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The kinetics of gas-phase processes in systems containing carbon and sulphur

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ABSTRACT. **Data on the kinetics of the processes in gas-phase systems containing carbon and sulphur, which are of considerable importance in the combustion of sulphur-containing fuels, the reduction of industrial sulphur-containing gases, the industrial preparation of sulphur, etc., have been reviewed.**

The bibliography contains 87 references.

Contents

I. Introduction 1140
II. The role of sulphur compounds and their transformation in the combustion and oxidation of hydrocarbons 1140
III. The gas-phase reduction of sulphur dioxide by hydrocarbons 1143
IV. The formation of carbon disulphide and carbonyl sulphide in gas-phase processes 1148
V. The kinetics and mechanism of the processes in the C–S–O system 1148
VI. The combined oxidation, photolysis, and radiolysis of carbon- and sulphur-containing compounds 1150
VII. The reaction of carbon- and sulphur-containing molecules in atmospheric processes 1152

I. Introduction

The kinetics of gas-phase reactions involving even basic sulphur-containing molecules have not been well studied. The principal results have been obtained in studies of the transformation of sulphur-containing compounds in the atmosphere,[1,2] their role in combustion and high-temperature corrosion,[3,4] and a number of model reactions (the oxidation of hydrogen sulphide,[5] carbon disulphide,[6] and various others). There has recently been a steady increase in the practical importance of gas-phase processes involving both sulphur-containing and carbon-containing compounds. These include the purification and processing of sulphur-containing natural gases,[7,8] the reduction of concentrated industrial sulphur-containing gases by hydrocarbons,[9,10] the production of gaseous sulphur[9,11] and carbon disulphide,[12] etc. The need to develop new industrial processes and to optimise existing ones arouses a natural interest in the kinetics and mechanism of these reactions. Unfortunately, there have been very few studies of the kinetics of gas-phase reactions involving compounds of sulphur and carbon, except for several model reactions (the oxidation of CS_2 and COS). There are very few published data on the rate constants of elementary reactions involving carbon- and sulphur-containing species.[13] Difficulties arise when attempts are made to extend generally accepted ideas about the decisive role of radical processes in complex gas-phase reactions, so clearly demonstrated in the description of the oxidation of hydrocarbons, to the kinetics of processes involving sulphur-containing molecules.

The present review attempts to summarise available data on the kinetics of gas-phase processes in systems containing compounds of sulphur and carbon.

II. The role of sulphur compounds and their transformation in the combustion and oxidation of hydrocarbons

The concentration of sulphur in different types of hydrocarbon fuel varies over a very wide range, in some cases amounting to several tens percent. The interest in the chemistry of combustion processes involving sulphur compounds is related to three basic problems: 1, the direct influence of sulphur compounds on combustion processes; 2, atmospheric pollution by sulphur-containing combustion products, principally SO_2;[3] and 3, high-temperature corrosion involving sulphur compounds, where a fundamental role is played by SO_3 molecules.[4,14]

A practically exhaustive review of work on combustion in sulphur-containing systems carried out up to 1972 has been published.[15] The presence of sulphur even in quantities less than 1%, particularly in rich mixtures, has a significant influence on all the characteristics of a process, namely temperature, rate of flame propagation, carbon formation, and the formation of NO_x. These effects are a direct manifestation of the chemistry of sulphur, primarily its influence on the concentration of radicals in the flame. The chemistry of sulphur compounds in hydrogen flames has been studied in most detail. Since the same processes predominate in hydrocarbon flames, it is appropriate to examine them briefly in this section.

Both experiments and numerical modelling show that even in rich flames, SO_2 is the predominant sulphur-containing compound, irrespective of the compound in which sulphur is introduced into the flame, although for rich mixtures the formation of H_2S, S_2, and other reduced compounds of sulphur is much more favourable from the thermodynamic viewpoint.[16] On the other hand, even in very lean mixtures it is rarely possible to detect sulphur trioxide SO_3 in quantities greater than several percent of the SO_2 concentration, and this also shows poor agreement with the result expected for thermodynamic equilibrium.[15] Elemental sulphur S_2 is the sulphur-containing species of second importance in flames, but its

concentration also does not reach the equilibrium values. The increase in the SO_2 concentration in rich flames leads to a predominant increase in the formation of S_2 from H_2S.[16]

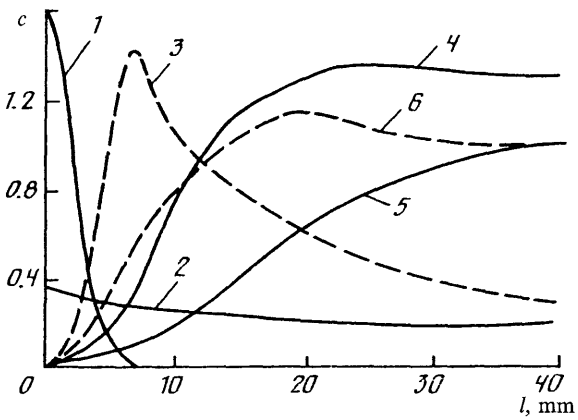
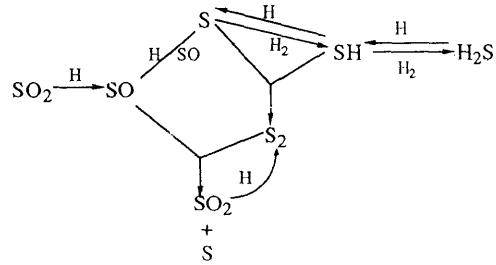


Figure 1. Experimental concentration profiles (*c* is the mole fraction) of the products in a laminar hydrogen flame $H_2/O_2/Ar$ containing 3% SO_2 (φ = 2.0, [Ar] = 37%, p = 150 torr);[16] *1*, 12.8[O_2]; *2*, 10[SO_2]; *3*, 400[SO]; *4*, 300[S_2]; *5*, 300[H_2S]; *6*, 4000[SH]; *l* is the distance along the flame.

An important feature of sulphur-containing flames is their two-stage character. Even after the principal combustion processes are complete, sulphur compounds continue to undergo continuous processes of rearrangement, associated with a change in temperature and the concentration of radicals. A detailed experimental and theoretical study of sulphur-containing hydrogen flames[16] has shown that the principal intermediate product, from which all reduced compounds of sulphur are formed, is SO, which is rapidly formed in the main reaction zone in the presence of high concentrations of radicals, but its concentration decreases sharply when the main combustion process is complete (Fig. 1). Reduced compounds of sulphur (S_2, SH, H_2S) begin to be formed after the maximum concentration of SO has been passed, and the S_2 and H_2S concentration profiles are approximately the same. An important role in the chemistry of sulphur compounds in flames is played by diffusion processes. Practically all reduced compounds of sulphur formed in the later stages of the process diffuse back into the zone of lower temperatures and higher concentrations of radicals, where they undergo exothermic reactions to give more highly oxidised compounds. An important conclusion from the work cited,[16] confirmed by mathematical modelling, is that all the reduced compounds of sulphur are produced by the intermediate formation of S atoms, as shown in the diagram for the transformations of sulphur-containing compounds in a laminar hydrogen flame in the zone corresponding to the completion of the main oxidation processes



The most significant influence of sulphur on the processes in flames is related to its catalytic action in radical recombination processes. According to the proposed mechanism[17]

$$H + SO_2 + M \longrightarrow HSO_2 + M,$$
$$H + HSO_2 \longrightarrow H_2 + SO_2,$$
$$OH + HSO_2 \longrightarrow H_2O + SO_2,$$

the presence of sulphur has a significant influence on the concentration of radicals driving the chain process. Thus according to calculations,[16] the presence of up to 3% sulphur lowers the maximum concentration of H atoms by a factor of two, and their concentration in the post-combustion zone by a factor of more than ten. This naturally leads to the experimentally observed decrease in the rate of propagation of the flame and to the increase in the temperature in relatively cold rich flames by almost 100 K.[16,18]

Although the principal active sulphur-containing species S, SO, and SH have been identified experimentally in flames, attempts to record the presence in flames of the radicals HSO_2 and HSO_3, which according to existing ideas are responsible for the catalytic recombination of radicals, have as yet been unsuccessful, despite the fact that, according to calculations, HSO_2 is formed very rapidly in the flame, and the estimated $H-SO_2$ bond energy exceeds 48.5 kcal mol^{-1} and possibly reaches 63 kcal mol^{-1}.[19] Nevertheless, the real existence of these radicals can hardly be doubted. Their exclusion from the kinetic schemes gives values for the concentrations of reduced compounds of sulphur which are 10–100 times lower than the values actually observed. In addition to indications of the formation of these radicals in solid matrices, there are experimental indications of the existence in the gas phase of HSO_3 radicals with a lifetime of about 1 μs.[20] The catalytic influence of SO_2, which lowers the concentration of radicals in the flame, brings about a significant shift in the distribution of sulphur-containing species towards the formation of more highly reduced compounds of sulphur.[16]

There are experimental indications[21] of the possible existence under certain conditions of the opposite effect of promotion of slow oxidation processes by the reaction

$$HO_2 + SO_2 \longrightarrow SO_3 + OH,$$

but this requires more detailed study.

The formation and decomposition of sulphur trioxide are the most important processes in the zone after sulphur-containing flames. As already noted, even in a large excess of oxygen SO_3 is rarely formed in quantities greater than several percent of the SO_2 concentration. Nevertheless, the presence of even these small quantities of SO_3 is of considerable importance for the kinetics and

more particularly the technology of combustion processes. The principal channel for the formation of SO_3 is the reaction

$$O + SO_2 + M \longrightarrow SO_3 + M,$$

so that, for example, the quantity of SO_3 formed in the oxidation of carbon monoxide, where the concentrations of oxygen atoms are high, is much greater than in hydrogen and hydrocarbon flames. For the same reason, the addition to the flame of substances which react rapidly with oxygen atoms leads to a significant decrease in the SO_3 concentration.[15] These questions are closely related to the problems of corrosion by sulphur.

