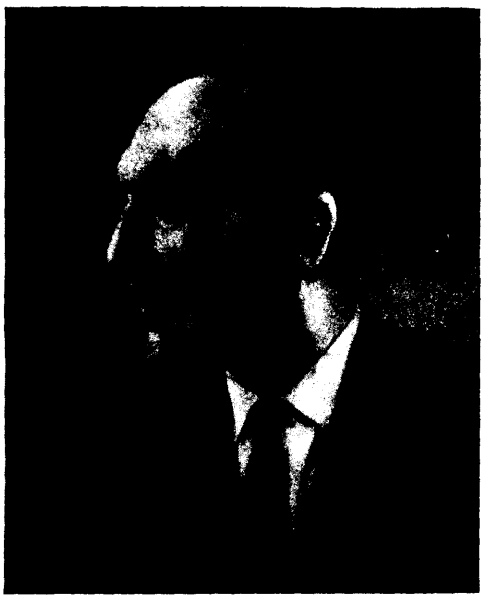
RUSSIAN CHEMICAL REVIEWS
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NIKOLAI NIKOLAEVICH SEMENOV

Dear Nikolai Nikolaevich,

The whole Soviet scientific community, all chemists in our great Motherland warmly greet and congratulate you on the day of your glorious anniversary.

Your fundamental discoveries in the fields of chain reactions, of combustion, and of explosive processes have deservedly brought you world-wide recognition.

You won the deep gratitude of the Soviet peoples as an untiring propagandist for and organiser of science. Throughout your brilliant life you have been a convinced and staunch champion of the unity of theory and practice.

It is gratifying to realise that you come to your jubilee in the prime of your creative powers and your untiring talent for scientific organisation.

Together with all Soviet scientists the Editorial Board of the journal "Uspekhi Khimii" sends you its greetings and most sincere wishes for health and ever new successes in your many-sided activities.

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STUDY OF THE KINETICS AND MECHANISM OF BRANCHED CHAIN REACTIONS IN THE GAS PHASE

A. B. Nalbandyan

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I. INTRODUCTION

The present Review gives a brief account of the principal results obtained in investigations, conducted mainly at the Institute of Chemical Physics of the USSR Academy of Sciences during the past five to six years, in the field of branched chain reactions, the theory of which has been developed by Semenov. Thanks to the powerful research tools which have appeared comparatively recently — electron spin resonance (e.s.r.), electronic computers, etc. — it has become possible to undertake a broad testing of the mechanisms which have been suggested for complex chemical processes and to study new systems in which, with rare exceptions, it had not been possible to establish the nature of the active species responsible for the development of the chain processes.

Forty years ago Semenov and his students at the Leningrad Physicotechnical Institute, in a study of the quenching of the luminescence of the combustion products from a mixture of phosphorus vapour and oxygen, observed the remarkable phenomenon of lower and upper limits of spontaneous combustion. During 1926–1930 the phenomenon of ignition limits was discovered also in sulphur vapour–oxygen, carbon monoxide–oxygen, and hydrogen–oxygen mixtures[1-8]. Investigations showed that practically no reaction took place below the lower or above the upper limit. It was sufficient, however, to raise slightly the pressure of the mixture near the lower limit, or lower it when above the upper limit, for the mixture to ignite instantly. The investigators noticed that the lower and upper limits possessed unusual properties. For example, the lower pressure limit is lowered by increasing the diameter of the vessel. Under identical conditions, dilution of the reactant mixture with an inert gas results in a fall in the limiting pressure of the combustible mixture. In other words, a mixture which does not inflame at a given pressure immediately ignites if an inert gas is added to it. On the other hand, the partial pressure of the reactant mixture at the upper limit falls sharply if it is diluted with an inert gas. All these and many other phenomena discovered at the same time and later do not fit into the framework of classical chemical kinetics.

In order to explain these astonishing phenomena, Semenov[2-9] put forward a theory of chain branching in chemical reactions, according to which the combustion of a gaseous mixture involves the direct participation of atoms and free radicals, the so-called active centres or chain carriers. Atoms and radicals react with the starting materials to form the final product and a new active particle. The latter again reacts, to give the reaction product and an atom or a free radical as new active particle. In this way an unbranched chain reaction arises and is propagated in the gas mixture, a phenomenon known since the discovery of the photochemical chlorination of hydrogen by Bodenstein[10]. The ignition of fuel mixtures is due to the branching of chains, i.e. to the appearance from time to time, at some link or links in the developing chains, of more than one active particle. These additional active centres also become centres of new chains. As a result, an avalanche-like increase in the number of active centres occurs in the system after a brief interval, and hence also in the reaction velocity, which we perceive as ignition. Mathematical analysis of the growth in the number of active particles in the reactant mixture shows that in this case the increase obeys the law $N = N_0 e^{\varphi t}$, where φ is a positive quantity.

The lower and upper limits of spontaneous ignition observed experimentally by Semenov were explained by the destruction of active centres or chain carriers. According to Semenov's theory, the lower limit is associated with heterogeneous destruction of chains, and the upper limit with their homogeneous destruction. This theory provided a quantitative description of the experimentally observed ignition limits and their properties.

According to the theory of the limits, absence of ignition is explained by the rate of destruction of active centres on the walls or in space exceeding the rate of branching. Ignition occurs only when the rate of branching of chains is greater than the rate of destruction of active centres. The lower ignition limit is determined by equality of rates of branching and of heterogeneous destruction of active centres, and the upper limit by equality of the rates of branching and of homogeneous destruction of chain carriers. The experimentally observed decrease in the lower pressure limit with increase in diameter of the reaction vessel and with dilution of the mixture by an inert gas are brilliantly explained by Semenov's theory of the limits. With a reaction vessel of larger diameters, the average time taken by an active particle to diffuse to the walls of the vessel is longer, and consequently the probability is higher of its entering into new branching reactions before destruction on the walls. Additions of an inert gas should act similarly to an increase in pressure. With dilution of the reactant mixture, the mean residence time of an active centre in free volume increases, since diffusion is slower. The decrease in the partial pressure of the reactant mixture at the second limit and the second limit itself are well and quantitatively explained by the theory of branched chain processes on the assumption that in space an active centre is destroyed in a three-body collision[9,11], while the branching reaction is bimolecular. The rate of branching will then increase in proportion to the pressure of the reactant gas, while the rate of termination will increase according to the square of the pressure. With rise in pressure, these rates can obviously become equal when the pressure reaches a certain value, and above this pressure the mixture will cease to ignite. When part of the reactant gas is replaced by an inert gas, the number of three-body collisions remains constant, while the rate of branching falls. For this reason ignition ceases at a lower partial pressure of the reactant gases as the pressure is raised.

Semenov's theory of branched chain processes very soon obtained world-wide acceptance. An immense number of papers appeared, in which numerous examples were given of reactions occurring by a branched chain mechanism. It became evident that chain reactions are not rare exceptions. An urgent need therefore arose for a detailed study of the kinetics and mechanism of chain processes. It was obvious that the conscious control of a chemical process was indissolubly linked with a knowledge of the detailed mechanisms of actual chain reactions. Thus in 1930 a second important period began of further development and testing of the theory of chain reactions. In the study of the mechanism of complex chemical processes, each comprising the aggregate of a series of elementary reactions of atoms and free radicals with the starting materials and intermediate products, the question first arises of the nature and reactivity of the active particles responsible for development of the process.

At the outset of the development of the theory of branched chain reactions, the combustion of hydrogen provided the

example on which a quantitative check of the theory came to be made. This reaction, while being less complicated than others, nevertheless possessed many features in common with other complex reactions.

As a result of the great efforts made by investigators in various countries, the following most probable mechanism became generally accepted for the combustion of hydrogen at pressures not exceeding atmospheric

$$H_2+O_2 \rightarrow 2OH, \quad (0)$$

$$OH+H_2 \rightarrow H_2O+H, \quad (1)$$

$$H+O_2 \rightarrow OH+O, \quad (2)$$

$$O+H_2 \rightarrow OH+H, \quad (3)$$

$$H \xrightarrow{walls} {}^1/_2 H_2, \quad (4)$$

$$O \xrightarrow{walls} {}^1/_2 O_2, \quad (5)$$

$$H+O_2+M \rightarrow HO_2+M, \quad (6)$$

$$OH \xrightarrow{walls} {}^1/_2 H_2O_2. \quad (7)$$

It is assumed in this scheme that hydrogen and oxygen atoms and the hydroxyl radical are the active centres responsible for chain propagation and branching in mixtures of hydrogen and oxygen, i.e. for reactions (1)–(3).

Much was done by workers to prove that these active species were involved in the combustion of hydrogen. Indirect evidence of their important role is provided by experiments on the action of hydrogen and oxygen atoms on the range of ignition of hydrogen–oxygen mixtures and on the length of the induction periods preceding ignition.

It was shown in the Institute of Chemical Physics of the USSR Academy of Sciences that the effect of hydrogen atoms is to raise the upper limit of spontaneous ignition, while the range of ignition is displaced to lower temperatures [12]. The action of oxygen atoms is far stronger. In the presence of high concentrations of oxygen atoms, produced in an electric discharge, an upper limit cannot be detected. The ignition temperature of the reactant mixture falls from 400°C to room temperature [13]. It was also established [14] that the induction period preceding ignition is markedly shortened under the influence of hydrogen and oxygen atoms.

A great success of the theory of branched chain reactions was provided by the direct experimental proof of the formation of high concentrations of hydroxy-radicals in low-pressure flames of hydrogen with oxygen. Using the method of line absorption spectroscopy [15], Kondrat'ev and his collaborators [16-18] showed that, in a low-pressure hydrogen–oxygen flame at pressures somewhat exceeding that at the lower limit, the concentration of hydroxy-radicals is several thousand times as great as the equilibrium value under the conditions of the flame. Avramenko's investigations [18] showed that the reaction velocity, determined from the quantity of water formed, varies linearly with the total concentration of hydroxy-radicals.

