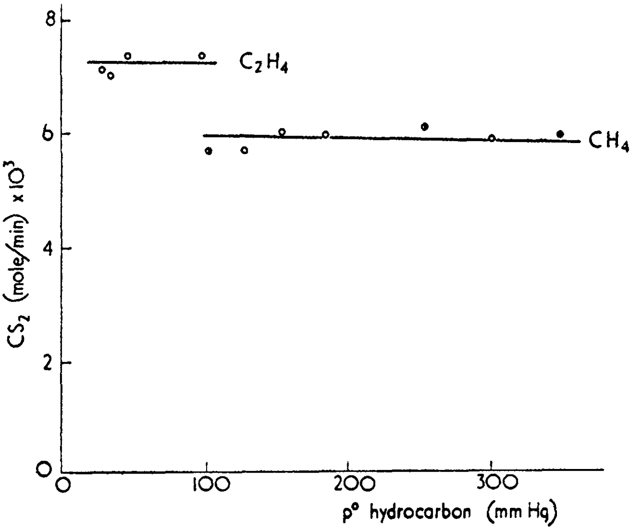

FIG. 2.—Moles of CS_2 per min, × 10^3, against initial partial pressure of hydrocarbon in mm; $p^{\circ}_{S_2}$ 254 mm; feed rate 300 cm³ at s.t.p. per min.

Upper curve: C_2H_4 and S_2 1223° K; lower curve: CH_4 and S_2 1250° K.

○ ◑ refer to runs carried out with CH_4 on two different samples of the catalyst.

All calculations on this reaction were made neglecting the volume change, since this in no case exceeded 3 %.

It will be seen that the rate, far from falling off with time, as would be expected from the results of fig. 1, increases steadily throughout the run, until very near the end when the reaction stops rather abruptly: the curves for CS_2, H_2S and H_2 are concave upwards throughout almost the whole course of the reaction until near the end when they turn over abruptly and become horizontal. This abrupt approach to equilibrium is also clearly suggested by the results already given in table 3. A further point of interest is that although the amounts of S_2 and H_2 in the product gases were found to be equal to those in the reactants, there appeared to be a substantial quantity of carbon missing, amounting to 6½ % at $t = 0{\cdot}9 \times 10^{-2}$ min: this missing carbon, as percentage of C_1, is shown on the curve marked " missing C ".

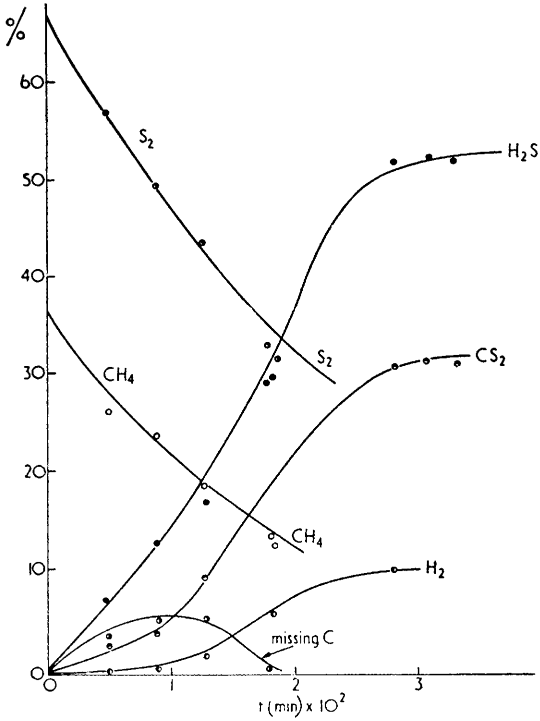

FIG. 3.—Percentage composition of N_2-free product as a function of contact time t (min) × 10^2; temp. 1200° K. $p^{0}_{CH_4}$ 135 mm; $p^{0}_{S_2}$ 245 mm.

That a reaction rate increases with time can often be explained by the formation of an intermediate compound. Now Bryce and Hinshelwood [10] have shown that when the higher hydrocarbons (ethane to octane) react with sulphur, then at as low a temperature as 600° K a reaction occurs producing unsaturated hydrocarbons and H_2S: the reaction was homogeneous and in the initial stages the number of double bonds produced greatly exceeded the number of molecules of H_2S. This was therefore described as a catalysed pyrolysis, and a chain mechanism was suggested.

It therefore appeared likely that the special shape of the reaction curves of fig. 3 could be explained by assuming that CH_4 first reacts with S_2 to give ethylene (or possibly some other higher unsaturated hydrocarbon) and that the ethylene then reacts further with S_2 to give CS_2. This would also explain the existence of the carbon deficit: for if ethylene were present it would appear in the analysis as CH_4.