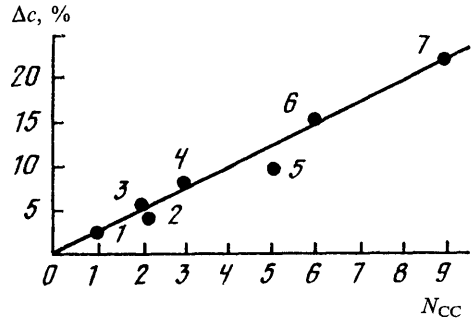


Figure 2. Influence of sulphur dioxide on the ignition limits of hydrocarbons; Δc, % is the required increase in the concentration of hydrocarbons for the addition of 20 torr SO_2 to its mixture with 200 torr oxygen (T = 700 °C);[15] N_{CC} is the number of C–C bonds in the hydrocarbon; *1*, ethane; *2*, acetone; *3*, ethylene; *4*, acetylene; *5*, n-hexane; *6*, cyclohexane; *7*, benzene.

The above processes involving sulphur-containing molecules predominate to the same extent in both hydrogen and hydrocarbon flames, and have been briefly examined here in order to give a more complete picture of the role of sulphur in oxidation processes. A specific feature of sulphur-containing hydrocarbon flames is the formation of CS_2, COS, and organosulphur compounds, and this has been much less extensively studied. Very little is known about the influence of SO_2 on the kinetics of the slow oxidation of hydrocarbons. It has been shown[22] that even at 200–250 °C the addition of SO_2 to a reaction mixture containing methane, n-hexane, methanol, or dimethyl ether leads to the formation of SO_3. In other studies of the slow oxidation of organic compounds,[23] however, only the presence or formation of oxides of nitrogen in the mixture led to appreciable consumption of SO_2, and from this it was suggested that at temperatures below 700 °C the rate of the reaction of SO_2 with oxygen-containing radicals (apart from O atoms) is negligible. The inhibiting influence of SO_2 is also revealed by the need to increase the partial pressure of the organic compounds in order to return the mixture to the ignition region.[23] In the ignition process, SO_2 apparently competes with the fuel for the chance to react with free radicals. A good correlation is observed between the quantity of added hydrocarbon required to compensate the influence of a given quantity of SO_2 and the number of C–C bonds in the molecule (Fig. 2). Since the rapid oxidative decomposition of the organic molecule must be preceded by the rupture of C–C bonds, the observed correlation suggests that SO_2 in some way is able to prevent this rupture.

The kinetics of the formation of sulphur-containing products have been studied[3] for different oxidation conditions and different hydrocarbons and sulphur-containing molecules. Flames of propane, methane, acetylene, and also hydrogen and its mixtures with carbon monoxide in the temperature range 1580–1800 K were studied. The sulphur-containing additives used were 0.23 mol% thiophen C_4H_4S and H_2S or 0.23–0.4 mol% SO_2. The relative deviation of the composition of the mixture from the stoichiometric fuel : oxidant ratio varied in the range φ = 0.6–1.7.

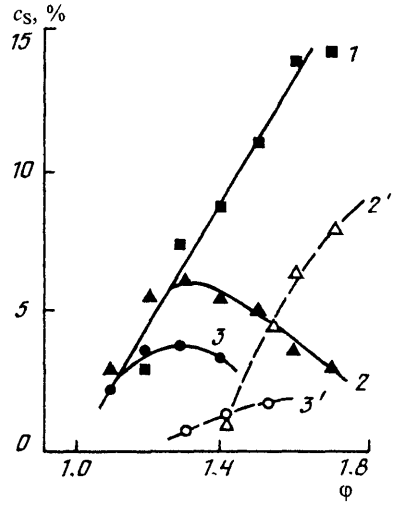


Figure 3. Concentration of sulphur (c_S) as hydrogen sulphide (*1–3*) and cabron disulphide (*2',3'*) in hydrogen and hydrocarbon flames for different values of φ (T = 1802 K, p = 0.92 atm);[3] *1*, H_2; *2,2'*, C_2H_2; *3,3'*, C_3H_8.

In the combustion of hydrocarbons with the addition of H_2S or SO_2, the following stable sulphur-containing products were detected: SO_2, SO_3, H_2S, COS, and CS_2. When C_4H_4S was used as the sulphur-containing additive, it was also detected in the combustion products. Other organosulphur molecules, including thiols, were not detected. For non-hydrocarbon flames, in addition to SO_x, only H_2S was detected. As already noted, SO_2 is always the predominant product. In lean mixtures, not more than 2–3% of the total sulphur is present as SO_3, and in rich mixtures the total concentration of sulphur in all other compounds (H_2S + COS + $2CS_2$ + C_4H_4S) does not exceed 20% (the sulphur concentration balance was determined for a propane flame at 1700 K). The type of compound containing the added sulphur had no significant influence on the yield of H_2S, CS_2, and COS. In contrast to the linear increase in the yield of H_2S in a hydrogen flame with increase in φ, in hydrocarbon flames this increase takes place only up to a certain value of φ, which corresponds to the start of the appearance of CS_2 and COS (Fig. 3). The start of the decrease in the H_2S concentration also coincides with the appearance of appreciable

quantities of unburned carbon, indicating the preferential formation of CS_2 and COS with increase in the quantity of unburned hydrocarbon in the gases. As shown below (section III), CS_2 in fact becomes the principal primary sulphur-containing product when there is a large deficit of oxygen in the system.

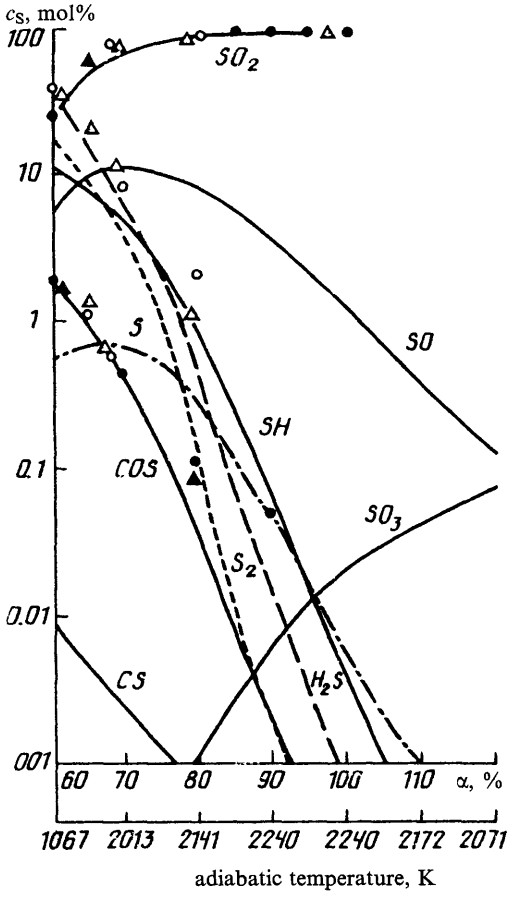


Figure 4. Equilibrium distribution of sulphur-containing components in a propane–air flame at an initial SO_2 concentration of 1%; the points correspond to the experimental data;[15,24] α is the fuel : air ratio (as a percentage of the stoichiometric ratio).

Increase in temperature naturally increases the part played by labile compounds of sulphur, so that in flames at 1500–2000 °C the equilibrium concentrations of these labile species may reach appreciable values. At these high temperatures, the attainment of the thermodynamically equilibrium composition of these products in the flames may be expected, but when the gases are cooled this equilibrium may be quenched before cooling is complete. Thermodynamic calculations of the composition of the products from hydrocarbon flames containing sulphur have been carried out.[24] The results are given in Fig. 4 as a function of the fuel : air ratio (as a fraction of the stoichiometric ratio $\varphi = 1$). Even with an air deficit of 20%, 90% of the sulphur is present as SO_2, and almost all the rest is present as SO. It is only at an air deficit of 40% that appreciable quantities of H_2S, S_2, and SH are present in addition to SO_2. With a 20% excess of air, however, less than 0.1% of the sulphur was present as SO_3. An interesting feature is that the calculation of the compositions of sulphur-containing hydrogen flames gives similar results.[4]

There have been practically no studies of the kinetics of the combined oxidation of hydrocarbons and sulphur-containing compounds at comparable concentrations. The practical interest in this topic is related primarily to the processing of natural gas with a high concentration (greater than 10%) of sulphur dioxide and the reduction of concentrated sulphur-containing gases by hydrocarbons. The marked difference in the reactivities of hydrogen sulphide and organosulphur compounds compared with that of alkanes, in particular methane, suggests that the processes involved in the oxidation of these compounds may be largely independent; this will be examined in more detail in section VI. Some data on the influence of high SO_2 concentrations on the combustion of mixtures of natural gas with air and oxygen have been published.[25] The tip of the peninsula of the range of flame propagation in a natural gas–air–carbon dioxide mixture corresponds to a concentration of 25% CO_2 in the mixture, whereas for sulphur dioxide this value is lowered to 16% SO_2. Since in the range 1100–1800 °C CO_2 and SO_2 have almost identical thermodynamic properties, the increased flame-extinguishing action of SO_2 compared with CO_2 is apparently related to the chemical inhibiting action of SO_2 on the chain process of methane combustion. For mixtures of natural gas and oxygen, the difference between the influences of CO_2 and SO_2 is even less marked, apparently because of the greater intensity of combustion of the oxygen flames.[25]

We carried out experiments to determine the range of stable combustion of methane–air mixtures containing up to 20% of added sulphur dioxide. The results agree well with published data.[25] Although sulphur dioxide shows a slightly stronger inhibiting action than carbon dioxide, the difference is not so dramatic as might have been expected from the results of studies using low concentrations of sulphur dioxide. With increase in the concentration of sulphur dioxide, the chemistry of the processes taking place evidently changes, and the role of sulphur dioxide is not limited to its participation in the catalytic recombination of radicals, particularly in the combustion of rich mixtures, where it may become the supplier of the additional oxygen required for oxidation. The results indicate that the stable combustion of methane–air mixtures containing up to 20% sulphur dioxide is possible in principle.

Unfortunately, up to the present it has apparently not even been possible to construct more or less adequate kinetic models of the transformation of sulphur-containing compounds in the combustion of hydrocarbons, and all attempts undertaken in this direction have been largely speculative in character.

III. The gas-phase reduction of sulphur dioxide by hydrocarbons

The largest group of kinetic studies of systems containing carbon and sulphur has been carried out on the reduction of industrial sulphur-containing gases by various hydrocarbons. Solid, liquid, and gaseous hydrocarbons have been used,[9] but the use of gaseous hydrocarbons (natural gas) appears to be most fully developed.