Experimental results obtained in this work were used to determine the rate constant of reaction (1), which was

$$k_1 = 7\times10^{-12}\sqrt{T}\,e^{-\frac{10\,000}{RT}} \text{ cm}^3\,\text{s}^{-1}\,\text{mol.}^{-1},$$

Semenov [19] estimated the rate constant k_2 of the branching reaction (2) from Koval'skii's data [20]. Its activation energy was close to 18 kcal. The activation energy of reaction (3) was estimated as 6 kcal from experimental data obtained by Harteck and Kopsch [21] for two temperatures in a study of the interaction of atomic oxygen with hydrogen. The latest, more accurate data of Azatyan et al. [22] give values for the rate constants of the elementary reactions (2) and (3) of respectively

$$k_2 = 1.3\times10^{-10}e^{-\frac{15\,900}{RT}} \text{ cm}^3\,\text{s}^{-1}\,\text{mol.}^{-1}$$

$$k_3 = 1.1\times10^{-10}e^{-\frac{11\,700}{RT}} \text{ cm}^3\,\text{s}^{-1}\,\text{mol.}^{-1}.$$

According to the scheme given above for the combustion of hydrogen, the rates of reactions (1)–(3) are respectively

$$w_1 = k_1[OH][H_2];\ w_2 = k_2[H][O_2];\ w_3 = k_3[O][H_2].$$

For one intermediate temperature near which investigations are usually made, e.g. for $T = 600°$, the ratios of the rate constants can be written in the form

$$k_1[H_2]:k_2[O_2]:k_3[H_2] = \frac{k_1[H_2]}{k_2[O_2]}:1:\frac{k_3[H_2]}{k_2[O_2]} = 46\frac{(H_2)}{(O_2)}:1:7.6\frac{(H_2)}{(O_2)}.$$

For hydrogen-rich mixtures, e.g.

$$[H_2]:[O_2] = 9:1\quad k_1[H_2]:k_2[O_2]:k_3[H_2] = 415:1:68.$$

This means that the inequality

$$k_2[O_2] \ll k_3[H_2] \ll k_1[H_2]$$

should hold in very hydrogen-rich mixtures with oxygen.

The reciprocals of the rate constants

$$\frac{1}{k_1[H_2]};\quad \frac{1}{k_2[O_2]}, \text{ and } \frac{1}{k_3(H_2)},$$

measure the life of the corresponding active centres from the moment at which they appear until they undergo fresh reactions. Hence $t_H \gg t_O \gg t_{OH}$, where t is the life of the corresponding active species. From this inequality it follows that, in very hydrogen-rich mixtures, the concentration of hydrogen atoms should considerably exceed those of oxygen atoms and hydroxy-radicals. In an equimolecular mixture [H] > [O] > [OH]. In an $[H_2]:[O_2] = 1:9$ mixture, [O] > [H] > [OH].

Assuming the above mechanism as a basis, Semenov [23,24] studied in 1943 the kinetics of the burning of hydrogen-rich mixtures with oxygen at pressures somewhat exceeding that at the lower limit of spontaneous ignition. The investigations showed that under these conditions only the variation in the concentration of hydrogen atoms and their destruction on the walls of the reaction vessel need be taken into account. Changes with time in the concentrations of oxygen atoms and hydroxy-radicals can be neglected, since their concentrations are far lower than that of the hydrogen atoms. Simultaneous solution of the equations for time variation in the concentrations of atomic hydrogen and of one of the starting materials — oxygen — led Semenov to the important conclusion that large quantities of hydrogen atoms are formed in a low-pressure flame, the relative concentration of which may in some cases reach more than 20% of the initial hydrogen.

This cardinal conclusion of the theory was confirmed by experiments made by Kondrat'eva and Kondrat'ev [25], who used a thermoelectric probe method to detect hydrogen atoms and measure their concentration. Two fine thermocouples in very narrow thin-walled quartz sheaths were placed in a stationary low-pressure flame obtained under flow conditions. On the tip of the sheath of the first thermocouple was deposited a layer of $ZnOCr_2O_3$, a substance on which hydrogen atoms recombine at every collision. The tip of the second thermocouple was washed

with nitric acid, in order to minimise the recombination of atoms striking the surface. This thermocouple served to measure the flame temperature. These workers recorded temperature differences in the flame reaching under certain conditions 300 deg. This difference was obviously associated with the heat of reaction of atoms and radicals vigorously recombining on the surface of the thermocouple coated with $ZnOCr_2O_3$. From the equation which they deduced to link ΔT with the relative concentration ξ of hydrogen atoms, Kondrat'eva and Kondrat'ev obtained ξ = = 0.45. This value agrees very well with ξ = 0.51 calculated by means of Semenov's formula. It followed from the excellent agreement between the theoretical conclusions and experiment that, in very hydrogen-rich mixtures with oxygen, the lower ignition limit should be determined mainly by the two reactions of atomic hydrogen — the branching reaction $H + O_2 \rightarrow OH + O$ (2) and the loss of hydrogen atoms on the walls of the reaction vessel (4) — for the loss of oxygen atoms and hydroxy-radicals on the walls can be neglected under these conditions.

After 1930 it was increasingly remarked that the lower limit of spontaneous ignition depends not only on the diameter of the reaction vessel and on inert additions but also on the surface state and nature of the material of the reaction vessel[26-30]. This was allowed for in the theory of the lower limit by introducing a new parameter ϵ, the coefficient of recombination of active particles on the surface[31-33]. Variation in ϵ with surface state and material could be explained by the experimentally observed hundredfold variation in the pressure at the lower limit. At the same time several communications appeared in the literature[34,35] on the very strong action on the lower limit of thin metallic rods placed coaxially in the reaction space. The theory of this phenomenon was given by Semenov[33], who, on the hypothesis of an intense destruction of active centres on the surface of the thin rods, obtained an equation enabling the coefficient of recombination of the active centres to be linked with the lower limit and the diameters of reaction vessel and rod. The action of the thin rods on the lower limit of a stoichiometric mixture of hydrogen and oxygen was used[36] to determine the recombination coefficients of the active species. For this purpose thin rods ($d \simeq 0.1$ cm) of various substances were introduced by means of a movable electromagnet into a reaction vessel which had first been treated with $K_2B_4O_7$ (a substance on which recombination of hydrogen atoms is very poor), and the lower limits were determined in the absence and in the presence of the rods. The apparatus used is shown diagrammatically in Fig. 1. The ignition limit in these experiments was determined by rapidly admitting the mixture from the subsidiary volume B into the reaction vessel A. The rods were introduced and withdrawn by means of the movable electromagnet.

The results in Table 1 for a vessel having d = 1.83 cm show that the lower limit is raised to the greatest extent in

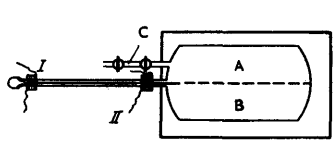


Fig. 1. Diagram of apparatus for studying the effect of rods on the lower ignition limit: A) reaction vessel; B) subsidiary vessel; C) electric furnace; I) and II) positions of rod.

TABLE 1.

Material of rod	Diameter of rod, cm	Temp., °C	Lower limit, mmHg, in vessel	
			without rod	with rod
Stainless steel	0.1	440	0.94	7.0
Gold	0.05	440	0.94	8.2
Tungsten	0.145	540	0.32	4.0
	0.1	440	0.53	10.3
Graphite	0.1	490	0.53	10.3
	0.1	530	0.42	7.8
	0.1	558	0.30	6.5
Quartz	0.1	440	0.94	2.34
Quartz washed with HF soln.	0.1	440	0.94	1.48

the presence of rods coated with $ZnOCr_2O_3$ and made of graphite. The experimental data in Table 1 and the corresponding equations deduced on the basis of Semenov's theory were used to calculate the recombination coefficients ϵ of active particles on the surfaces investigated. The calculated results in Table 2 show that, depending on the material and state of the surface, the recombination coefficient may vary by factors of 10^4. The substances investigated can be arranged in a sequence according to their activity towards the recombination of active particles. The first place in this sequence is occupied by $ZnOCr_2O_3$ and graphite, which are followed by gold, platinum, tungsten, stainless steel, quartz which has been washed with HF solution, and finally Pyrex which has been treated with HF solution. In 1924 Bonhoeffer[37] studied the recombination of atomic hydrogen on various metals, and arranged the latter in the sequence — platinum, palladium, tungsten, iron, etc. — according to their activity. A comparison of this sequence with that obtained from experiments on the effect of the rods on the lower limit of ignition of hydrogen-rich mixtures with oxygen provides information on the identity of the recombining species.

An interesting phenomenon which clearly demonstrates the branched chain character of the combustion of hydrogen is that, if a hydrogen–oxygen mixture is transferred to a reaction vessel in which a graphite or other rod has previously been placed, ignition may be observed provided that the pressure of the mixture is higher than that of the lower limit p_1 in the presence of the rod. At pressures $p < p_1$ ignition does not occur: the mixture ignites only when the rod is withdrawn from the vessel. A rod placed in a reaction vessel may be likened to a powerful pump, which extracts all the hydrogen atoms from the reaction zone. On removal of the rod, the concentration of atomic hydrogen increases very rapidly, and the mixture ignites. By placing in the reaction vessel a series of rods of varying efficiency in bringing about the recombination of hydrogen atoms, it was possible to ignite the same mixture several

TABLE 2. Recombination coefficients of atomic hydrogen on various surfaces.

Material of rod	T, °C	ϵ_H
$ZnOCr_2O_3$	490	1.0
Graphite	490	1.0
Gold	440	$9.8 \cdot 10^{-2}$
Platinum	388	$8.9 \cdot 10^{-2}$
Tungsten	540	$5.7 \cdot 10^{-2}$
Stainless steel	440	$2.8 \cdot 10^{-2}$
Quartz	440	$5 \cdot 10^{-4}$
Quartz washed with HF soln.	440	$3 \cdot 10^{-4}$
Pyrex washed with $K_2B_4O_7$ soln.	440	$1.9 \cdot 10^{-5}$

times by successively withdrawing rods from the reaction zone. The method described here of controlling the ignition of gaseous mixtures by means of rods strongly recalls the control of the radioactive disintegration of uranium nuclei by means of cadmium rods or boron steel rods, which strongly absorb fission neutrons. This analogy does not appear fortuitous when it is remembered that the above reaction of the combustion of hydrogen and the nuclear disintegration of uranium are both branched chain processes.

II. STUDY OF THE KINETICS AND MECHANISM OF THE COMBUSTION OF HYDROGEN AND CARBON MONOXIDE BY THE e.s.r. METHOD

1. Kinetics and Mechanism of the Combustion of Hydrogen at Low Pressures

The possibility of identifying directly all types of active centres involved in chain propagation in the oxidation of hydrogen, and of measuring their absolute concentrations, has appeared comparatively recently, after the discovery of the phenomenon of electron spin resonance (e.s.r.)[38] and construction of the appropriate instruments[39]. A great advantage of the e.s.r. method is that it permits the detection, without disturbance to the course of the reaction, not only of atoms but also of many radicals. The method was first used in the study of gas-phase chemical reactions, by Panfilov et al.[40] in the Institute of Chemical Physics of the USSR Academy of Sciences in 1960. They examined a low-pressure flame in hydrogen–oxygen mixtures with the aim of detecting atomic hydrogen and measuring its concentration. For this purpose they used the flow technique illustrated diagrammatically in Fig. 2. The low-pressure flame was established in a quartz tube *1* heated by the electric furnace *3*, placed directly above the EPR-12 cavity *2*. At pressures slightly exceeding that of the lower limit these workers found, in full agreement with Semenov's conclusions, immense concentrations of atomic hydrogen, which under certain conditions reached 10–15% of the initial hydrogen. Subsequently Panfilov[41] made a detailed study of the kinetics of the combustion of hydrogen as a function of the composition of the mixture. By measuring directly the concentration of hydrogen atoms and the variation in the concentration of molecular oxygen during the reaction, he showed that the rules deduced by Semenov, neglecting the wall destruction of oxygen atoms and hydroxy-radicals on the surface of the reaction vessel in hydrogen-rich mixtures, were completely satisfied.