Accordingly ethylene itself was allowed to react with sulphur; a mixture of C_2H_4 and S_2 was passed over the catalyst at 1223° K at a fixed flow rate, the initial partial pressures of S_2 being 254 mm and of CH_4 varying between 29 and 100 mm. The results are shown in the upper curve of fig. 2. The rate of formation of CS_2 from ethylene is seen to be of the same order as that from CH_4. Furthermore, this high rate is achieved even at low partial pressures of C_2H_4, the rate appearing in fact independent of the partial pressure; this is an important point since if C_2H_4 is an intermediate compound it will need to react sufficiently fast at low concentrations. The evidence obtained is seen, therefore, to be consistent with the idea that ethylene is formed as an intermediate compound: and, as will be shown below, the results with higher hydrocarbons also suggest the formation of unsaturated intermediate compounds.

CH_4—without S_2—was also passed over the catalyst at 1250° K at flow rates of from 100 to 300 cm^3/min and with partial pressures varying between 100 and 300 mm. No change in volume occurred, no hydrogen was formed, and no carbon deposited. In fact the CH_4 appeared to survive unchanged for a contact time of 10^{-2} min. It is clear therefore that if C_2H_4 is an intermediate in the formation of CS_2 it must be formed by the action of S_2 on the CH_4—either catalytically or homogeneously—and not by direct reaction of CH_4 on the catalyst.

The reaction of H_2 and S_2 to form H_2S according to eqn. (8) was investigated in a short series of runs at 1250° K on 3 g of the same alumina catalyst, the flow rate being 300 cm^3/min. The results are given in table 4 in terms of moles of H_2S formed per min. The initial partial pressure of S_2 was held constant at 100 mm, whilst that of H_2 was varied between 100 and 250 mm.

TABLE 4

$p^{\circ}_{H_2}$ (mm)	100	150	200	250
H_2S (mole/min) × 10^3	0·13	0·20	0·29	0·31

If the results are compared with those of fig. 1, 2 and 3 it will be seen that the rate of reaction of H_2 with S_2 to form H_2S is of an order of magnitude comparable with that of the formation of H_2S from CH_4 and S_2. The reverse reaction $2H_2S = 2H_2 + S_2$ was also investigated, and shown to proceed at a substantial rate. It remains an open question therefore whether the H_2S and the H_2 formed in the reaction of CH_4 and S_2 are primary products, or whether one is formed as a secondary product from the other. The rather late appearance of the H_2 in the reaction of $CH_4 + S_2$, as compared with the H_2S (see fig. 3), suggests the possibility that the H_2 may be a secondary product.

If the formation of CS_2 from CH_4 goes through C_2H_4 as intermediate compound at 1200° K, it is possible that the same route will be followed at the much lower temperatures used by previous workers [1-5] especially in view of the observation of Bryce and Hinshelwood that unsaturated hydrocarbons could be formed at as low a temperature as 600° K.

HIGHER HYDROCARBONS

Experiments were carried out in which pentane, heptane or benzene was allowed to react with S_2 on 3 g of catalyst in the mullite tube. The liquid hydrocarbon was evaporated into a N_2 stream, which was combined with the S_2-bearing N_2 stream before entry to the reaction tube.

Runs were carried out with heptane at 1273° K, at a total feed flow rate of 100 cm^3 at s.t.p. per min, the initial partial pressure of C_7H_{16} being 30 mm and of S_2 255 mm, with the object of finding a suitable catalyst. The results, using 3 g of catalyst in each case are shown in table 5.

TABLE 5.—CHOICE OF CATALYST FOR HIGHER HYDROCARBONS

catalyst	% CS_2 produced	notes
pptd Al_2O_3	0	catalyst clogged with heavy tars
silica gel	0	" " " "
pptd MoS_2	28	tars on surface of catalyst
NiO co-pptd with Al_2O_3	29	" " "
V_2O_5 " " "	31	" " "
V_2O_5 " " " after 3 runs	22	results reproducible

Unexpectedly no CS_2 was produced with the alumina catalyst which had been used for CH_4, although considerable amounts of tar, H_2S, and some thiophen were among the products. Of the other catalysts tried, vanadium pentoxide co-precipitated with alumina was the most active, giving 31 % of CS_2 to start with, but falling to 22 % after 3 runs, at which level it remained steady and reproducible.

Using 3 g of the vanadium pentoxide catalyst runs were now carried out with pentane, heptane and benzene. The results are given in table 6. The second and third columns give the initial partial pressures in mm of hydrocarbon and of S_2 in the feed. In these experiments a considerable increase in volume on reaction is to be expected, and in the absence of a complete analysis, including hydrocarbons, it would be difficult to deduce the volume of the product: the amounts of CS_2, H_2S and unsaturateds are therefore expressed as moles % of the moles of S_2 + hydrocarbon in the feed. The % unsaturateds refers to the percentage of double bonds as determined by the bromine titration method.