The high-temperature homogeneous reduction of concentrated sulphur-containing gases by natural gas has passed industrial tests at

the Noril'sk mining and metallurgical combine for processing waste gases from metallurgical processes with a sulphur dioxide concentration of up to 20%. The concentrated sulphur-containing waste gases are purified, and commercial sulphur is produced.[10] At the high-temperature reduction stage, the yield of sulphur is 55–60%. The total yield of sulphur with allowance for subsequent catalytic completion of reduction by the Klaus method is 80–85%. The process was first patented in 1933,[26] and tested industrially in the nineteen-forties,[27,28] but not even the most general ideas about its mechanism have been published.

Available data on the thermodynamics of the reduction of sulphur dioxide by methane show that the reaction can take place almost to completion at temperatures of 1250–1350 °C. Data on the composition of the equilibrium gaseous mixtures, found with allowance for side reactions, have been published.[29] They show that the equilibrium yield of sulphur increases with increase in temperature and with increase in the molar ratio $SO_2:CH_4$, reaching 100% at $SO_2/CH_4 = 2$ and $T > 1300$ °C. In addition, the equilibrium yield of sulphur increases with decrease in pressure.

Some of the first studies of the kinetics of the heterogeneous–homogeneous reduction of sulphur dioxide by methane were carried out by Yushkevich and co-workers,[30] Zawadzki and co-workers,[31] and Walker.[32] Yushkevich studied the kinetics of the two-stage reduction of sulphur dioxide by methanol at 700–1000 °C on bauxite with subsequent conversion of the gaseous sulphur compounds at 370 °C on the same catalyst. At a sulphur dioxide concentration of 14.7%, a ratio $SO_2/CH_4 = 2$, and a flow rate of 350 h^{-1}, the yield of sulphur was 85% at 900 °C, 82% at 800 °C, and 13% at 700 °C. According to these studies, the reaction is heterogeneous–catalytic up to a temperature of 1000 °C, and the products at thermodynamic equilibrium should be sulphur or carbon disulphide.[32] At low ratios $N = SO_2/CH_4$, that is in an excess of methane, reduction to hydrogen sulphide takes place.

Zawadzki[31] studied the process in quartz reactors at a ratio $N = 2.2-3.4$ and temperature of 820–1135 °C, and found that on quartz the reaction takes place only at $T > 800$ °C; up to 1050 °C the reaction is apparently heterogeneous, and above 1050 °C it takes place in the gas phase. In addition to elemental sulphur, large quantities of COS and CS_2 are formed. The formation of large quantities of COS is not consistent with thermodynamic considerations, so that the authors cited suggested that on quartz the reaction is retarded at an intermediate stage, and that carbonyl sulphide is unstable and can decompose in two directions:

$$COS \longrightarrow CO + S,$$
$$2COS \longrightarrow CS_2 + CO_2.$$

Berkman and Kushnir[33] made a detailed study of the methane process in a quartz flow reactor, and they consider that the conclusion that large quantities of COS are formed is based on unreliable methods of analysis, and that carbon disulphide is the principal and primary product of the non-equilibrium reduction of sulphur dioxide by methane. The influence of the reagent ratio $N = SO_2/CH_4$ on the composition of the products at 800 °C was also studied. The results show that the principal reduction product in all cases is carbon disulphide and that its yield is almost independent of the reagent ratio and corresponds to approximately two thirds of the reduced sulphur. The sum $H_2S + S$ is therefore also almost constant, and over a wide range of $N > 0.4$ the principal product is sulphur, and hydrogen sulphide becomes the predominant product only at very high methane concentrations ($N < 0.4$). The methane oxidation products CO and CO_2 are present in the approximate ratio 2:1.

Increase in temperature increases the extent of the reduction (at a constant rate of supply of the gases $V = 22$ ml min^{-1}) and decreases the yield of carbon disulphide.[33] The decrease in the yield of carbon disulphide at low values of N (excess of the reducing agent) leads to an increase in the yield of hydrogen sulphide for a constant yield of sulphur. At high values of N the decrease in the yield of carbon disulphide is accompanied by an increase in the yield of sulphur, and there is practically no hydrogen sulphide. The methane oxidation products are CO and CO_2; at $N < 1$, as a result of a deficit of the oxidising agent SO_2, increase in temperature leads to a marked increase in the yield of CO, whereas at $N > 2$ the yield of carbon dioxide increases. The rate (extent) of the reduction at 800 °C also depends on the type of quartz (non-transparent quartz is approximately two times more active) and on the time for which it has been used.[33] The catalytic activity gradually decreases by a factor of almost four, and neither heating in a stream of oxygen nor treatment with hot acids increases the established catalytic activity of the quartz. The relative distribution of the sulphur-containing products of the reduction of sulphur dioxide by methane, however, is not influenced by the difference in the catalytic activities of different types of quartz, or by change in the contact time, or by the decrease in the activity with time, which influence only the extent (that is the rate) of the reduction.

The methane reduction of sulphur dioxide at concentrations of 10–100% and at higher temperatures up to 1250 °C has been studied.[29] The process was carried out in quartz flow reactors with an internal diameter of 4–23 mm and a length of 38–100 mm at a constant flow rate of the mixture of 2.4 litre h^{-1}. The separation of carbon was observed in the reaction zone at 900 °C and sometimes at 1100 °C, but not at 1250 °C. Experiments were also carried out on the reduction by domestic gas, shown by chromatographic analysis to contain about 14% ethane, 80% propane, and some methane and nitrogen. The results of the experiments at 1100 °C and 1250 °C were approximately the same as those for the reduction by methane.

It has been concluded[29,32] that the rate of the reduction of sulphur dioxide by methane is controlled by the rate of its thermal decomposition. Describing the rate of the thermal decomposition of methane by the first-order equation:

$$-\frac{d[CH_4]}{dt} = K[CH_4] = A\exp(-E/RT)\,[CH_4]$$

and taking for the rate constant the value $k = 7.08 \times 10^{13} \exp(-87250/RT)$ s^{-1}, the authors cited[29] calculated the kinetics of the thermal decomposition of methane and compared them with the experimentally observed kinetics of the transformation of sulphur dioxide. Satisfactory agreement between the calculated and experimental curves was obtained.

The conclusion[34,35] that sulphur dioxide reacts with methane only after oxygen is used up is interesting. These results were obtained in a study of the kinetics of the reaction and the yield of products in the $SO_2-CH_4-O_2$ system under flow conditions in the presence of a catalyst ($T = 732-831$ °C).

Some data of interest for an understanding of the mechanism of the process were also obtained in practical work on the extraction of sulphur from rich metallurgical gases. In particular, the technological parameters of the high-temperature process depend markedly on the initial concentration of oxygen in the gases being

processed,[36] the presence in the gases of water vapour (up to 5–7% in real gases), and other factors. Increase in the oxygen concentration leads to a decrease in the degree of conversion; in addition, oxygen brings about additional heating of the reaction mixture by the heat of the reaction.[9] Published studies[36] showed that the extent of the reduction of sulphur dioxide by methane depends on the flow rate of supply of the reagents.

A detailed study of the kinetics of the reduction of sulphur dioxide by methane in the temperature range 1000–1360 K has been carried out.[37,38] The process was carried out under static conditions in quartz reactors with a diameter of 21–46 mm. The kinetics of the process were followed from the infrared and ultraviolet spectra of the reagents and products.

The following equations of first-order reactions were obtained for the maximum rate of consumption of the reagents:

$$-\frac{d[CH_4]}{dt} = 6.5\cdot10^{10}\exp(-72000/RT)\,[CH_4]\ cm^{-3}\ s^{-1}$$

$$-\frac{d[SO_2]}{dt} = 2.7\cdot10^{9}\exp(-64000/RT)\,[SO_2]\ cm^{-3}\ s^{-1}.$$

These results indicate that the rate of consumption of methane in this system and the rate of the thermal decomposition of pure methane practically coincide.[39] In any case, in the temperature range 1100–1500 K the rates of these processes do not differ by a factor of more than 2, which is much smaller than the scatter in the experimentally determined rates of the thermal decomposition of methane.[40] The activation energy of the decomposition of methane in this system (72 ± 3 kcal mol^{-1}) is close to the activation energy of the thermal decomposition of pure methane.[39,40] The good agreement between the rate of the thermal decomposition of pure methane, the rate of consumption of methane in the system and the rate of reduction of sulphur dioxide (with allowance for the stoichiometry of the reaction) shows that the thermal decomposition of methane is in fact the limiting stage of the process.

Figure 5 gives the kinetics of the reduction of sulphur dioxide by methane at a ratio $SO_2:CH_4 = 2:1$ and $T = 1200$ K. The similar behaviour of the starting materials can be clearly seen, indicating that their decompositions are limited by the same processes. As in the thermal decomposition of pure methane,[39] the kinetic curves show a section corresponding to acceleration of the reactions, that is the process is self-accelerating. The highest rate of decomposition of methane in this reaction is proportional to its concentration and depends very little on the concentration of sulphur dioxide. The maximum rate of change in the sulphur dioxide concentration is proportional to the concentration of sulphur dioxide and the concentration of methane, but only until the stoichiometric ratio $SO_2:CH_4 = 2$ is reached. At higher concentrations of methane it no longer influences the maximum rate of decomposition of sulphur dioxide.[37]

The principal primary product of the reduction of sulphur dioxide is carbon disulphide, and the start of appreciable formation of this product coincides with the end of the induction period; the highest concentration is reached at the same time as the highest rate of consumption of sulphur dioxide and methane. Its concentration subsequently decreases rapidly to almost zero. The highest concentration of carbon disulphide corresponds to almost 70% of the total change in the concentration of sulphur dioxide at that moment ($2[CS_2]_{max} \simeq 0.7\Delta[SO_2]_{t_{max}}$), and with allowance for its partial decomposition it can be stated that not less than 95% of the sulphur dioxide is converted initially into carbon disulphide. Thus carbon disulphide is not merely the principal but the only primary product of the reduction of sulphur dioxide by methane.

The formation of another sulphur-containing product, namely carbonyl sulphide, is observed much later, and its highest concentration is reached after the stage corresponding to the rapid decomposition of sulphur dioxide and methane. It is therefore a secondary product, formed most probably by the familiar reactions of carbon disulphide with other products of this process

$$CS_2 + CO_2 \longrightarrow 2COS,$$
$$CS_2 + H_2O \longrightarrow COS + H_2S.$$

In these reactions, only a small fraction of the carbon disulphide is apparently removed, since the highest concentration of COS is approximately one fifth of the highest concentration of carbon disulphide, although the concentration of carbon oxide sulphide decreases much more slowly than that of carbon disulphide, and COS is one of the stable end products.