The technique of using e.s.r. to study gas reactions has recently been considerably improved. It has become possible[42,43] to investigate low-pressure flames directly inside the e.s.r. cavity. Platinum wires (d = 0.2 mm) arranged along the walls of the reaction vessel and enclosed in a quartz sheath have been used to heat the reaction mixture. Such a reaction vessel, when placed inside an e.s.r. cavity, has hardly any effect on the Q factor of the latter, although the sensitivity of the instrument is slightly diminished. Tubes of larger diameter have come to be used[44], which enables flames to be obtained at lower pressures.

Using a reaction vessel heated with platinum filaments[43] and placed in an e.s.r. cavity, Balakhnin et al.[45] were in 1964 the first to observe the e.s.r. spectrum of oxygen atoms in a low-pressure hydrogen–oxygen flame (at 580° and 6 mmHg). The concentration of atomic oxygen proved to be very high. It depended greatly on the composition of the mixture. In a mixture containing ~ 15% of hydrogen and 85% of oxygen, atomic oxygen represents about 5% of the total pressure or 0.3 mmHg. The investigations showed that the concentration of oxygen atoms, while being greatest in oxygen-rich mixtures, fell as hydrogen was added. In an equimolecular mixture the concentrations of oxygen and hydrogen atoms are comparable, and in hydrogen-rich mixtures the concentration of hydrogen atoms far exceeds that of oxygen atoms. The first qualitative result obtained is fully consistent with conclusions drawn from an examination of the ratio of the kinetic constants described in the Introduction to the present Review.

In the same year 1964 Balakhnin et al.[46], employing a quartz reaction vessel with an absorbing cell completely filling the cavity, observed higher concentrations of hydroxy-radicals in low-pressure hydrogen–oxygen flames. Work with a new design of absorbing cell has shown[47-50] that the microwave absorption spectrum of hydroxy-radicals is due to electric dipole transitions, the intensity of which exceeds by several orders of magnitude that of the usual e.s.r. lines caused by magnetic dipole transitions. The concentration [configuration (?) (Ed. of Translation)] of the absorbing cell used enabled not only hydroxy-radicals but also hydrogen and oxygen atoms to be detected, since it covers antinodes both of magnetic and of electric components of the ultrahigh-frequency (UHF) field.

Fig. 3 gives the e.s.r. spectra of H and O atoms and OH and OD radicals recorded in low-pressure hydrogen–oxygen and deuterium–oxygen flames.

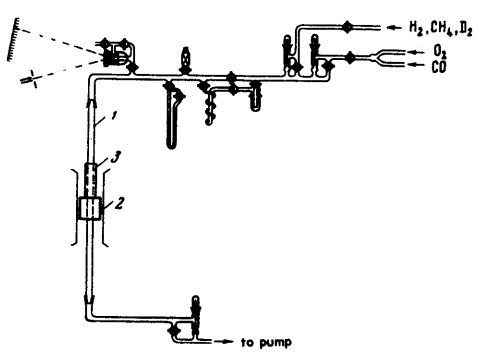


Fig. 2. Diagram of flow apparatus for the e.s.r. study of low-pressure flames.

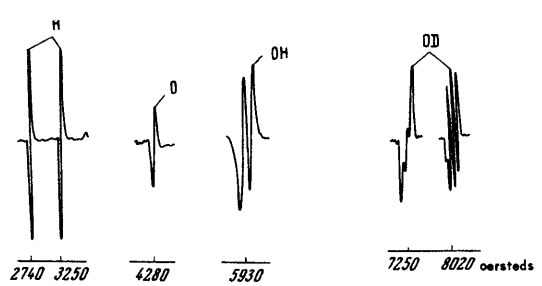


Fig. 3. Electron spin resonance spectra of H and O atoms and of OH and OD radicals obtained in low-pressure H_2–O_2 and D_2–O_2 flames.

The first stage has recently been completed[51] of investigations on the measurement of the absolute concentrations of hydrogen and oxygen atoms and hydroxy-radicals in low-pressure hydrogen–oxygen flames as functions of the composition of the mixture. In Fig. 4 the concentrations of hydrogen and oxygen atoms are plotted on the same scale, while for hydroxy-radicals the scale has been increased hundredfold. Fig. 4 also shows the variation in the quantity of water formed. The first striking feature is the parallelism between the curves for the variation in the concentration of hydroxyl and water, which pass through a maximum in the vicinity of the equimolecular composition. As noted in the Introduction, proportionality between the total concentration of hydroxyl and the quantity of water formed was at one time established by Avramenko. Such a relation arises directly from the mechanism of the oxidation of hydrogen, according to which the reaction velocity is given by the formula $w = k_1[OH][H_2]$. As was to be expected, the contribution of reaction (7), the destruction of hydroxyl on the walls, is negligible.

Fig. 4 shows that the concentration of atomic oxygen is a maximum for a mixture containing about 20% of hydrogen and 80% of oxygen. As the reactant gas is enriched with hydrogen, the concentration of oxygen atoms drops sharply. In a mixture containing 80% of hydrogen and 20% of oxygen, the concentration of oxygen atoms is $\sim 10^{14}$ cm^{-3}, while that of atomic hydrogen in this mixture is a maximum, amounting to approximately 1.3×10^{16} cm^{-3}, which exceeds the concentration of oxygen atoms by a factor of > 100. On replacement of part of the hydrogen by oxygen, the concentration of hydrogen atoms falls linearly. At the point corresponding to 20% H_2 + 80% O_2 the concentration of oxygen atoms exceeds that of hydrogen atoms by more than 50%. In an equimolecular mixture the concentration of hydrogen atoms exceeds that of oxygen atoms by a factor of about 10. However, in view of the fact that the rate constant for the destruction of oxygen atoms exceeds the corresponding constant for hydrogen atoms by a factor of about 5,[52] the heterogeneous recombination of oxygen atoms cannot be neglected. The greater rate of loss of oxygen atoms in comparison with hydrogen atoms is confirmed by curves *2* and *1* for the variation in their concentrations

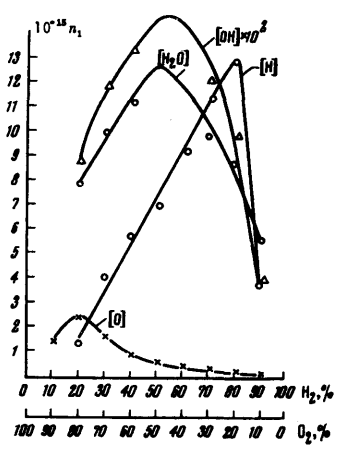


Fig. 4. Dependence of concentrations of H and O atoms and of OH radicals, and of the quantity of water formed, on the composition of the H_2–O_2 mixture.

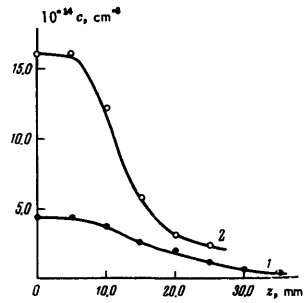


Fig. 5. Fall in concentration of atoms with distance between furnace and resonator: 1) H; 2) O.

with distance (Fig. 5), obtained by e.s.r. measurements[53] on the combustion products extractable from the reaction zone at a high linear velocity.

If the absolute concentrations of all the active centres in the combustion zone can be calculated[54–56], with simultaneous measurement of the quantity of water formed and of oxygen consumed, it will be possible to attempt to estimate the rate constants for the elementary reactions (1)–(3).

According to the above scheme for the burning of hydrogen, the reaction velocity is

$$\frac{d[H_2O]}{dt} = k_1[OH][H_2].$$

It is assumed that the contribution of reaction (7), loss of hydroxy-radicals on the walls, which also results ultimately in the formation of water, is small. By means of this equation, with the dependence of $[H_2O]$, [OH], and $[H_2]$ on time of contact known, it is not difficult to calculate k_1. Such determinations have been made for an equimolecular mixture at p = 2.86 mmHg and four temperatures (900°, 943°, 993°, and 1052°K). The following expression was obtained for k_1

$$k_1 = (2 \pm 0.8) \times 10^{-10} e^{-\left(\frac{86\,100 \pm 1200}{RT}\right)} \text{ cm}^3 \text{ s}^{-1} \text{ mol.}^{-1},$$

which can be regarded as showing good agreement, within the limits of experimental error, with the value measured by Avramenko and Lorentso[57].

The rate constant k_2 of reaction (2) was calculated by means of the equation

$$\frac{d(O_2)}{dt} = -k_2[H][O_2].$$

Measurements were made, under the conditions described above, of the quantity of oxygen consumed and of the absolute concentrations of hydrogen atoms as functions of the time of contact. The value obtained for k_2 was

$$k_2 = (1.7 \pm 0.7) \times 10^{-10} e^{-\left(\frac{16\,600 \pm 1200}{RT}\right)} \text{ cm}^3 \text{ s}^{-1} \text{ mol.}^{-1},$$

which agrees well with many earlier determinations[22,58–63].

We have seen above that in hydrogen-rich mixtures with oxygen, [H] ≫ [O] ≫ [OH]. In this case the loss of oxygen atoms and hydroxy-radicals on the walls can be neglected, and hence it can be assumed that

$$\frac{d[O]}{dt} = \frac{d[OH]}{dt} = 0.$$

From the scheme for the combustion of hydrogen we have

$$\frac{d[O]}{dt} = k_2[H][O_2] - k_3[O][H_2] = 0, \quad (1)$$

$$\frac{d[OH]}{dt} = -k_1[OH][H_2] + k_2[H][O_2] + k_3[O][H_2] = 0. \quad (2)$$

Subtracting Eqn.(2) from (1), we obtain

$$\frac{[O]}{[OH]} = \frac{k_1}{2k_3}. \quad (3)$$

Measurements of this concentration ratio for hydrogen-rich mixtures showed that at 993°K and 2.55 mmHg its value was [O]/[OH] = 3. At this temperature $k_1 = 2.4 \times 10^{-12}$ cm³ s⁻¹.