Table 6

hydrocarbon	p_0 (mm) hydro-carbon	p_0 (mm) S_2	temp °K	contact time (min) × 10^2	products			$\frac{\text{unsat.}}{H_2S}$
					CS_2 %	H_2S %	unsat. %	
pentane *with* catalyst	30	330	1273	0·43	2	7		
				0·64	8	10		
				1·28	25	38		
				2·56	26	38		
			1373	0·4	5	10	31	3·1
				0·6	10	15		
				1·2	31	44		
				2·4	29	43	20	0·46
			1473	0·37	10	12	38	3·2
				0·55	28	25		
				1·11	39	38		
				2·22	40	38	18	0·48
heptane *with* catalyst	30	255	1273	0·43	4	9		
				1·29	39	37		
			1373	0·6	12	16		
				1·2	38	31		
			1473	0·37	12	18		
				1·11	42	33		
benzene *with* catalyst	30	255	1273	0·43	3	11	31	2·9
				0·64	9	16		
				1·29	21	20		
			1373	0·4	5	13	24	1·8
				0·6	20	16		
				1·2	34	20	6	0·3
			1473	0·37	5	13		
				1·11	31	19		
				2·22	33	20		
pentane *without* catalyst	30	330	1273	0·43	0	4	12·0	3·0
				0·64	0	5		
				2·56	0	20	8·0	0·4

As with CH_4, the rates of reaction of the higher hydrocarbons increase with time. The rate of production of CS_2 increases even more than that of H_2S since the initial production of CS_2 is delayed relative to that of H_2S. The reaction ends abruptly, the acceleration continuing up till the time no reactant is left: this recalls the behaviour with CH_4 as shown in table 3 and fig. 3. These effects can also be seen in fig. 4 where the % products are plotted against contact time for pentane at 1373° K.

As with CH_4 the form of the present reaction curves can be attributed to a two-stage mechanism: in the first stage, double bonds would be formed by the action of S_2 on the reactant hydrocarbon; in the second, the double bonds would react to form CS_2. In certain cases therefore the amount of double bonds formed was determined on the liquid product as shown in the table. The last column gives the ratio of unsaturateds to H_2S. With benzene the % unsaturateds could only be determined rather roughly owing to the strong coloration of the solution by anthracene which was shown to be present in detectable amounts. As found by Bryce and Hinshelwood, the ratio [unsaturated]/[H_2S] is much larger than unity during the early stages of the reaction where it usually has a value of about 3: later it falls to well below unity.

Thus there is a rapid production of unsaturateds at the beginning of the reaction and a rapid production of CS_2 in the later stages during which the percentage of unsaturateds diminishes, which clearly suggests that CS_2 is produced in a secondary reaction from the unsaturateds which are the primary products.

It will be seen from the bottom of table 6 that when pentane and sulphur are passed through a tube containing no catalyst, a much smaller production of unsaturateds was recorded, and no CS_2 was produced. It is therefore concluded that the production of unsaturateds is due principally to heterogeneous catalysis, and not, as found by Bryce and Hinshelwood at lower temperatures, to homogeneous reaction only.

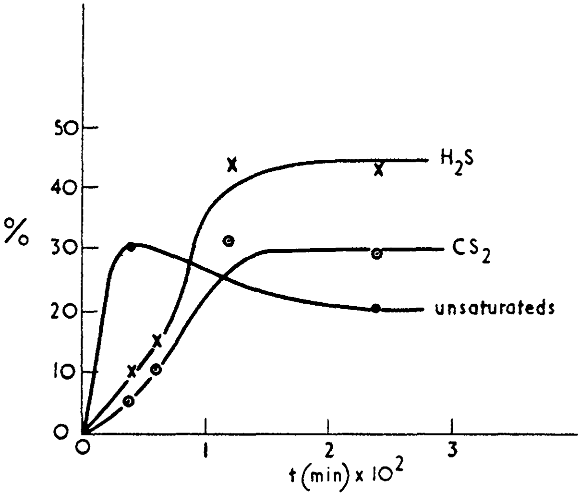

FIG. 4.—Pentane; temp. 1373° K; moles of CS_2, H_2S and unsaturateds, as a percentage of N_2-free moles of feed, against contact time, t (min) × 10^2.

The fact that the Al_2O_3 catalyst, which was effective for CH_4, was entirely inactive with higher hydrocarbons, for which the V_2O_5 catalyst had to be used, can perhaps be attributed not to any inability of the Al_2O_3 to catalyse the production of CS_2 itself, but to the fact that the catalyst became covered with heavy tarry products: it may be supposed that the vanadium catalyst was able to break down these heavy hydrocarbon tars and thus to free its surface for CS_2 production.

It is to be noted that the " unsaturateds " recorded in table 6 were *liquid* hydrocarbons; they could not therefore have been ethylene. It is, however, possible that these liquid unsaturateds are further broken down to C_2H_4, and that it is C_2H_4 which then reacts with S_2 to form CS_2. Some confirmation of this view might be seen in the fact that the rates of production of CS_2 are of much the same order for CH_4 as for higher hydrocarbons. The alternative is to suppose that the higher unsaturated hydrocarbons themselves react with S_2 to give sulphur compounds which then break down progressively to give CS_2 as the final product.

Regarding the work as a whole it may be concluded that the formation of CS_2 from hydrocarbons and sulphur passes through two stages, in the first of which unsaturateds are formed, and in the second the unsaturateds react with sulphur to give CS_2. With CH_4 it is likely that ethylene is the principle unsaturated intermediate: with higher hydrocarbons, the identities of the unsaturated intermediates are not yet known.

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