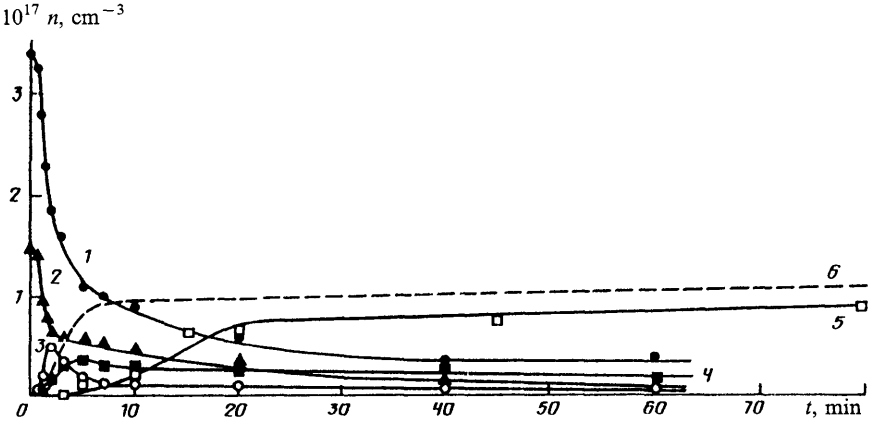


Figure 5. Kinetics of the change in the concentration of the products; $T = 1200$ K; $p = 440$ torr; $[SO_2] = 10\%$; $[CH_4]_0 = 5\%$;[38] *1*, SO_2; *2*, CH_4; *3*, CS_2; *4*, COS (relative units); *5*, H_2S; *6*, S_2 (estimated).

Hydrogen sulphide is a tertiary product of the reduction of sulphur dioxide by methane, since its formation begins after the highest concentrations of CS_2 and COS have been reached and is apparently directly related to their decomposition. In a large excess of sulphur dioxide, the formation of hydrogen sulphide is not observed at all, or takes place after a long time as a result of reactions between secondary reaction products. The highest yield of hydrogen sulphide (about 100%) is observed only with identical concentrations of sulphur dioxide and methane.

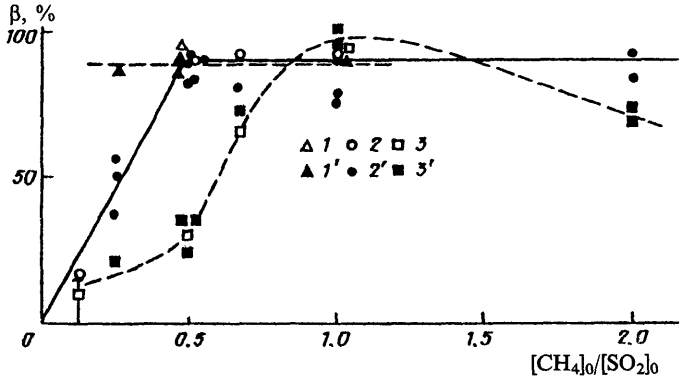


Figure 6. Dependence of the extent of the transformation of the reagents (β) on the ratio $[CH_4]_0/[SO_2]_0$; T = 1200 K; p = 440 torr;[38] *1*, $\Delta CH_4/(CH_4)_0$; *2*, $\Delta SO_2/(SO_2)_0$; *3*, $H_2S/\Delta SO_2$; reaction time: *1*–*3*, 30–50 min; *1'*, *2'*, *3'*, 60–80 min.

The formation of elemental sulphur begins at practically the same time as the formation of carbonyl sulphide. Thus sulphur is also a secondary product of this reaction, and its concentration fairly rapidly reaches a stationary level. For a ratio $SO_2:CH_4$ = 2, corresponding to the overall equation

$$2SO_2 + CH_4 \longrightarrow CO_2 + 2H_2O + S_2,$$

the distribution of sulphur in the principal products for fairly long reaction times at 1200 K is as follows: S_2 ~65, H_2S ~25, $SO_2 \leqslant 9$, and COS ~1%, that is the actual overall equation for the reaction is approximately:

$$4SO_2 + 2CH_4 \longrightarrow 2CO_2 + 3H_2O + H_2S + 5/4S_2 + 1/2SO_2.$$

At a higher concentration of methane, corresponding to a ratio $SO_2:CH_4$ = 1, the composition of the final products changes sharply towards the formation of hydrogen sulphide ($H_2S \geqslant 86\%$, $SO_2 \leqslant 9\%$, $COS \leqslant 4\%$, $S_2 + CS_2 < 1\%$), that is the relative yield of hydrogen sulphide $(H_2S/\Delta SO_2)_\infty$ tends to 100% (Fig. 6). This corresponds to the equation

$$SO_2 + CH_4 \longrightarrow CO + H_2O + H_2S.$$

With an even greater excess of methane, the relative yield of hydrogen sulphide again decreases. Here we should expect the appearance of the principal products of the thermal decomposition of methane, primarily hydrogen, C_2 hydrocarbons, and solid carbon.

Thus in the reduction of sulphur dioxide by methane, the following sequence of transformations of sulphur-containing products takes place:

$$SO_2 \rightarrow CS_2 \rightarrow COS \text{ and } S_2 \rightarrow H_2S.$$

The decomposition of carbon disulphide, which is the direct precursor of all other reaction products, is the next limiting stage of the process after the thermal decomposition of methane. It is therefore extremely important to determine the mechanism and rate of its transformation in this system. Published data[38] indicate that the decomposition of carbon disulphide involves its direct reaction with sulphur dioxide (Fig. 7). The rate of the thermal decomposition of pure carbon disulphide is one tenth of that in the $SO_2 + CH_4$ reaction. The presence of methane increases the rate of the decomposition of carbon disulphide at 1200 K by a factor of ~3, but only the reaction with sulphur dioxide can explain the observed kinetics of the decomposition of CS_2 in the $SO_2 + CH_4$ system.[38]

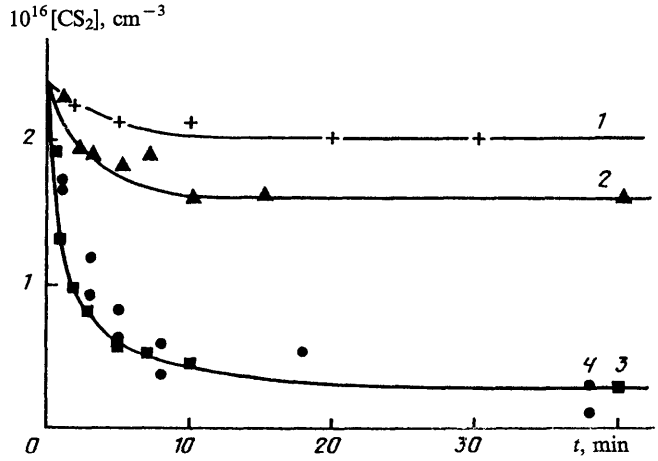


Figure 7. Kinetics of the decomposition of carbon disulphide; T = 1200 K, p = 440 torr; the initial concentrations of carbon disulphide are reduced to the same value $[CS_2]_0 = 2.4 \times 10^{16}$ cm^{-3};[38] *1*, thermal decomposition of CS_2; *2*, reaction of $CS_2 + CH_4$, $[CH_4]_0 = 1.75 \times 10^{17}$ cm^{-3}; *3*, reaction of $CS_2 + SO_2$, $[SO_2]_0 = 3.5 \times 10^{17}$ cm^{-3}; *4*, reaction of $SO_2 + CH_4$, $[SO_2]_0 = 3.5 \times 10^{17}$ cm^{-3}, $[CH_4]_0 = 1.75 \times 10^{17}$ cm^{-3}.

The extent of the transformation of sulphur dioxide in a deficit of methane increases regularly with increase in the concentration of methane in accordance with the stoichiometric ratio $\Delta[SO_2] = 2[CH_4]_0$. When this stoichiometric ratio and higher concentrations (an excess) of methane are reached, the degree of transformation of sulphur dioxide exceeds 90%.

The degree of transformation of sulphur dioxide into hydrogen sulphide (the relative yield of hydrogen sulphide) $H_2S/\Delta SO_2$ in a deficit of methane also increases regularly from $\leqslant 20\%$ at CH_4/SO_2 = 1:8 to ~30% at the stoichiometric ratio CH_4/SO_2 = 1:2 and to almost 100% at CH_4/SO_2 = 1:1, after which it

decreases again to 70% at $CH_4/SO_2 = 2:1$. Thus by controlling the ratio of methane and sulphur dioxide it is possible to control the ratio of the final concentrations of sulphur dioxide and hydrogen sulphide in the reaction products.

There are practically no published data on the kinetics of the reduction of sulphur dioxide by other gaseous hydrocarbons, except for acetylene.[41] The interest in acetylene is due to the fact that it is the principal hydrocarbon product of the thermal decomposition of methane,[39,40] and may play an important role in the high-temperature reduction of sulphur dioxide.

Studies in the temperature range 1000–1200 K[41] showed many common features in the reduction of SO_2 by methane and by acetylene, although acetylene reacts with SO_2 several times more rapidly. In this temperature range, simultaneous thermal decomposition of acetylene takes place,[42] and the rate of decomposition of acetylene under the conditions of the work cited[41] was much greater than the rate of change in the concentration of sulphur dioxide; the temperature dependence was approximately the same for these processes, and corresponded to an activation energy of ~45 kcal mol^{-1}. At lower temperatures (1000 K), a short period of auto-acceleration which is usually observed in the thermal decomposition of acetylene,[42] was noted.

The markedly different rates of the thermal decomposition of acetylene and the reduction of sulphur dioxide, together with the zeroth order of the rate of reduction of SO_2 with respect to acetylene, indicate that the reduction involves the reaction of sulphur dioxide with the thermal decomposition products of acetylene.