Eqn. (3) yielded for k_3 the value

$$k_3 = (0.3 \pm 0.1) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1},$$

which is also close to that found previously by other workers [22,64].

2. Kinetics and Mechanism of the Combustion of Carbon Monoxide in the Presence of Small Additions of Hydrogen

Another system which obeys the laws of branched chain reactions is the combustion of carbon monoxide in the presence of small additions of hydrogen, water vapour, or any other substance which can act as hydrogen-donor. It is assumed [22,66,67] that the combustion of carbon monoxide in the presence of hydrogen at low pressures takes place in conformity with the above scheme for the combustion of hydrogen, except that reaction (1) is replaced by the reaction

$$OH + CO \rightarrow CO_2 + H, \quad (8)$$

in which the same chain carriers — hydrogen and oxygen atoms and hydroxy-radicals — are assumed as before. The rate constants of almost all the elementary reactions are known.

It is readily seen that, when the added hydrogen constitutes a few or a fraction of one per cent of the whole mixture, reaction (3), together with the chain-branching reaction (2), becomes rate-determining. Under these conditions the rates of reactions (2) and (3) are comparable. Similar considerations [22] show that, with low H_2 contents in the mixture, reaction (5) — the loss of oxygen atoms on the surface of the reaction vessel — begins to compete with reaction (3). Hence follows the necessity for taking into account reaction (5) together with the loss of hydrogen atoms. The contribution of reaction (7) is very small in comparison with that of reaction (8), which occurs at a very high rate (high rate constant [57]

$$k_8 = 4.8 \times 10^{-13} \sqrt{T}\, e^{-\frac{5700}{RT}} \text{ cm}^3 \text{ s}^{-1},$$

and high concentration of carbon monoxide).

It is to be expected from the above that the concentration of hydrogen and oxygen atoms would be comparable, and that of hydroxy-radicals considerably lower. With the appearance of the e.s.r. method it became possible to test quantitatively the scheme for the combustion of carbon monoxide. Investigations were first made of low-pressure carbon monoxide–oxygen flames containing various quantities of hydrogen. A flow-type apparatus was used with a quartz reaction vessel heated by an electric furnace. Active particles were sought among the reaction products about 10 mm below the end of the electric furnace. A stoichiometric mixture of carbon monoxide and oxygen was studied, with variation in the amount of hydrogen added, in the temperature of the vessel from 580° to 700°, and in the pressure of the reacting gases from 2 to 10 mm. Hydrogen atoms were first detected in a $2CO + O_2 + xH_2$ mixture by Azatyan et al. [68] in 1961. Measurements made by these workers showed that, when the partial pressure of hydrogen is varied from 0.06 to 0.39 mmHg, with a total pressure of the reactant gas of 4.3 mmHg, the partial pressure of hydrogen atoms varies from 0.04 to 0.1 mmHg, which constitutes some 10% of the initial hydrogen concentration.

In the same year 1961 Azatyan et al. [69] observed high concentrations of atomic oxygen with the reaction vessel at 607–650° and 5.5 mmHg, and measured the concentration of atomic hydrogen under the same conditions. At low hydrogen contents the concentration of atomic oxygen exceeded that of atomic hydrogen. With increase in the hydrogen content, the concentration of oxygen atoms rapidly reached a maximum and then fell sharply, while the concentration of atomic hydrogen steadily increased, becoming several times greater than that of oxygen atoms. In some cases the sum of the partial pressures of hydrogen and oxygen atoms reached 2% of the total pressure.

Quite recently, in 1965, Gershenzon et al. [70], using a reaction tube with an expanded portion which completely fills the e.s.r. cavity, have observed large concentrations of hydroxy-radicals among the products of the combustion of carbon monoxide in the presence of hydrogen.

The distribution curves for all active species measured in this work are reproduced in Fig. 6, from which it is seen that the concentration of hydroxy-radicals is much lower than those of hydrogen and oxygen atoms, which are comparable. At low contents of molecular hydrogen the concentration of oxygen atoms exceeds that of hydrogen atoms. Thus all types of active centres responsible for the development of a branched chain reaction have been detected in the carbon monoxide–oxygen system containing small additions of molecular hydrogen, and their absolute quantities have been measured. The concentrations of these species were in qualitative agreement with estimated values obtained on the basis of the known rate constants for the elementary reactions (8), (2), and (3).

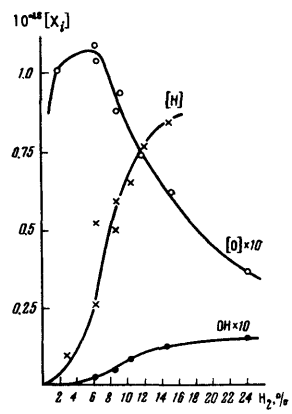


Fig. 6. Variation in concentration of H and O atoms and of OH radicals in $2CO + O_2$ mixture with percentage content of hydrogen.

On the basis of the values obtained for almost all the rate constants of the elementary reactions constituting the mechanism of the combustion of hydrogen at pressures close to the lower ignition limit, the first attempt was made to describe the kinetics of the combustion of these mixtures in the spontaneous ignition peninsula. For this purpose the following system of kinetic equations was set up to describe the time variation in all the starting materials and intermediate products

$$\frac{\partial [H]}{\partial t} = k_1 [OH][CO] - k_2 [H][O_2] + k_3 [O][H_2] + D_H \Delta^2 [H];$$

$$\frac{\partial [O]}{\partial t} = k_2 [H][O_2] - k_3 [O][H_2] + D_O \Delta^2 [O];$$

$$\frac{\partial [OH]}{\partial t} = 2k_2 [H_2][O_2] - k_1 [OH][CO] + k_2 [H][O_2] + k_3 [O][H_2] + D_{OH} \Delta^2 [OH];$$

$$\frac{\partial [CO]}{\partial t} = -k [OH][CO];$$

$$\frac{\partial [O_2]}{\partial t} = -k_0 [H_2][O_2] - k_2 [H][O_2];$$

$$\frac{\partial [H_2]}{\partial t} = -k_0 [H_2][O_2] - k_3 [O][H_2],$$

at $t = 0$, we have [H] = [O] = [OH] = 0. The boundary conditions are[33] $n_w \pm S(du/dx)_w = 0$, where n_w is the concentration of active centres near the wall and $S = 4\lambda/3\epsilon$, λ being the mean free path and ϵ the coefficient of destruction of active particles.

This set of differential equations cannot be solved analytically. It has been studied on an EVM-20 electronic computer.

The mixture $2CO + O_2$ was examined[70] with a content of molecular hydrogen varying from 1.5% to 10% at a total pressure of 1–8 mmHg and at the three temperatures 853°, 893°, and 923°K. The diameter of the reaction tube was 10 mm.

The first three equations of the above set contain diffusion terms representing the loss of active centres on the walls. In solving the system, the question arose of the possibility of replacing it by the simpler term $k(x)$, where k is the rate constant of heterogeneous chain termination and (x) the concentration of active centres. In the diffusion-controlled range of the loss of active centres, we have[24,71] $k = 23.2D/d^2$, where D is the diffusion coefficient of the active centres and d the diameter of the reaction vessel. In the kinetically controlled region of heterogeneous chain termination, $k = \epsilon u/d$ where ϵ is the recombination coefficient of active particles on the surface of the reaction vessel and u their thermal velocity. As long ago as 1931 Bursian and Sorokin showed[72] that, when the extent of combustion of the starting materials was small, i.e. in the initial stages of the process, such substitution is permissible, provided that the reaction velocity is limited by the reaction of one type of active centre, which is destroyed at each collision with the wall.

In 1943 Semenov[33] showed that such substitution was also possible when the rate-controlling active centre recombines on the wall in the kinetically controlled range, i.e. when $k = \epsilon u/d$. In order to establish the possibility of such substitution with more than one rate-controlling active centre (in this case three) and when the burning-up of the starting materials is not neglected, the solution was undertaken of the two sets of differential equations, with diffusion terms and with $k(x)$ terms. Values for the rate constants of the elementary reactions employed in the combustion of hydrogen (Table 3) were used in the solution.

TABLE 3.

Reaction	Value of constant	Ref.
$H_2 + O_2 \rightarrow 2OH$	$10^{-12} e^{-\frac{45\,000}{RT}}$ cm³ s⁻¹	24
$OH + CO \rightarrow CO_2 + H$	$4.8\times10^{-13}\sqrt{T}\,e^{-\frac{5700}{RT}}$ cm³ s⁻¹	57
$OH + H_2 \rightarrow H_2O + H$	$7\times10^{-13}\sqrt{T}\,e^{-\frac{10\,000}{RT}}$ cm³ s⁻¹	57
$H + O_2 \rightarrow OH + O$	$1.3\times10^{-10} e^{-\frac{15\,900}{RT}}$ cm³ s⁻¹	22
$O + H_2 \rightarrow OH + H$	$1.1\times10^{-10} e^{-\frac{11\,700}{RT}}$ cm³ s⁻¹	22
walls $H \rightarrow {}^1/_2 H_2$	$13.1\sqrt{T}\,e^{-\frac{5400}{RT}}$ s⁻¹	52
walls $O \rightarrow {}^1/_2 O_2$	$60\sqrt{T}\,e^{-\frac{6100}{RT}}$ s⁻¹	52
walls $OH \rightarrow {}^1/_2 H_2O_2$	$k_7 = k_5$	

The value of k_7 at high temperat res being unknown, it was taken to be equal to k_5.

Fig. 7 illustrates the solutions as the variation of the concentrations of active species with time. The points represent the solution of the simplified system. Agreement is seen to be good throughout the curves. Consequently replacement of the diffusion terms by $-k(x)$ is permissible in this case, too. In conformity with the branched chain character of the reaction, the curves representing the growth in active particles with time show an induction period, which becomes shorter with rise in temperature and in pressure. The concentration of active centres rapidly reaches a maximum, and then falls slowly. At points corresponding to maximum populations of the active centres, the concentrations of hydrogen and oxygen atoms are comparable, while the concentration of hydroxy-radicals is considerably lower. At small hydrogen concentrations the concentration of oxygen atoms exceeds that of hydrogen atoms. All these results agree well with experimental data, which is evidence of the correctness of the rate constants used for the individual elementary reactions in solving the set of equations.

An attempt was made to vary the rate constants — k_4, k_5, and k_7 — for the loss of active centres. When operating in the kinetically controlled range of heterogeneous chain termination, the surface of the reaction vessel was

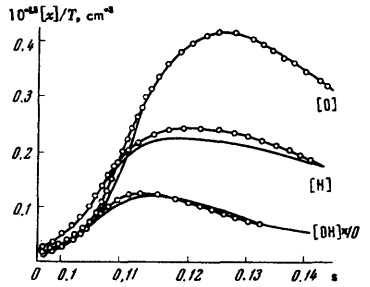


Fig. 7. Kinetics of the formation of active species in the $2CO + O_2 + 1.5\%\ H_2$ flame (theoretical curves).

quite often changed from one experiment to another, which directly affected the recombination constants. Analysis showed that the magnitude of the constant k_5, for the loss of oxygen atoms on the walls, had the greatest effect, with small additions of hydrogen, on the concentration of all types of active centres. The probable reason is that under these conditions the rate of reaction (3) considerably exceeds the rate of branching (2).

III. METHOD OF DETERMINING RATE CONSTANTS OF THE PRIMARY REACTIONS OF HYDROGEN AND OXYGEN ATOMS WITH VARIOUS COMPOUNDS

A good knowledge of detailed mechanisms of the combustion of hydrogen and carbon monoxide in the vicinity of their limits of spontaneous ignition enabled Azatyan et al.[22] to propose a new, improved method for determining the rate constants of the elementary reactions of hydrogen and oxygen atoms with various substances. The method is based on a remarkable property of chain processes, their high sensitivity to chemically active impurities. It is well known that minute additions of such substances are able to change sharply the reaction velocity, increasing or decreasing it several hundredfold or thousandfold. Thus, for example, small additions of iodine vapour to a mixture of hydrogen and oxygen can markedly diminish the rate of burning of hydrogen and considerably narrow the range of spontaneous ignition[73]. Fig. 8 gives the upper limit of ignition for a hydrogen–oxygen mixture (curve *1*) as a function of temperature. Curves *2* and *3* have been obtained for the same mixture but containing 0.004% and 0.006% of iodine. The lowering of the limit is obviously associated with the bulk removal of hydrogen atoms: $H + I_2 \rightarrow HI + I$. The iodine atom is known to be considerably less active than the hydrogen atom, and is unable to continue the hydrogen-oxidation chain.

Small additions of hydrocarbons, aldehydes, alcohols, acids, and many other substances have similar effects to iodine on the rate of burning of hydrogen. The action of various quantities of ethane on the lower limit of spontaneous ignition of the mixture $4H_2 + O_2$ can be cited as an example of the inhibiting action of small additions of a hydrocarbon[74]. It is seen from Fig. 9 that the lower limit gradually rises with increasing content of ethane in the mixture.

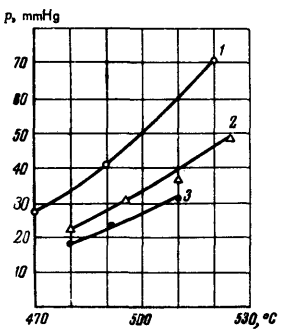


Fig. 8. Effect, on the upper ignition limit of $2H_2 + O_2$, of small additions (%) of iodine vapour:
1) 0; 2) 0.004; 3) 0.006.

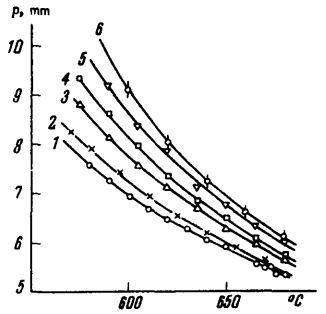


Fig. 9. Temperature dependence of lower ignition limit of $4H_2 + O_2 + xC_2H_6$ mixture for different values of x (%):
1) 0; 2) 0.0995; 3) 0.2006; 4) 0.3004; 5) 0.4070; 6) 0.4982.

Very clear cases exist of the promotion of burning by the presence of small additions of active substances. Such an example is provided by the combustion of carbon monoxide in oxygen containing small amounts of hydrogen, which we have examined previously[22,75]. As is known, an absolutely dry mixture of carbon monoxide and oxygen does not ignite, or does so, if at all, under different pressure and temperature conditions. However, it is sufficient to add a few per cent of hydrogen or water vapour to make the mixture readily ignitable. Fig. 10 illustrates how a carbon monoxide–oxygen mixture can be more readily ignited as the concentration of hydrogen added to it increases[22,75]. It was found that not only hydrogen and water vapour but also all compounds whose molecules contain hydrogen — all hydrocarbons and many other substances — possess these properties. As example of the promoting action of small additions we may cite the dependence of the lower carbon monoxide–oxygen limit on the presence of ethane[76]. It is seen from Figs. 9 and 11 that additions of ethane inhibit burning in one system and promote it in another. This dual effect of the same substance on rate of burning was found not only for different systems but also in the

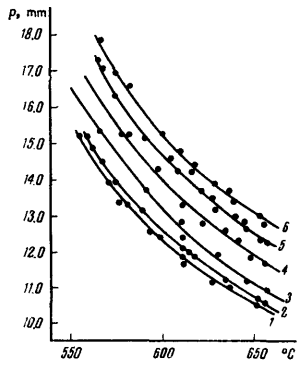


Fig. 10. Temperature dependence of lower limit of $2CO + O_2 + xH_2$ mixture for different values of x (%):
1) 3.79; 2) 3.28; 3) 2.14; 4) 1.48; 5) 1.06; 6) 0.78.

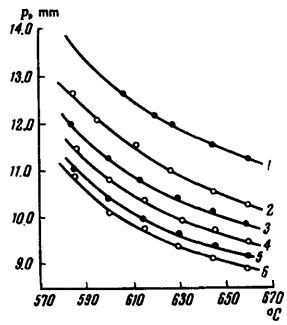


Fig. 11. Temperature dependence of lower ignition limit of $2CO + O_2 + xC_2H_6$ mixture for different values of x (%):
1) 0.0225; 2) 0.0389; 3) 0.0555; 4) 0.074; 5) 0.097; 6) 0.141.

same system[75,76]. If, for example, the concentration of ethane in the carbon monoxide–oxygen reactant mixture is further increased, a point is reached at which the limit begins to rise[76], as is well seen from Fig. 12. The dual effect of the simplest hydrocarbon, methane, on the lower carbon monoxide–oxygen limit was first reported in Ref. 77.

Let us consider in sequence the causes of the inhibiting action of small additions of active impurities on the combustion rate of hydrogen and its limits, and the dual effect of these substances on the combustion of carbon monoxide and oxygen and its lower limit of spontaneous ignition. The work of Voevodskii and Tikhomirova[78] simultaneously with that of Baldwin[59] showed that the inhibiting action of ethane and other hydrocarbons on the hydrogen–oxygen ignition limits is due to the additional homogeneous loss of hydrogen atoms by the reaction

$$H + C_2H_6 \rightarrow H_2 + C_2H_5. \quad (9)$$

followed by the reaction

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2. \quad (10)$$

The result of reactions (9) and (10) is to replace an active hydrogen atom by a relatively inactive HO_2 radical.

Investigations of low-pressure hydrogen–oxygen flames by the e.s.r. method show that the concentration of all

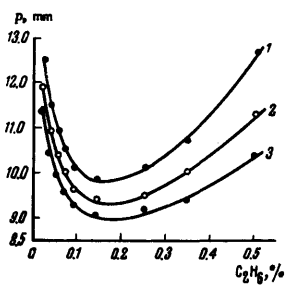


Fig. 12. Dependence of lower limit of spontaneous ignition of $2CO + O_2$ on percentage of C_2H_6 in mixtures at (°C):
1) 610; 2) 630; 3) 650.

active species — carriers of the chain oxidation of hydrogen — drops sharply on addition of the inhibitor. In this connection, the condition for the lower ignition limit in hydrogen-rich mixtures with oxygen must be written

$$2k_2[O_2][H] = k_4[H] + k_9[RH][H].$$

The left-hand side determines the rate of branching, and the right-hand side is the sum of terms determining the rates of loss of hydrogen atoms on the walls and in bulk. Hence the concentration of oxygen at the lower limit $[O_2]$ is determined by the equation

$$[O_2] = \frac{k_4}{2k_2} + \frac{k_9}{2k_2}[RH], \quad (A)$$

from which it is seen that, in full agreement with experiment, additions of an active impurity tend to raise the lower limit. When $[RH] = 0$, we have $[O_2] = k_4/2k_2$, the ratio of the rate constants for loss [of atomic hydrogen] (4) and branching (2).

The accelerating effect of small additions of various compounds RH, which act as hydrogen-donors in the combustion of carbon monoxide, can be explained by the following reactions of chain propagation and branching

$$OH + CO \rightarrow CO_2 + H, \quad (8)$$
$$H + O_2 \rightarrow OH + O, \quad (2)$$
$$O + RH \rightarrow OH + R. \quad (11)$$

Thus it is suggested that atomic oxygen, on interaction with the active additive, abstracts a hydrogen atom from the latter to form a hydroxy-radical. The flame of a carefully purified and dried mixture of carbon monoxide and oxygen has been studied by the e.s.r. method in the presence of over a score of different hydrogen-donors. The additives comprised methane, ethane, propane, butane, ethylene, propene, methanol, ammonia and several of its derivatives, and many other compounds[75,79,82]. In all cases large concentrations of hydroxy-radicals and hydrogen and oxygen atoms were detected, which increased as the impurity content increased to a certain value [RH] depending on the temperature and the nature of the additive. The inhibiting action of high concentrations [RH] is obviously due to reaction (9), which results in the bulk loss of hydrogen atoms. The e.s.r. measurements show that the concentration [RH] at which the limit begins to increase is followed by a sharp drop in the concentration of hydrogen and oxygen atoms and hydroxy-radicals[80].

The combustion of carbon monoxide in the presence of an active impurity RH can be represented by the sequence of elementary reactions (1)–(9). Mathematical analysis of the scheme by means of Semenov's method of steady-state concentrations[83] yields the following final expression for the ignition condition[76]

$$[O_2]_l^{CO} = \frac{k_4}{k_2}\left(1 + \frac{k_9[RH]}{k_4}\right)\left(1 + \frac{k_5}{k_{11}[RH]}\right), \quad (B)$$

from which it follows, in complete agreement with experiment, that the lower limit should have a high value in a mixture of carbon monoxide and oxygen ($[RH] \rightarrow 0$). With addition to it of an active impurity RH, the pressure at the lower ignition limit will fall with [RH] until reaction (9) begins to compete with reaction (2). With further increase in the impurity content beyond this concentration [RH], which can be termed a critical concentration, the lower limit begins to rise. When hydrogen is the added substance, this condition is written[22]

$$[O_2]_l^{CO} = \frac{k_4}{2k_2}\left(1 + \frac{k_5}{k_3[H_2]}\right). \quad (C)$$

where $[O_2]_1^{CO}$ is the oxygen concentration at the lower limit of the carbon monoxide–oxygen mixture containing various additions of hydrogen, and the k are the rate constants of the corresponding elementary reactions.