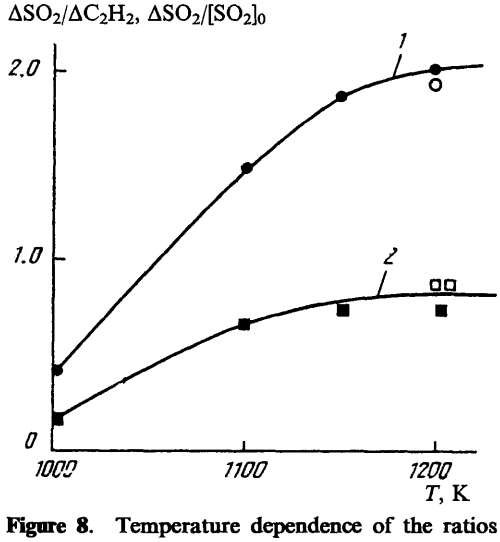


Figure 8. Temperature dependence of the ratios $\Delta SO_2/\Delta C_2H_2$ and $\Delta SO_2/[\Delta SO_2]_0$; black points—reactor with diameter 21 mm; open points—reactor with diameter 46 mm;[41] *1*, $\Delta SO_2/\Delta C_2H_2$; *2*, $\Delta SO_2/[SO_2]_0$.

In addition to sulphur, the principal sulphur-containing products of the process, recorded from their infrared spectra, are CS_2 and COS. As in the reaction of SO_2 with CH_4,[38] CS_2 is the principal and apparently the only primary product of the decomposition of sulphur dioxide. The formation of COS takes place much later, and is probably associated with the decomposition of CS_2 in the presence of SO_2. The highest concentrations $[CS_2]_{max}$ and $[COS]_{max}$ are apparently determined only by the rate of reduction of sulphur dioxide, and therefore are also independent of the initial concentration of acetylene. In an excess of acetylene, the formation of carbon is observed. Small quantities of methane are also formed, evidently by thermal decomposition.

Increase in temperature increases the ratio of the change in the concentration of sulphur dioxide to the change in the concentration of acetylene $\Delta SO_2/\Delta C_2H_2$ from 0.4 to 1000 K to 2.0 at 1200 K (Fig. 8). This may be related to a change in the mechanism and hence in the products of the thermal decomposition of acetylene, in which polymerisation products predominate at $T < 1200$ K, while at higher temperatures there is an increase in the contribution made by processes involving small radicals.[42] Another reason may be a change in the mechanism of the reaction of sulphur dioxide with the thermal decomposition products of acetylene. Evidence that the reduction of sulphur dioxide involves the thermal decomposition products of acetylene is provided by the change in the quantity $\Delta SO_2/\Delta C_2H_2$ during the reaction (Fig. 9). As the thermal decomposition products are used up, this ratio increases from zero to ~1.5 at 1100 K and ~2 at 1200 K. The degree of reduction of sulphur dioxide $\Delta SO_2/[SO_2]_0$ increases with increase in temperature is approximately the same way as the quantity $\Delta SO_2/\Delta C_2H_2$ (Fig. 8).

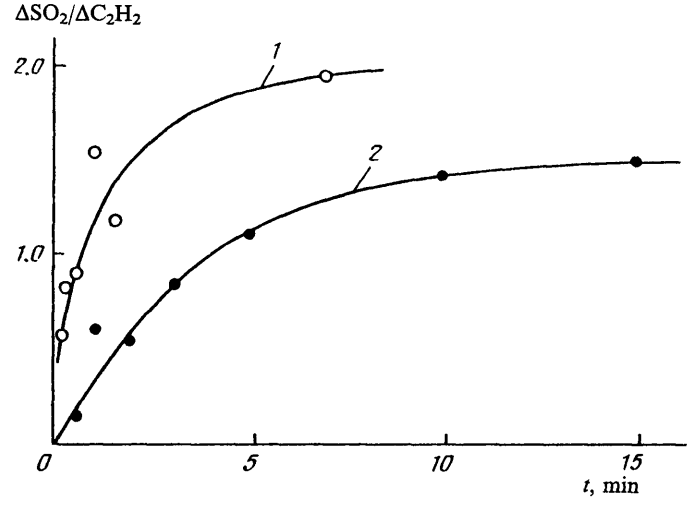


Figure 9. Time dependence of the ratio $\Delta SO_2/\Delta C_2H_2$; p = 440 torr, reactor diameter 21 mm; *T*, 1200 K; *2*, 1100 K.[41]

Thus the reduction of sulphur dioxide by acetylene and the reduction of sulphur dioxide with methane have a number of common features. From available data on the reaction of sulphur dioxide with methane and with acetylene, an attempt can be made to formulate some general conclusions about the mechanism of the reaction of SO_2 with hydrocarbons.

1. The limiting stage of the process is the thermal decomposition of the hydrocarbon.

2. The presence of sulphur dioxide does not lead to significant changes in the kinetics of the decomposition of the hydrocarbon.

3. A decisive role in the reduction is played by the reaction of SO_2 with the thermal decomposition products, primarily H_2.[43,44]

4. The rate of reduction is linearly dependent on the sulphur dioxide concentration.

5. The primary and apparently the only primary stable product of the reduction of SO_2 is CS_2. The sulphur-containing products are formed by the sequence

$$SO_2 \rightarrow CS_2 \rightarrow COS \text{ and } S_2 \rightarrow H_2S.$$

6. The subsequent decomposition of CS_2 involves its reaction with SO_2 to give COS, S_2, and other products.

7. The final degree of reduction of sulphur dioxide increases smoothly to 90–100% with increase in the hydrocarbon : sulphur dioxide ratio. At the same time the extent of the transformation of sulphur dioxide into elemental sulphur decreases.

IV. The formation of carbon disulphide and carbonyl sulphide in gas-phase processes

Carbon disulphide is one of the most important chemical products, and is required for the production of synthetic fibres, flotation reagents, vulcanisation accelerators, poisons, etc. In the nineteen-sixties, the intensive introduction of new industrial methods for obtaining carbon disulphide from natural gas and sulphur began, making it possible to establish large-scale fully automated processes.[12,45] The industrial process is carried out in the presence of a catalyst at a temperature up to 660 °C and a degree of transformation of methane up to 96%.[12] The kinetics of the process have been studied.[46] A large number of new studies are published annually on the technology of the production of carbon disulphide by this method using different modifications of the catalyst and different process conditions.[12,45] Heavier hydrocarbons containing three or more carbon atoms react readily with sulphur, and give a large quantity of carbon disulphide for every molecule of original sulphur and a correspondingly smaller quantity of hydrogen sulphide per molecule of carbon disulphide formed. The reaction of sulphur with higher hydrocarbons takes place much more rapidly with almost 100% conversion. In the catalytic process, however, the presence of propane and heavier hydrocarbons leads to the formation of carbon and tarry substances, including their formation on the catalyst, and also to the production of thiols, thiophens, and organic sulphides, so that the natural gas is purified beforehand to remove these hydrocarbons.[12]

In addition to catalytic methods, purely homogeneous methods have been proposed for carrying out this process at higher temperatures.[47–53] Patents have been published on the synthesis of carbon disulphide from paraffin hydrocarbons at 700–1300 °C,[47] accompanying petroleum gases,[48] and other hydrocarbons. A method for obtaining carbon disulphide by the reaction of saturated hydrocarbons with sulphur vapour and sulphur dioxide at 500–900 °C in 0.1–2 s has been described.[49] The disadvantages of this method are the low yield of CS_2 (42.5–50%) and the formation of side products. To eliminate these disadvantages, it is suggested that alkenes, dialkenes and heavier hydrocarbons be used as the carbon-containing starting material.[53] The process takes place at 500–900 °C at atmospheric or elevated pressure in 1.5–4 s with a yield of up to 80–91%. It is known, however, that unsaturated hydrocarbons, reacting with sulphur, give a large quantity of organic sulphur compounds as side products.[45] The kinetics of the gas-phase reaction of sulphur vapour with hydrocarbons have not been studied.

It has been suggested that carbon disulphide can be obtained by the reaction of sulphur vapour with carbon monoxide at 510–650 °C both in the gas phase[54] and in the presence of a catalyst.[55]

The use of various waste gases containing sulphur and hydrogen sulphide as the sulphur-containing starting material for the synthesis of carbon disulphide and carbon oxide sulphide is of considerable practical interest. A 26–70% yield of carbon disulphide at 1180 °C and 1280 °C without the use of a catalyst has been reported,[56] but other workers[57] obtained no carbon disulphide in the products of the homogeneous reaction in quartz tubes at temperatures of 900–1100 °C. Only the addition of a catalyst (kaolin impregnated with $K_2Cr_2O_7$) made it possible to obtain a 50% yield of CS_2,[57] so that it was suggested[45] that the quartz surface of the assembly in the work cited[56] had a catalytic action. Although the synthesis of CS_2 from methane and hydrogen sulphide has not yet found practical application, it has been suggested that this process may be promising if oxygen-containing gases or free oxygen are added to the reaction mixture.[45]

The formation of carbon disulphide and carbon oxide sulphide in the reaction of sulphur dioxide with methane was detected even in early studies.[31–33] This gas-phase process has been used with the simultaneous supply of sulphur vapour and sulphur dioxide for reaction by the hydrocarbon.[49,53] The kinetics of the formation of carbon disulphide and carbonyl sulphide by the reaction of sulphur dioxide with methane, acetylene, and carbon monoxide have been the subject of a series of detailed studies[37,38,41,58,59] (see sections III and V).

V. The kinetics and mechanism of the processes in the C–S–O system

The oxidation of carbon disulphide and carbonsyl sulphide is one of the most extensively studied gas-phase processes in the chemistry of sulphur. The available experimental data cover a wide range of temperatures (300–2000 K) and pressures (1–2000 torr) and include reactions under flow and static conditions, atomic flames, and experiments in shock tubes.[6] In addition, published data[13] on the rate constants of the elementary reactions in these processes have been used to construct a sufficiently adequate kinetic model, providing a satisfactory description of the published experiments.[6] An analysis of the kinetic model made it possible to select the most important reactions for the oxidation of CS_2:

$$CS_2 + O = CS + SO, \quad CS + O = CO + S,$$
$$CS_2 + O = COS + S, \quad S + O_2 = SO + O,$$
$$SO + O_2 = SO_2 + O,$$

and the oxidation of COS:

$$COS + O = CO + SO, \quad CO + SO = CO_2 + S,$$
$$COS + O = CO_2 + S, \quad CO_2 + S = CO + SO,$$
$$SO + O = S + O_2, \quad S + O_2 = SO + O.$$

Application of the mechanism being discussed to the conditions at low temperature $T \simeq 353–493$ K showed it to be inadequate. The calculated reaction rate was found to be too low. At low

temperatures, a fairly large contribution is apparently made by heterogeneous processes and reactions involving more complex intermediate species, not included in the kinetic scheme.