Unlike the method based on determination of lower limits in the kinetically controlled region of heterogeneous chain termination[84], the reaction is conducted in the diffusion-controlled region of heterogeneous destruction of active centres in the proposed method[75]. An advantage of this is the excellent reproducibility and the associated far greater accuracy of the constants obtained. Azatyan's detailed investigations[75] have shown that chain termination in the diffusion-controlled region is completely ensured by coating the walls of the reaction vessel with magnesium oxide. Let us examine the principle underlying the determination of the rate constants of reactions (9) and (3), with the combustion of hydrogen-rich mixtures with oxygen and of carbon monoxide–oxygen mixtures containing small additions of hydrogen as examples, for which purpose we consider in succession the equations to the lower limit (A) and (B), in which the heterogeneous chain-termination constants k_4 and k_5 can be calculated[75]. With cylindrical vessels

$$k = \frac{23.2\,D}{d^2} = \frac{23.2}{d^2} D_{stp}\,\frac{760}{(273)^{1.5}}\,\frac{T^{1.5}}{p} \quad \text{or} \quad k = k^0\frac{T^{1.5}}{p}$$

where

$$k^0 = \frac{23.2}{d^2} D_{stp}\,\frac{760}{(273)^{1.5}}, \qquad (D)$$

D_{stp} being the diffusion coefficient of the corresponding active centre at standard temperature and pressure. Substituting for k_4 and k_5 in Eqn. (A) and replacing concentrations by pressure, we can rewrite the equation for the lower limit in a hydrogen-rich mixture with oxygen in the form

$$pp_{O_2} = \frac{k_4^0 T^{2.5}}{2k_2 \times 10^{19}}\left[1 + \frac{k_9 \times 10^{19}}{k_4^0 \times T^{2.5}}\,pp_{RH}\right]$$

where p is the pressure of the reactant mixture at the limit, and p_{O_2} and p_{RH} are the pressures of oxygen and the added impurity at this limit. When plotted as pp_{O_2} against pp_{RH} this is the equation to a straight line.

Fig. 13 shows the series of straight lines obtained by recalculating the lower limits as a function of temperature for the various additions of ethane shown in Fig. 9. The experimental points are seen to fit well on straight lines for the different temperatures. These straight lines make intercepts $a = k_4^0 T^{2.5}/2 \times 10^{19} k_2$ on the ordinate axis, and have a slope of $\tan\alpha = k_9/2k_2$. Dividing the latter by the former and taking logarithms, we obtain

$$\log\frac{\tan\alpha \cdot T^{2.5}}{a} = \log\frac{k_9^0 \cdot 10^{19}}{k_4^0} - \frac{E_9}{4.57} \times \frac{1}{T}$$

which represents a linear variation of $\log[T^{2.5}(\tan\alpha)/a]$ with $1/T$. Results calculated from the data in Fig. 13 are plotted in Fig. 14. In this case, too, the points lie on a straight line. From the slope of the straight line we can readily determine E_9, the activation energy of reaction (9), and from the intercept we can find k_9^0.

In this way rate constants have been determined for many elementary reactions of atomic hydrogen with molecules of various active impurities added to a hydrogen–oxygen mixture. A test of the method is provided by the boundary condition (A): at [RH] = 0 the intercepts a (Table 4) made by the straight lines on the ordinate axis at

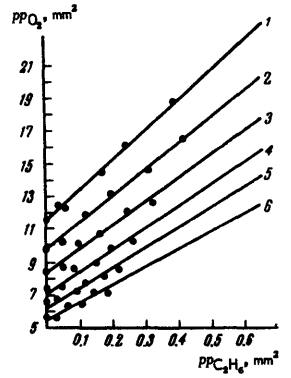


Fig. 13. Dependence of pp_{O_2} on $pp_{C_2H_6}$ at (°C):
1) 580; 2) 600; 3) 620; 4) 640; 5) 660; 6) 680.

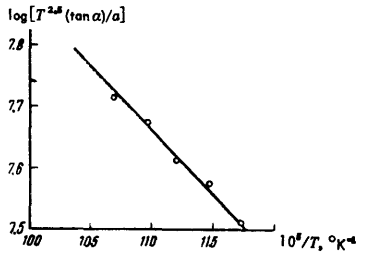


Fig. 14.

TABLE 4.

T, °C	a, mm²	$p^{H_2}p^{H_2}_{O_2}$, mm²
580	11.6	11.6
600	9.8	9.70
620	8.3	8.4
640	7.10	7.40
660	6.20	6.5
680	5.50	5.60

different temperatures should be identical with the product $p^{H_2}p^{H_2}_{O_2}$. The scatter of the values given as example in Table 4 is seen to be small.

The method can also be tested by the value of the branching rate constant k_2, which can be determined from the relationship $a = k_4^0 T^{2.5}/2 \times 10^{19} k_2$ and compared with the published value. This relationship can be rewritten in the form

$$\log\frac{a}{T^{2.5}} = \log\frac{k_4^0}{2k_2^0 \cdot 10^{19}} + \frac{E_2}{4.57} \times \frac{1}{T}.$$

The variation required by the equation is shown in Fig. 15, values of a having been taken from Table 4. The slope of the resulting straight line was used to calculate E_2, and the intercept on the ordinate axis gave k_2^0. The overall formula obtained for the constant was

$$k_2 = 2.1 \times 10^{-10} e^{-\frac{16\,600}{RT}}\ \text{cm}^3\ \text{s}^{-1}\ \text{mol.}^{-1},$$

in good agreement with the corresponding published value.

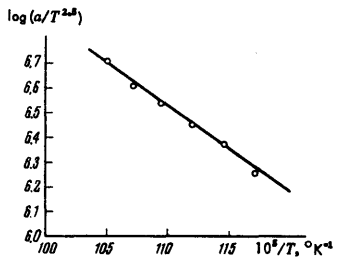


Fig. 15.

Let us now consider the method of determining the rate constant of reaction (3), for which purpose we use Eqn. (C) for the lower limit of ignition of a carbon monoxide–oxygen mixture in the presence of hydrogen. Substituting for k_4 and k_5, and replacing the concentrations $[O_2]^{CO}$ and $[H_2]$ by pressures, we can write the equation in the form

$$pp_{O_2} = \frac{(k_4^0)^{CO} \cdot T^{2.5}}{2k_2 \cdot 10^{19}} \left[1 + \frac{(k_5^0)^{CO} \cdot T^{2.5}}{k_3 \cdot 10^{19} \cdot pp_{H_2}} \right],$$

where p is the pressure at the lower limit of $2CO + O_2 + xH_2$, and p_{O_2} and p_{H_2} are the partial pressures of oxygen and hydrogen at this limit. The superscript CO attached to k_4^0 and k_5^0 indicates that these parameters relate to the above mixture. When plotted as pp_{O_2} against $1/pp_{H_2}$, this equation represents a straight line.

Fig. 16 shows the results of analysing the experimental data plotted in Fig. 10, and gives the temperature dependence of the lower ignition limit with various contents of hydrogen in the $2CO + O_2$ reactant mixture. The experimental data are seen to fit the corresponding curves well in Fig. 16. These curves make intercepts $b = k_4^0 T^{2.5}/2 \times 10^{19} k_2$ on the ordinate axis, and the slope of the straight lines is

$$\tan\alpha = \frac{(k_4^0)^{CO} \cdot T^{2.5}}{2k_2 \cdot 10^{19}} \times \frac{(k_5)^{CO} \cdot T^{2.5}}{k_3 \cdot 10^{19}}.$$

The logarithm of their ratio is

$$\log \frac{\tan\alpha}{b \cdot T^{2.5}} = \log \frac{(k_5^0)^{CO}}{10^{19} \cdot k_3^0} + \frac{E_3}{4.57} \cdot \frac{1}{T},$$

where E_3 is the activation energy of reaction (3), and k_3^0 is the preexponential factor.

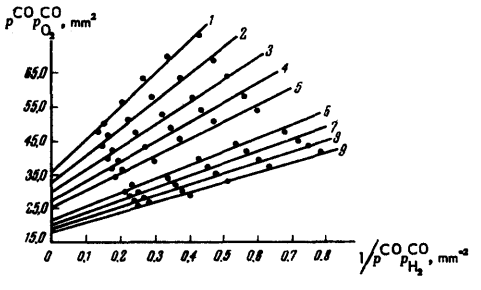


Fig. 16. Dependence of pp_{O_2} on $1/pp_{H_2}$ at (°C): 1) 570; 2) 580; 3) 590; 4) 600; 5) 610; 6) 630; 7) 640; 8) 650; 9) 660.

Fig. 17 shows that the dependence of $\log[(\tan\alpha)/bT^{2.5}]$ on $1/T$ calculated from the data plotted in Fig. 16 fit well on a straight line in this case, too. The slope of the line gave E_3, and the intercept on the vertical axis k_3^0. The expression obtained for the rate constant of the reaction was

$$k_3 = 1.1 \times 10^{-10} e^{-\frac{11\,700}{RT}} \text{ cm}^3 \text{ s}^{-1} \text{ mol.}^{-1}.$$

The value obtained[22] of E_3 = 11.7 kcal mole^{-1} considerably exceeds that calculated from the experiments of Harteck and Kopsch, and is somewhat higher than that given in Ref. 64. As has been shown above, the best agreement with experiment is obtained in fact with this value of E_3.

Let us consider the significance of the intercepts b made by the straight lines on the ordinate axis (Fig. 16) in the case of carbon monoxide–oxygen mixtures containing small additions of hydrogen. Writing Eqn. (D) for carbon monoxide–oxygen mixtures containing small additions of hydrogen and also for hydrogen–oxygen mixtures, and dividing the former by the latter, we obtain

$$(k_4^0)^{CO} = (k_4^0)^{H_2} \frac{(D_{stp})^{CO}}{(D_{stp})^{H_2}},$$

where $(D_{stp})^{CO}$ and $(D_{stp})^{H_2}$ are the respective diffusion coefficients of hydrogen atoms in the two mixtures under normal conditions. Substituting $(k_4^0)^{CO}$ in the formula for b, we have

$$b = \frac{(k_4^0)^{H_2} \cdot T^{2.5}}{2k_2 \cdot 10^{19}} \cdot \frac{(D_{stp})^{CO}}{(D_{stp})^{H_2}},$$

or, since

$$\frac{(k_4^0)^{H_2} \cdot T^{2.5}}{2k_2 \cdot 10^{19}} = p^{H_2} \cdot p_{O_2}^{H_2},$$

$$b = p^{H_2} \cdot p_{O_2}^{H_2} \cdot \frac{(D_{stp})^{CO}}{(D_{stp})^{H_2}}.$$

This means that the straight lines should make intercepts on the vertical axis[75] which are numerically equal to the product $p^{H_2} p_{O_2}^{H_2}$ at the lower limit of the hydrogen–oxygen mixture multiplied by the ratio of the diffusion coefficients of hydrogen atoms in the $CO + O_2 + xH_2$ and $H_2 + O_2$ mixtures. (When considering the lower limits of hydrogen–oxygen mixtures in the presence of RH, it was obviously necessary to take into account the appropriate correction D^{RH}/D^{H_2}. Since, however, the diffusion coefficients of hydrogen atoms in a hydrogen–oxygen mixture are very little changed by the addition of up to 1% of RH, this ratio can be taken as unity.) Azatyan's calculations showed[75] that $D^{CO}/D^{H_2} \simeq 0.72$. Comparison of the lengths of the intercepts b with the corresponding product obtained from

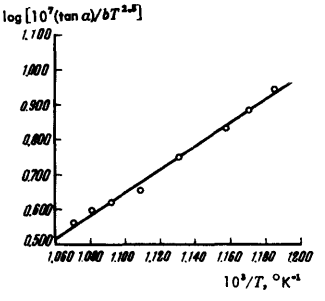


Fig. 17.