Since there is an extensive literature on the oxidation of CS_2 and COS, including reviews (see Ref. 6 and references therein), the kinetics and mechanism are examined in detail below for only one of the reactions in the C–S–O system, namely the thermal SO_2 + CO reaction.

The interest in carbon monoxide as reducing agent for sulphur dioxide is related to the fact that it is formed unavoidably when the reducing agent used is carbon or coke, whose use has been proposed for the preparation of sulphur from industrial gases containing SO_2.[60] As early as the eighteen-eighties, Berthelot and others showed that CO can reduce SO_2 slowly to give free sulphur. For example, the reaction of SO_2 and CO in a porcelain tube at 1000–1200 °C gave elemental sulphur and carbon dioxide, and also small quantities of carbonyl sulphide.[61] In the absence of a catalyst this reaction is slow, even at 800 °C, but is catalysed by almost any heated surface; the resulting reaction is of first order.[62]

Koval'skii and co-workers[63,64] showed by separate calorimetry that when Al_2O_3 is used as catalyst, the reduction of sulphur dioxide by carbon monoxide is a homogeneous reaction taking place by a chain mechanism, but chain initiation takes place on the surface of the catalyst. An appreciable quantity of carbonyl sulphide was formed in the reaction, and adding COS and sulphur increased the reaction rate.

From an analysis of the ESR spectra of the frozen products of the reaction of carbon monoxide and sulphur dioxide over bauxite at p = 1 atm and T = 600 °C it was concluded that SO is one of the species propagating the chain in the reduction of sulphur dioxide by carbon monoxide.[65] An excess of SO_2 relative to the stoichiometric ratio $CO:SO_2$ = 2 led to a decrease in the reaction rate, and an excess of CO to an increase.

The composition of a thermodynamicaly equilibrium SO_2–CO mixture at temperatures of 400–1000 K, including systems containing added water, oxygen, and carbon dioxide, has been calculated.[66] It was shown tht at 473 K almost complete reduction of sulphur dioxide by carbon monoxide is possible, but traces of water and oxygen lower the equilibrium yield of elemental sulphur.

The kinetics of the gas-phase CO + SO_2 reaction in static quartz reactors have been studied at temperatures of 1100–1360 K using infrared and ultraviolet spectroscopic analysis of the products.[58,59] Under these conditions, change in the surface:volume ratio of the reactor and in pressure in the range 60–300 torr had no influence on the reaction. The effective activation energy of the process, determined from the rate of removal of sulphur dioxide, was 46 kcal mol^{-1}. An interesting feature is that this value practically coincides with the activation energy of the formation of CO_2 in this reaction (E = 48.3 kcal mol^{-1}), obtained in shock waves at temperatures of 1770–2453 K.[67] It was established that the rate of change in the SO_2 concentration is independent of the concentration of SO_2 and is linearly dependent on the CO concentration. As in other studies,[64] the principal intermediate reaction product is carbonsyl sulphide. In contrast to the catalytic process at a lower temperature,[64] however, where the highest yield of COS reached 45%, in the gas-phase process at 1215 K and a reagent ratio $CO:SO_2$ = 2:1 the highest concentration of carbonyl sulphide was only 5–8% of the initial concentration of sulphur dioxide. At the moment when a highest COS concentration of 25–50% is reached, however, all the sulphur liberated at this stage by the decomposition of SO_2 is present as COS. An estimate taking account of the rate of decomposition of carbonyl sulphide itself showed that at least 80% of the SO_2 decomposed is converted initially into COS, and its lower concentration compared with published data[64] is due to the higher rate of its decomposition at a high temperature.

Experiments with the addition of carbonyl sulphide (up to 30% of the initial concentration of SO_2) to the original mixture showed[59] that in contrast to the catalytic process,[63,64] these additives have no significant influence on the kinetics of the decomposition of sulphur dioxide. The concentration of carbonyl sulphide itself decreased very rapidly, with practically the characteristic decomposition time of pure CO, to a quasi-stationary level close to the quasi-stationary concentration of COS in the reaction without the addition of this product. The decomposition of COS under these conditions apparently takes place to a considerable extent independently of the reduction of sulphur dioxide and does not make a significant contribution to the rate of radical initiation. The decomposition of COS in the presence of only one of the original reagents, SO_2 or N_2 (a five-fold excess relative to COS) was about three times more rapid than that in the reaction being studied. In the mixture with SO_2, a simultaneous slow decrease in the concentration of sulphur dioxide was observed. This is apparently related to the reaction of SO_2 with carbon monoxide formed by the decomposition of COS, taking place more rapidly than the decomposition of COS. The decrease in the quantity of CO_2 corresponded approximately to the stoichiometry of the reaction of SO_2 and the CO formed. Attempts to detect CS_2 in the decomposition of COS were unsuccessful, that is the reaction

$$2COS \rightleftharpoons CO_2 + CS_2$$

takes place to only a small extent, and the principal reaction is

$$COS \rightleftharpoons CO + S.$$

The extent of the decomposition of COS under these conditions was greater than 95%. The decomposition of COS is much slower in the presence of CO than in the presence of SO_2 or N_2. This may be a consequence of the influence of CO on the back reaction. Only traces of CS_2, corresponding to not more than 3% of ΔCOS, were detected. The presence of CO in the original mixture explains the slower rate of decomposition of COS in the reaction being studied, compared with the decomposition of pure COS. The extent of the decomposition also decreases as a result of the displacement of the equilibrium. Overall it can be stated that the reaction of CO and SO_2 takes place with the formation of COS and is accompanied by the subsequent and to a large extent independent decomposition of COS, mainly by the second reaction. The influence of the starting materials on the decomposition of COS reduces mainly to the influence of CO on the displacement of the equilibrium by the back reaction.

The estimated activation energy of the decomposition of COS lies in the range 30–46 kcal mol^{-1}. Since this value is approximately half the energy of the removal of a sulphur atom from a COS molecule (73.7 kcal mol^{-1}), it has been suggested[59] that the decomposition takes place by a bimolecular mechanism *via* the formation of a linear complex

$$OC-S + S-CO \longrightarrow CO + S_2 + CO,$$

which is endothermic to the extent of about 40 kcal mol^{-1}. This mechanism of the decomposition would indicate that the fact that added COS has no influence on the reaction rate is due to the absence of atoms and radicals from the reaction products.

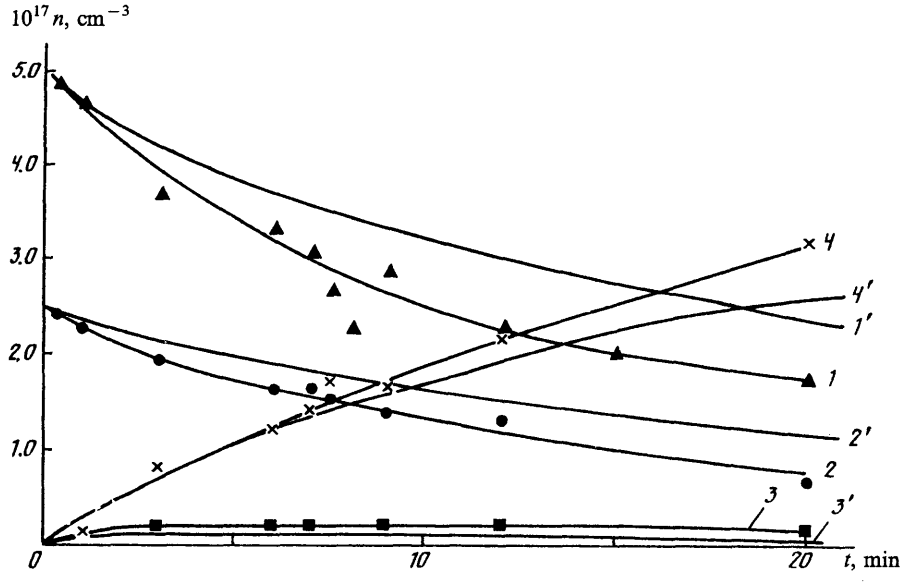


Figure 10. Kinetics of the change in the concentration (n) of the products of the reaction of sulphur dioxide with carbon monoxide at $CO:SO_2 = 2:1$ and $T = 1215$ K;[59] *1,1'*, CO; *2,2'*, SO_2; *3,3'*, COS; *4,4'*, CO_2; *1–4*, experiment; *1'–4'*, calculation.

Figure 10 gives the experimental kinetic curves for the reaction of sulphur dioxide with carbon monoxide. Attempts to detect the formation of other products, including S_2O, from infrared absorption at 679 cm^{-1} were unsuccessful. Only traces ($\leqslant 10^{15}$ cm^{-3}) of CS_2 were detected. Figure 10 also gives the results of calculations of the kinetics of this reaction using the kinetic model of the processes in the C–S–O system.[6] Satisfactory agreement was obtained between the experimental and calculated curves for all the observed products, confirming the reliability of the general model of the processes in the C–S–O system developed in the work cited.[6] Table 1[59] gives an abbreviated model of the reaction of CO and SO_2, obtained by selecting the most important reactions of the model[6] without introducing any changes to the values of their rate constants. Since the difference between calculations using the abbreviated scheme in Table 1 and calculations using the complete scheme does not exceed 15%, it can be stated that this simplified scheme gives the basic mechanism of the reduction of sulphur dioxide by carbon monoxide.

VI. The combined oxidation, photolysis, and radiolysis of carbon- and sulphur-containing compounds

The combined thermal oxidation, photolysis, and radiolysis of carbon- and sulphur-containing compounds is now being intensively studied. The aim of these studies is to find ways of processing sulphur-containing natural gas or purifying it from organosulphur compounds.