TABLE 5.

Reaction	k_0, $cm^3\ s^{-1}\ mol.^{-1}$	E, kcal $mole^{-1}$	Ref.
$H + O_2 = OH + O$	$1.3 \cdot 10^{-10}$	15.9 ± 0.8	22
$H + CH_4 = H_2 + CH_3$	$2.0 \cdot 10^{-11}$	10.6 ± 1.0	75
$H + C_2H_6 = H_2 + C_2H_5$	$1.0 \cdot 10^{-10}$	9.5 ± 1.0	74
$H + C_2H_4 = H_2 + C_2H_3$	$1.5 \cdot 10^{-11}$	7.2 ± 1.0	86
$H + C_3H_8 = H_2 + C_3H_5$	$T = 640°$	$k = 4.8 \cdot 10^{-13}$	87
$H + NH_3 = H_2 + NH_2$	$0.68 \cdot 10^{-10}$	13.7 ± 0.6	88
$H + C_2H_5OH = H + C_2H_4OH$	$2 \cdot 10^{-11}$	8.1 ± 0.6	89
$H + n\text{-}C_3H_7OH = H_2 + C_3H_6OH$	$4.1 \cdot 10^{-11}$	6.4 ± 0.6	88
$H + n\text{-}C_4H_9OH = H_2 + C_4H_8OH$	$3.3 \cdot 10^{-11}$	5.1 ± 0.6	88
$O + H_2 = OH + H$	$1.1 \cdot 10^{-10}$	11.7 ± 0.7	22
$O + CH_4 = OH + CH_3$	$0.94 \cdot 10^{-10}$	8.7 ± 0.8	75,85
$O + NH_3 = OH + NH_2$	$0.32 \cdot 10^{-10}$	10.0 ± 0.5	88
$O + C_2H_4 = OH + C_2H_3$	$2.3 \cdot 10^{-10}$	8.1 ± 0.5	86
$O + C_2H_6 = OH + C_2H_5$	$1.4 \cdot 10^{-10}$	7.5 ± 1.0	86
$O + C_3H_8 = OH + C_3H_7$	$1.8 \cdot 10^{-10}$	6.2 ± 1.0	90
$O + C_4H_{10} = OH + C_4H_9$	$T = 630°$	$k = 1.2 \cdot 10^{-11}$	90

direct measurements of the lower limit of spontaneous ignition of hydrogen–oxygen mixtures, with the correction D^{CO}/D^{H_2} taken into account, showed good agreement between experiment and calculation. The temperature dependence of b was used to calculate the rate constant of reaction (2) as

$$k_2 = 1.3 \times 10^{-10} e^{-\frac{15\,900}{RT}}\ cm^3\ s^{-1}\ mol.^{-1}.$$

Eqn. (B) must be used[85] to determine the rate constants of elementary reactions of the type (11). This equation contains, besides the unknown constant k_{11}, the rate constant k_9 of the reaction $H + RH \rightarrow H_2 + R$, which is found from experimental results on the dependence of the lower limit of hydrogen-rich mixtures with oxygen containing RH as impurity. In several cases the radical R, formed in reactions (9) and (11), may interact with oxygen to form a new active centre in the main oxidation chain:

$$R + O_2 \rightarrow R'CHO + OH. \qquad (12)$$

As a result, the condition for the lower limit will contain, together with the required constant k_{11}, the additional unknown factor $k_9/(k_9 + k_{10})$.

A method which has been suggested[75] for eliminating this factor is to consider simultaneously the conditions of the lower ignition limits for the mixtures $H_2 + O_2 + xRH$ and $CO + O_2 + xRH$ deduced with reaction (12) taken into account. Table 5 gives values for the rate constants of elementary reactions of hydrogen and oxygen atoms with the molecules of several compounds, determined from the displacement of the lower limits of hydrogen–oxygen and carbon monoxide–oxygen mixtures in the presence of small additions of these compounds.

IV. USE OF e.s.r. METHOD TO ESTABLISH THE SITE AT WHICH ATOMIC OXYGEN ATTACKS A COMPLEX MOLECULE

The e.s.r. method, applied to low-pressure flames, enables us to establish the point at which a complex molecule is attacked by atomic oxygen, as has been shown in the case of the methanol molecule[81]. A low-pressure carbon monoxide–oxygen flame has been studied in the presence of small additions of methanol. It was first shown that small additions of the latter, as of other hydrogen-donors, depress the lower ignition limit. Fig. 18 illustrates the dependence of the lower limit on the methanol content for two temperatures. The low-pressure flames in $2CO + O_2 + xCH_3OH$ mixtures were investigated in an apparatus of the type illustrated in Fig. 2. Previously dried and

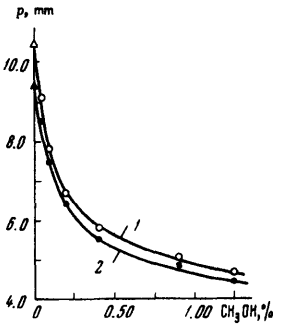


Fig. 18. Dependence of lower limit of spontaneous ignition of $2CO + O_2$ mixture on percentage content of methanol at (°C): 1) 670; 2) 690.

purified carbon monoxide was bubbled through methanol at 6°C, after which it was passed through a coil immersed in a thermostat at 0°C. The carbon monoxide saturated with the methanol vapour at 0°C was mixed through a regulating valve with a stream of carbon monoxide and oxygen, which had also first been purified and dried. The percentage of the alcohol in the stream was varied by changing the flow of carbon monoxide bubbled through it. Experiments were made over the temperature range 685–755°C at pressures of 3–7.4 mmHg with an initial alcohol content in the mixture of 0.86–1.7%. In all cases large quantities of hydroxy-radicals and hydrogen and oxygen atoms were observed in the flame. The presence of active species in the flame, as well as the depression of the lower limit with increasing concentration of methanol in the mixture, indicates that, as with the above promoters of the burning of carbon monoxide, the effective rate of chain branching is limited by the reaction of atomic oxygen with methanol, so that the mechanism of the combustion of carbon monoxide in the presence of methanol can be represented by the sequence of reactions

$$OH + CO \rightarrow CO_2 + H,$$
$$H + O_2 \rightarrow OH + O,$$
$$O + CH_3OH \rightarrow OH + CH_2OH \quad \text{or} \quad O + CH_3OH \rightarrow OH + CH_3O,$$
$$H \xrightarrow{\text{walls}} {}^1/_2 H_2,$$
$$O \xrightarrow{\text{walls}} {}^1/_2 O_2,$$
$$H + CH_3OH \rightarrow H_2 + CH_2OH.$$

It was stated above that hydroxy-radicals enter very rapidly into reaction (8). Hence by adding small quantities of CH_3OD or CD_3OH to the reacting mixture and determining the ratio of OH to OD, it might be possible to assess the point of attack. Since the maximum magnetic field strength in the EPR-2 apparatus does not exceed 6000 oersteds, whereas OD radicals are observed in stronger fields, the ratio [H]/[D] was measured on the assumption that they obeyed the same proportionality. Such substitution cannot influence the conclusion drawn by these authors, since two series of independent experiments were made with CH_3OD and CD_3OH. When CH_3OD was added as impurity, no lines at all due to D atoms were detected in the e.s.r. spectrum of the low-pressure flame. Yet the intensity of the lines due to hydrogen atoms exceeded the noise level by factors of 30–35. From the number of components in the spectrum of hydrogen and deuterium

atoms and the width of the lines, the ratio was found to be $[H]/[D] \geq 15$. This means that oxygen atoms attack preferentially the methyl group of the CH_3OD molecule. When CD_3OH was added, the low-pressure flame was found to contain large quantities of deuterium atoms and relatively few hydrogen atoms. The ratio was $[D]/[H] \simeq 6$. This means that oxygen atoms preferentially attack the CD_3 group on reaction with CD_3OH.

The change in the proportion of atoms which can be abstracted from the methyl group on passing from CH_3OD to CD_3OH is obviously associated with a difference in strength between the C–H and C–D bonds, and also between O–H and O–D, in methanol. If the difference in activation energy for abstraction by oxygen atoms of deuterium and hydrogen atoms from the methyl group is taken to be 1.2 kcal $mole^{-1}$,[91] the ratio of the rate of abstraction of a hydrogen atom from the methyl group to the rate of abstraction of a hydrogen atom from the hydroxy-group is 11. On a similar hypothesis concerning the abstraction of deuterium and hydrogen atoms from the hydroxy-group of the alcohol molecule CH_3OD, these workers showed that this ratio should exceed 8. It was thus established that at temperatures up to 755°C oxygen atoms attack preferentially the methyl group of the CH_3OH molecule.

V. INVESTIGATION OF SOME LOW-PRESSURE FLAMES BY THE e.s.r. METHOD

The above two systems unfortunately exhaust our fundamental knowledge of the detailed mechanisms of complicated chemical processes. During the forty years since the chain nature of the combustion of phosphorus was established, many new reactions which also obey the laws of branched chain reactions have been discovered: they give ignition limits which are sensitive to chemically active additions, to the diameter of the reaction vessel, to its surface properties, etc. Until recently, however, the active species — the carriers of chain oxidation — have not been identified in many systems. Great difficulties have arisen in this connection in constructing mechanisms for these reactions. We have seen above that optical spectroscopy has played a large part in developing the theory of chain reactions, in identifying hydroxy-radicals as one of the main chain-carriers, and in measuring their absolute concentrations. By this technique, incidentally, Emanuel'[92] discovered surprisingly large quantities of SO radicals in a slow chain reaction.