It has been shown that it is possible to carry out the chain thermal–radiation decomposition of hydrogen sulphide in the presence of carbon monoxide in the temperature range 60–650 °C;[68] the radiation-chemical yield of hydrogen $G(H_2)$ increased with increase in temperature, from 2 at 60 °C to 150 at 500 °C. According to the proposed scheme, carbon monoxide not only transfers excitation to the H_2S molecules but also reacts with the SH radical to give COS. Estimates[69] showed that it is possible to carry out the extensive purification of natural gas by the selective photodissociation of hydrogen sulphide by ultraviolet radiation to give hydrogen and elemental sulphur. This possibility was studied experimentally[70] in mixtures of hydrogen sulphide (0.5–10%) with CH_4, CO_2, and H_2 by irradiating with ultraviolet light with λ = 193 nm. Selective dissociation of H_2S took place down to concentrations lower than $10^{-3}-10^{-4}$ times the initial concentration. The formation of organosulphur compounds was not observed, and the concentration of methane remained unchanged. This result was attributed[70] to the small extent of the photodissociation of CH_4 and the low rate of the reactions of methane with the HS and S radicals formed by the photolysis of H_2S

$$HS + CH_4 \rightarrow H_2S + CH_3,$$
$$S + CH_4 \rightarrow HS + CH_3,$$

at $T < 600$ K. Because of their relatively low concentration, the reactions of S radicals with unsaturated compounds

$$S + C_2H_2 \rightarrow \text{products}$$

$$S + C_2H_4 \rightarrow \text{products}$$

have no significant influence on the purification process.

Experiments have been carried out on the combined incomplete oxidation of methane and hydrogen sulphide under static conditions at pressures of 350–440 torr and temperatures of 600–1000 K.[71] The process was carried out at concentrations of 0.3–10% hydrogen sulphide, 2.5–10% oxygen, and 5–90% methane (diluted with helium). The products were analysed from their infrared and

ultraviolet spectra (CH_4, H_2S, SO_2, CS_2, COS) and by chromatography (CH_3OH, C_2H_2, SO_2, and H_2O).

At temperatures of about 600 K it is possible to observe the kinetics of the consumption of H_2S and the accumulation of SO_2. In the absence of methane and with an excess of oxygen, practically all the H_2S is oxidised to SO_2. The presence of methane has little influence on the kinetics of the initial stage of the process, but the process becomes slower and stops at a certain residual stationary concentration of H_2S. Decrease in the oxygen concentration is accompanied by a decrease in the rate and extent of the oxidation of H_2S and the rate of formation and yield of SO_2, and by a decrease in the S_2/SO_2 ratio.

Table 1. Mechanism of the reduction of sulphur dioxide by carbon monoxide.[59]

Reaction	lg A, mol litre^{-1} s^{-1}	E, kcal mol^{-1}
$CO+SO_2 = CO_2+ SO$	9.78	55.0
$CO+SO = CO_2+ S$	9.78	10.9
$CO+S +M = COS+ M$	10.30*	1.8
$COS+M = CO+S+M$	11.28	64.0
$COS+SO = S_2 + CO_2$	8.40	8.3
$COS+S = CO + S_2$	9.23	4.0
$SO_2 + S = SO + SO$	9.78	16.8
$CO_2+S = CO + SO$	11.57	13.2

*mol^2 litre^{-2} s^{-1}.

With increase in temperature to 800 K there is a sharp increase in the rate of the decomposition of H_2S, and the SO_2 concentration passes through a maximum; both products reach stationary values of the concentration, which for H_2S correspond to half the initial value. At low concentrations (5%) of methane there is a slight decrease (~10%) in its concentration (Fig. 11). At a methane concentration of about 90% there is no change in its concentration within the accuracy of the measurements. The oxidation products contain an appreciable quantity of CS_2 and some COS; the concentrations of these products pass through a maximum when the stationary value of the concentration of SO_2 is reached. At the maximum the degree of transformation of H_2S into these products at $[H_2S] = [O_2] = [CH_4] = 10\%$ reaches the values $2CS_2/(H_2S)_0 \simeq 0.3$ and $COS/(H_2S)_0 \simeq 0.06$; the corresponding values for SO_2 and S_2 are about 0.3 and 0.35.

At even higher temperatures (900–1000 K) and concentrations $[H_2S] = [CH_4] = 10\%$ and $[O_2] = 5\%$, that is with a deficit of oxygen, H_2S decomposes completely ($t < 5$ s), but no formation of SO_2 is observed, that is the principal sulphur-containing product is now S_2.[71]

Depending on the ratio H_2S/O_2, two overall equations for the oxidation of hydrogen sulphide are possible:

$$2H_2S + O_2 \longrightarrow 2H_2O + S_2,$$
$$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2.$$

The fraction of hydrogen sulphide converted into sulphur dioxide naturally increases with the oxygen concentration. In the combustion of hydrocarbons containing a small quantity of sulphur compounds, practically all the sulphur is converted into SO_2.[16] Under the conditions of the work cited[71] in an excess of oxygen, the principal oxygen-containing product is again SO_2, but in the presence of methane the SO_2 formed is partly reduced to S_2 and even to H_2S, and this is a slower process than the actual oxidation of hydrogen sulphide (Fig. 11).

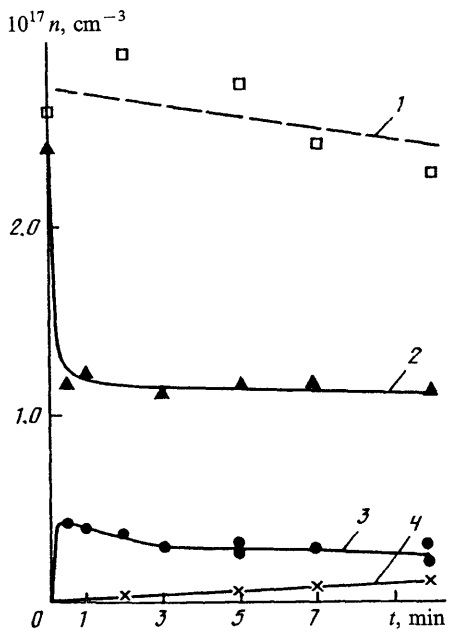


Figure 11. Kinetics of the oxidation of hydrogen sulphide in the presence of methane and the yield of products: *1*, CH_4; *2*, H_2S; *3*, SO_2; *4*, CS_2; T = 800 K, p = 440 torr, $[H_2S]$ = 5%, $[O_2]$ = 2.5%, $[CH_4]$ = 5%.[71]

Thus in the oxidation of methane containing a small quantity of hydrogen sulphide, the rapid partial oxidation of hydrogen sulphide to S_2 and SO_2, the ratio of which is determined by the oxygen concentration, is accompanied by the subsequent slower reduction by methane of the SO_2 formed to give S_2, and also by the reaction of S_2 with methane to give CS_2. It is only in a large excess of oxygen relative to hydrogen sulphide that almost complete transformation of H_2S with an almost 100% yield of SO_2 takes palce. The slow reduction of sulphur dioxide by methane (section III) limits the establishment of equilibrium in this system.

Figure 12 gives the dependence of the maximum rate of increase in the pressure W_{max} and the yield of products on the H_2S concentration. The presence of even 0.3% H_2S lowers the highest

reaction rate by a factor of 2, and 2% H_2S lowers it by a factor of about 4. The yield of methanol also decreases slightly.[71] Figure 13 gives the kinetics of the formation of the reaction products for a mixture containing 2% H_2S. In all the mixtures the concentration of methanol passes through a maximum. An interesting feature is that the transformation of H_2S is complete well before the end of the whole process.[17]

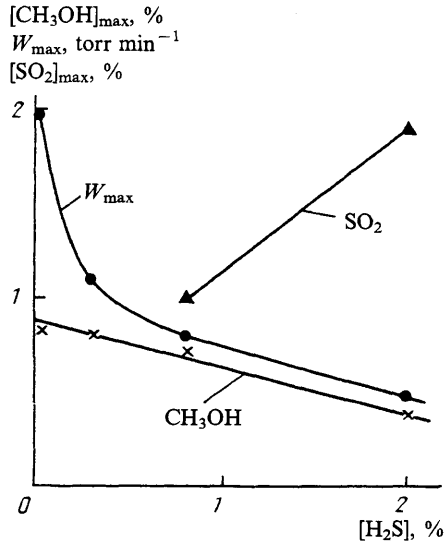


Figure 12. Dependence of the highest rate of oxidation of methane (W_{max}) and the highest yields of methanol [CH_3OH] and sulphur dioxide [SO_2] on the concentration of hydrogen sulphide; T = 723 K, p = 350 torr, [CH_4] = 80%, [O_2] = 10%, [H_2S] = 0.3–2%, remainder helium.[71]

Figure 12 shows that up to H_2S concentrations of 0.8% the highest concentration of methanol decreases by not more than 15%, indicating that it may be possible to use natural gas with a low sulphur concentration for its partial oxidation to methanol. Kinetic modelling of the incomplete oxidation of natural gas with a low sulphur concentration to give methanol at high pressures (100 atm) showed that in addition to a sharp decrease in the reaction time, even a slight increase in the yield of methanol can be expected. Even at a concentration [H_2S] $\simeq$ 1%, however, the conversion of hydrogen sulphide into sulphur dioxide is not complete. In view of the low reliability and incomplete nature of the kinetic data on the reactions of sulphur-containing compounds, however, it is difficult, without appropriate experimental studies, to evaluate the conclusions reached by modelling.

VII. The reaction of carbon- and sulphur-containing molecules in atmospheric processes

Sulphur is a relatively widespread element, and plays an important role in the circulation of the lithosphere and the atmosphere. On the earth's surface it is concentrated mainly in sulphide and sulphate ores, and in the ocean it is present mainly as dissolved sulphates. The principal sulphur-containing compounds in the atmosphere are sulphur dioxide, hydrogen sulphide, and other reduced compounds of sulphur, and also sulphate aerosols. Sulphur compounds do not accummulate in the atmosphere. Chemical cycles ensure a fine balance between the supply of sulphur to the atmosphere and its return to the earth's surface, although the increasing flux of sulphur originating from man's activities (207 million tons of SO_2 in 1976, 41.4% of the total supply of sulphur to the atmosphere[72]) is possibly displacing this equilibrium slightly.

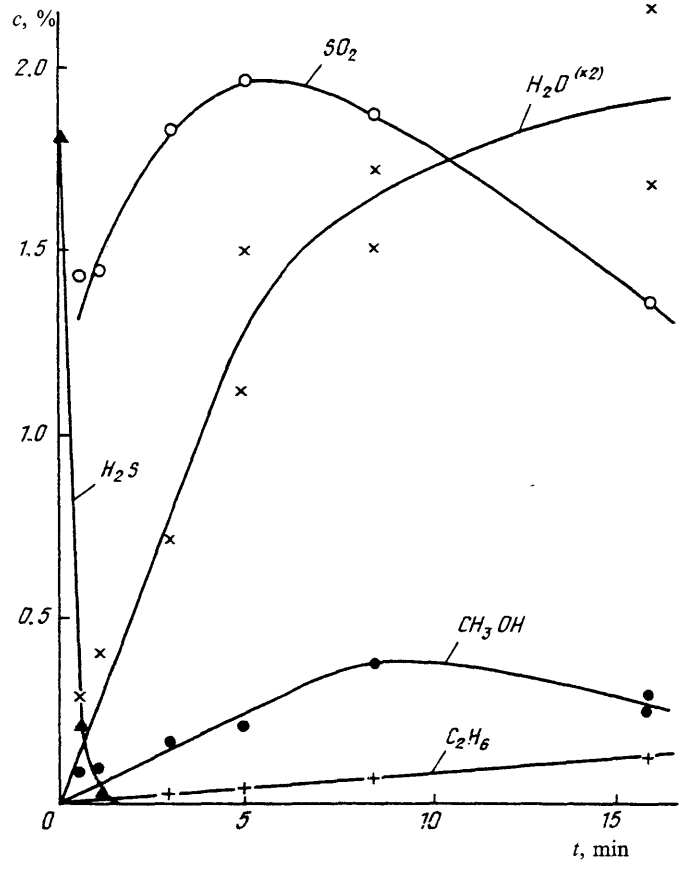


Figure 13. Kinetics of the formation of the products of the oxidation of methane in the presence of added hydrogen sulphide; T = 723 K, p = 350 torr, [CH_4] = 80%, [O_2] = 10%, [He] = 8%, [H_2S] = 2%.[71]

Most of the carbon in the atmosphere is present as carbon dioxide (~340 p.p.m.), methane (1.6–1.7 p.p.m.), and carbon monoxide (0.04–0.20 p.p.m.).[1]

Reduced carbon- and sulphur-containing molecules, whose concentration in the atmosphere is low, are oxidised mainly by

hydroxyl radicals to give finally carbon dioxide and more highly oxidised compounds of sulphur

$$OH + COS \rightarrow CO_2HS,$$
$$OH + COS \rightarrow CO + SOH,$$
$$OH + CS_2 \rightarrow COS + HS,$$
$$OH + CS_2 \rightarrow CS + SOH,$$
$$OH + CH_3SCH_3 \rightarrow \text{products}.$$

The photolysis of these compounds in the troposphere plays a relatively minor role. The hydroxyl radical is also involved in the conversion of SO_2 into H_2SO_4.

Methane also reacts initially with the hydroxyl radical to give methyl radicals

$$CH_4 + OH \longrightarrow CH_3 + H_2O,$$

which are then oxidised by O_2 in a series of reactions to give formaldehyde, whose subsequent photolysis gives carbon monoxide. Carbon monoxide from this source, and carbon monoxide entering the atmosphere directly, is oxidised further by OH radicals in a cyclic series of reactions, beginning with the reaction

$$CO + OH \longrightarrow CO_2 + H,$$

giving CO_2 as the final product. In the troposphere, about 70% of the OH radicals are used up in the reaction with CO, and 30% in the reaction with CH_4. Both processes give peroxide radicals:

$$H + O_2 + M \longrightarrow HO_2 + M,$$

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M,$$

which can react with sulphur dioxide:

$$ROO + SO_2 \longrightarrow RO + SO_3,$$

whose concentration in the atmosphere reaches about 1.1×10^{-10}.[1] If the rate constant of the reaction

$$CH_3OO + SO_2 \longrightarrow CH_3O + SO_3$$

were about $(5-10) \times 10^{-15}$ $cm^3 molecule^{-1} s^{-1}$, as has been reported,[73,74] it might play a decisive role in the sulphur cycle. Later work,[75,76] however, gave a much lower value for the rate constant of this reaction (5×10^{-17} $cm^3 molecule^{-1} s^{-1}$), so that this reaction apparently does not play a significant part in the sulphur cycle.

Among the reduced compounds of sulphur, entering the atmosphere mainly from the ocean surface, a relatively important part in the global sulphur cycle is played by organosulphur compounds, primarily dimethyl sulphide CH_3SCH_3, which annually supplies about 40 million tons of sulphur to the atmosphere.[77] Recently, therefore, considerable attention has been paid to the mechanism of the oxidation of dimethyl sulphide, dimethyl disulphide CH_3SSCH_3, and other organosulphur compounds in the atmosphere.[77,78] As in the case of other reduced compounds of sulphur, the principal chemical process responsible for the decomposition of CH_3SCH_3 and CH_3SSCH_3 in the atmosphere is their reaction with OH, and the principal product of the complex processes involved in their atmospheric oxidation is SO_2.[78]

The reaction of carbon- and sulphur-containing molecules may play a much greater role in the atmospheres of planets such as Venus, where the concentrations reach 96.5% CO_2, 0.003% CO, and 0.015% SO_2.[1] They apparently play a predominant role in the region of the atmosphere of Venus below the cloud layer. In view of the high temperatures (732 K on the surface of Venus) and pressures (90 atm) and the proximity of the surface, which catalyses the approach to equilibrium, it may be assumed in a first approximation that the thermodynamically equilibrium composition, perturbed by vertical transport processes, is established in this region. This equilibrium is apparently in fact established at the surface, but with increase in the distance from the surface the equilibrium begins to break down to a considerable extent, increasing the part played by kinetic processes in the formation of the composition of the atmosphere. As a result, the ascending and descending streams apparently have different chemical compositions. The ascending streams contain components originating in Venus' crust (for example COS, S_2, H_2S, etc.), and the descending streams contain the products of photolysis in the upper cloud layer (SO_3, Cl_2, O_2, etc.). On the surface, chemical equilibrium is apparently established for all the gases except CO and O_2, which in the tropospheres are not in equilibrium with one another or with the COS/SO_2 system.[1] The next most important elementary stages, beginning with the formation of SO, can describe the interconversion of various components:

$$SO_2 + CO \longrightarrow SO + CO_2, \qquad CO + S + M \longrightarrow COS + M,$$
$$SO + CO \longrightarrow S + CO_2, \qquad S + COS \longrightarrow S_2 + CO,$$
$$SO + SO_2 \longrightarrow S + SO_3, \qquad SO + COS \longrightarrow S_2 + CO_2.$$

Spectroscopic data obtained by cosmic probes confirm indirectly the presence of S_2, S_3, and subsequent oligomers of sulphur S_x up to the stable S_8.[1] The photo-dissociation of these molecules

$$S_x + h\nu \longrightarrow S^* + S_{x-1}$$

may be the source of excited S* atoms capable of reacting with molecules of water and carbon dioxide

$$S^* + H_2O \longrightarrow SH + OH,$$
$$S^* + CO_2 \longrightarrow SO + CO.$$

Excited atoms and molecules play an important part in the chemistry of the atmosphere. In particular, the reaction of excited molecules of sulphur dioxide with hydrocarbons may play an important role in the formation of sulphur-containing aerosols in industrial regions with a relatively high atmospheric concentration of hydrocarbons and sulphur dioxide. The high bond energy in the SO_2 molecule practically excludes the dirct photo-dissociation of this molecule in the atmosphere, and also all other reactions except further oxidation.[79] The formation of excited SO_2^* molecules in the atmosphere may open up alternative pathways in the reaction of SO_2 with carbon-containing molecules. It has been reported[80] that a large quantity of sulphur-containing products is formed when an air/sulphur dioxide/butane mixture is irradiated.

A study of the photochemical reactions in mixtures of SO_2 with alkanes on irradiation with light with $\lambda = 3130$ Å[81] showed the absence of processes involving the rupture of C–C bonds, since the products of the photolysis of SO_2 with isobutane and n-butane did not contain methane, ethane, or propane. A small quantity of C_8 hydrocarbons was detected. Only traces of oxygen-containing compounds—alcohols, aldehydes, and ketones—were detected. The principal products include sulphinic acids RS(=O)OH and other organic acids. Their low quantum yield and the low yields of hydrogen and the products of the recombination and disproportionation of alkyl radicals show that the reaction of SO_2 with RH does not involve radical chain reactions. For the most part the mechanism of the reaction of excited SO_2^* with hydrocarbons remains unclear.

A more obvious process is the reaction of SO_2^* with carbon monoxide

$$SO_2^* + CO \longrightarrow CO_2 + SO,$$

where the spin-allowed character of the formation of SO in the triplet ground state $X^3\Sigma^-$ and the excess excitation energy make the reaction in this direction possible, although the low quantum yield shows that the removal of oxygen, even from the excited SO_2^* molecule, is difficult[81] and still requires an activation energy of 4 kcal mol^{-1}.[82]

Calvert and co-workers carried out a series of studies of the reaction of the triplet excited molecules $SO_2(^3B_1)$ with alkanes,[83,84] alkenes, and aromatic hydrocarbons.[85,86] The activation energy of the quenching of $SO_2(^3B_1)$ by paraffinic hydrocarbons decreases regularly in the order: ethane, neopentane, propane, n-butane, cyclohexane, and isobutane, which corresponds to the decrease in the strength of the C–C bond in the molecule. These and other data indicate that for these compounds chemical quenching, probably involving the removal of a hydrogen atom, predominates. The rate constants of the quenching of $SO_2(^3B_1)$ by alkenes and aromatic hydrocarbons depend little on temperature and correspond closely to the number of binary collisions. These data confirm the hypothesis that the initial act of the reaction, determining the rate of the process, is the reaction between $SO_2(^3B_1)$ and the π-system in these compounds. The subsequent addition of $SO_2(^3B_1)$ to the double bond of the alkene gives a triplet biradical as an intermediate complex,[83] as in the reaction of $O(^3P)$ atoms with alkenes.[87] The principal stable products of the reaction of $SO_2(^3B_1)$ with alkenes are sulphinic acids, formed with an efficiency of 0.14–0.5 per collision.[85]

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The practical importance of the chemical reactions of carbon- and sulphur-containing compounds requires a deeper understanding of the kinetics of these reactions. New data in this field may lead to the improvement of a number of processes of technical importance.

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