In view of the above discussion, it appears that electron spin resonance may play a still larger part in the study of the mechanisms of complex reactions. This method enables many radicals to be detected, as well as atoms. A combination of electron spin resonance, optical spectroscopy, and kinetic methods for studying chemical processes will undoubtedly permit a more rapid penetration into the detailed mechanisms of chemical reactions.

In the light of the above, the authors whose work is discussed below have decided to undertake a detailed examination of several systems which had formed subjects of earlier investigations.

1. Reaction of Sulphur Vapour with Oxygen

The reaction of sulphur vapour with oxygen was one of the first in which Semenov and Ryabinin[3] discovered lower and upper limits of spontaneous ignition. However, there is no indication in the literature of the detection of any active centres in this system. On the basis of indirect evidence, associated with the behaviour of the system on combustion, Semenov[24] suggested that oxygen atoms were formed.

Sarkisyan et al.[93] report the first results of an e.s.r. investigation of a low-pressure flame of sulphur vapour in oxygen. A novel feature of the experimental technique, compared with that discussed above, is the evaporator reaction vessel used for work both with solids and with liquids whose vapours undergo combustion. The diagram (Fig. 19) shows that the vessel consists of two coaxial tubes *1* and *2*. The outer tube has a widened portion *3* in an e.s.r. cavity resonator, which enables magnetic and electric components of the UHF field to be used. Use of the vessel illustrated in Fig. 19 became possible as a result of the improvement described in another paper[44]. The sulphur was placed in the cup *4* of the inner tube. A gentle stream of an inert gas was supplied through this tube, and entrained the sulphur vapour by flowing over the sulphur heated by means of a special furnace *5*. The gases emerged through the nozzle *6* into the combustion zone, where they mixed with oxygen supplied through the outer tube. The temperature of the combustion zone was maintained by means of the furnace *7*. The inner tube could be moved vertically by means of the ground glass joint *8*, which made it possible to move the combustion zone. The part of the reaction vessel located in the resonator was heated by a stream of hot air. By lowering the combustion zone, the flame could thus be drawn into the resonator. Experiments were made at 300–400°C, and the pressure of the mixture was varied over the range 1.5–3 mmHg.

Under these conditions large quantities of SO radicals and O atoms were observed in the flame. Three single lines were observed for the SO radical, which coincided with published e.s.r. spectral lines for SO radicals obtained by means of an electric discharge in sulphur dioxide[94,95]

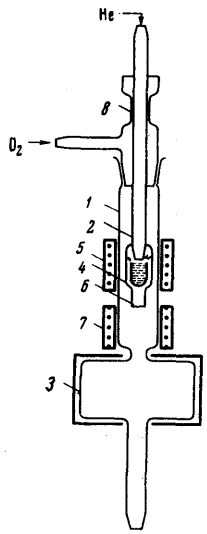


Fig. 19. Diagram of evaporator reaction vessel.

or by the reaction O + COS = CO + SO.[96] The concentration of oxygen atoms reached 25–30% of the initial oxygen, and that of SO was an order of magnitude lower. Experiments showed that small additions of methane resulted in a diminution in the concentration of oxygen atoms. At the same time lines were observed in the spectrum characteristic of the hydroxy-radical, their appearance obviously being due to the reaction $O + CH_4 \rightarrow OH + CH_3$.

In 1954 Semenov[98] considered the possible role of diradicals in chain reactions, and suggested the following mechanism for the diradical oxidation of sulphur vapour

$$S_8 = \dot{S}_7 + \dot{S},$$
$$\dot{S} + O_2 = \dot{S}O + \dot{O},$$
$$\dot{O} + S_8 = \dot{S}O + \dot{S} + S_6,$$
$$\dot{S}O + O_2 = SO_2 + \dot{O},$$
$$O + O_2 + M = O_3 + M,$$
$$SO_2 + O = SO_3,$$
$$O \xrightarrow{\text{walls}} {}^1/_2 O_2.$$

As we see, the main carriers of the diradical chain combustion of sulphur — oxygen atoms and SO radicals — have been detected. It will be shown further that sulphur atoms cannot be observed, either in this system or in other systems containing sulphur. The failure to detect sulphur atoms is obviously associated with their great reactivity, as a result of which their equilibrium concentration is considerably lower than the sensitivity of the e.s.r. instrument. Further investigation of the kinetics and the mechanism of the combustion of sulphur vapour will in the very near future enable the mechanism of this process to be finally established.

2. Investigation of Low-Pressure Carbon Disulphide–Oxygen Flames

The burning of carbon disulphide in oxygen was studied in detail by Kondrat'ev,[99] and was also investigated by Voronkov and Semenov[100]. The reaction was shown to develop by a branched chain mechanism. Using a flow technique, Kondrat'ev observed the interesting phenomenon of a sharp change in colour of the flame on passing from mixtures rich in oxygen to those poor in oxygen near the stoichiometric mixture. Analysis established the formation of COS and sulphur as intermediate products. The radical CS was detected in mixtures rich in carbon disulphide. The principal final reaction products were sulphur dioxide and carbon monoxide. Fig. 20 illustrates the yields of intermediate and final reaction products as functions of $\alpha = [O_2]/[CS_2]$. Spectroscopic investigations have shown that the concentration of CS radicals, which is very low near $\alpha \simeq 2.5$, increases rapidly as α decreases, i.e. with enrichment of the mixture with carbon disulphide.

As in previous work, the e.s.r. investigation of low-pressure carbon disulphide flames was conducted under flow conditions. The flame was produced in the part of the tube located in the e.s.r. resonator. Experiments were made over the temperature range 200–500°C and at 6 mmHg. The ratio α varied over the range 0.8–14. Azatyan et al.[101] observed large quantities of oxygen atoms in oxygen-rich mixtures, their spectrum being identified from the g factor of 1.5 and from the fine structure. The

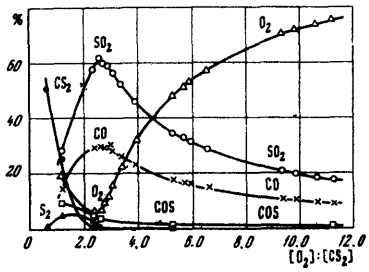


Fig. 20. Composition of combustion products of $CS_2 + O_2$ mixtures as function of $\alpha = [O_2]/[CS_2]$.

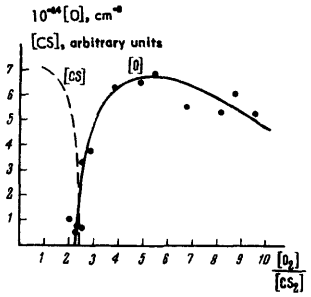


Fig. 21. Dependence of concentration of oxygen atoms on α.

assignment of the spectrum to atomic oxygen was also proved chemically: on addition of small amounts of molecular hydrogen to the reactant mixture, the concentration of oxygen atoms falls, while lines characteristic of the hydroxy-radical and hydrogen atoms appear, obviously as a result of the reaction $O + H_2 = OH + H$.

The dependence of the concentration of oxygen atoms on α is shown in Fig. 21, from which it is seen that at $\alpha \simeq 2.5$ the concentration is lower than the sensitivity of the e.s.r. instrument. Slight enrichment of the mixture with oxygen results in a sharp increase in the concentration of atomic oxygen. With further increase the concentration reaches a maximum and then slowly falls. Thus the atomic oxygen curve is, as it were, the mirror image of the curve for the variation in CS found by Kondrat'ev and included in the diagram on an arbitrary scale. This at first glance peculiar shape of the atomic oxygen curve seems to us to be due to reaction of the oxygen atoms with intermediate compounds, primarily with COS and S_2, which are the main intermediates in the region $\alpha < 2.5$. Quite recently a still further active species — the SO radical — has been detected in this system in the Institute of Chemical Physics of the USSR Academy of Sciences. Investigations will be continued on low-pressure carbon disulphide flames with the aim of elucidating the reaction mechanism.

3. Study of Low-Pressure Hydrogen Sulphide Flames

Great interest attaches to e.s.r. investigations of low-pressure hydrogen sulphide flames. It has been noted above that large quantities of SO radicals have been observed, and several of their properties studied, in the slow oxidation of hydrogen sulphide at pressures above the

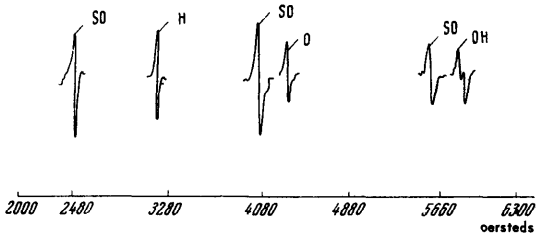


Fig. 22. Electron spin resonance spectrum of H and O atoms and OH and SO radicals detected in low-pressure hydrogen sulphide flames.

second limit of spontaneous ignition (100–200 mmHg). Emanuel'[92], and later Semenov[24], suggested mechanisms for the chain oxidation of hydrogen sulphide. The optical absorption spectra of SO, OH, and S_2 radicals had been observed[102] in the hydrogen sulphide flame before the e.s.r. method was applied. The absorption spectrum of sulphur monoxide — though in the form of the dimer S_2O_2 — has been observed[103] in the flash photolysis of hydrogen sulphide–oxygen mixtures under isothermal conditions. Mass-spectroscopic examination of the flame near the third limit indicates the existence of the S_2O radical[104]. The HS radical has not yet been detected in the flame.

Sachyan and Nalbandyan[105] have been able to observe large concentrations of hydrogen atoms and oxygen atoms in an e.s.r. study of low-pressure hydrogen sulphide flames using a heated reaction vessel placed in the e.s.r. resonator. Experiments were made at pressures up to 10 mmHg over the temperature range 350–450°C. In these experiments a signal due to atomic oxygen was detected at low hydrogen sulphide contents, but disappeared when the latter reached 25% of the whole mixture. The signal of atomic hydrogen was found at a hydrogen sulphide content of ~ 15% of the initial mixture, and became more intense as the latter increased to 45–50%.

In order to detect spectra possessing electric dipole transitions, a quartz cell completely filling the resonator was used. An electric furnace was placed above the resonator, which was heated up with hot air both to eliminate the formation of a deposit in the quartz tube and also in order to ignite the combustible mixture directly in the resonator space in the wide part of the quartz tube. Under these conditions Gershenzon et al.[106] observed the signals of hydroxy-radicals in the form of an unresolved doublet, and also three single signals in different parts of the magnetic field, due to the SO radical. Fig. 22 shows the spectra of the hydrogen and oxygen atoms and the OH and SO radicals obtained. It was expected that HS radicals would also be present in the flame, but all searches, in different systems and under different conditions, were fruitless. This is, perhaps, due to rapid reaction of HS radicals with oxygen.

We see that, among the systems discussed above, the mechanism of the combustion of hydrogen sulphide is the most complicated.

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