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Pentan Isomers Compound Flame Front Structure

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REPORT 1

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Preface

The following paper has been written by Z. A. Mansurov, A. W. Mironenko, D. U. Bodikov, and K. N. Rachmetkaliev of the Al-Farabi Kazakh State National University, Almaty, Kazakhstan as part of a collaboration with LLNL in the field of combustion chemistry. The fuels considered in this study, and the temperatures and pressures investigated, are extremely relevant to ongoing projects at LLNL related to chemistry of engine knock in spark-ignition, internal combustion engines. In the present paper, the group led by Professor Mansurov provides a review of the field of low temperature hydrocarbon oxidation and experiments carried out in the past at the Kazakh State National University. In future reports, the same group will discuss new experimental studies of oxidation under the same conditions of isomers of pentane. This work is intended to investigate the role that fuel molecular structure plays in determining knock tendency in engine combustion.

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Charles K. Westbrook
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INTRODUCTION

Investigations of flame structure of stabilized cool flames is of important value for determination of regularities of fuel conversion in both cool and hot flames. According to the contemporary ideas the cool flame is considered to be a precursor of the hot flame and therefor, processes occuring here should affect directly on the structure of hot flame forming after cool flame.

In Kasakh National University the investigation of the cool flame oxidation and cool flame structure had been started in 1970 with the purpouses:

-elaboration of the flat cool one- and two-stages flame stabilisation methods for studying front flame structure,

-discovery and identification of radicals and stable intermediats in cool flame front including H-atoms and studying of their distribution in the flame front.

In the Report 1 a short analytical literture servey on cool flames investigation has been presented, and arrangements and methods of the investigation of distribution of active centres and stable intermediates as well as results of studying of the cool flame front structures of butane, pentane, hexane and diethyl ether obtained in our laboratory have been alsu discribed.

SHORT ANALYTICAL LITERATURE SURVEY.

The gaseous hydrocarbon oxidation proceeds in a rather broad temperature and pressure region where various chain reactions are observed. The area of the low temperature oxidation includes slow oxidation, cool flames and two-stage ignition, in which the cool flame is the first stage. The investigation of the hydrocarbon cool flames and their derivatives is of considerable interest due to their important role in a number of fields:

a) low temperature oxidation [1-4];

b) combustion processes occuring in the internal motor engine [5]. It is of great interest from the point of view of environmental pollution with the incomplete oxidation products in engines;

c) problems concerning technical safety in chemical industry since cool flames are potential sources of low temperature centres of ignition at fuel concentrations corresponding to the upper concentraion limit of the ignition [6-8];

d) development of new direction that is thecnological combustion related to obtaining products of incomplete combustion (aldehydes, alcohols, oxide compounds and unsaturated hydrocarbons) in flame conditions [9-13];

Cool flames were known by H.Davi as early as in 1816 [14] and they were studied by W.H.Percin (1881) [15]. The systematic investigation of cool flames was conducted by M.Prettre and his co-wokers [16] for a long period (1935-1960). Further, they were studied by a range of researchers [17-21]. A.S. Sokolik and his co-wokers [22] investigated the appearance of cool flames flashes in the internal combustion engines (ICE) and found the interrelation of the ICE detonation with the cool flame process. The chemical kinetic oxidation processes were studied by Ch. K. Westbrook [23], who offered a kinetic model of the ICE fuel oxidation interpreting an action of anti-detonators.

Investigations of flame structure of stabilized cool flames is of important value for determination of regularities of fuel conversion in both cool and hot flames. It should be noted that there is a small number of researches aimed to study the front structure of stabilized cool flames.

There are about ten works in which profiles of stable initial, final and intermediate compounds distribution have been obtained. Still less reserches are devoted to the determination and distribution of active intermediate radicals and atoms [24-34].

In stabilized cool flames at the certain initial temperature and flow rate a spacing evolution of the conversion of initial, intermediat and final substances arises, that allow to measure temperatures and conduct zond samples [24,26,30] which are impossible under the static conditions due to extremely short duration of the process.

The diethyl ether-air flame which does not reqiure considerable heating of the fuel mixture for its stabilization is the most studied cool flame[24,25,31-34]. Constructions of a vertical tube reactor, flat bunner as well as the conditions of cool flame generation are described in the Ref.[35].

M.B. Neiman and his co-workers [17,18,31] studied the kinetics of accumulation and further conversion of acetaldehyde and formaldehyde in the stationary cool flame of diethyl ether. It was shown that the specific activity of acetaldehyde fast fell near the cool flame region while the acetaldehyde group did not take part in the formaldehyde formation.

Townend found experimentaly [21] that cool flames were able to be spread into the fuel mixture at room temperature without heating.Semenov explained this phenomenon by means of square-law autocatalysis [61].

B.G. Agnew and J.T. Agnew applied the procedure of sampling with a quartz microzond with the further analysis by combined chromatography and mass-spectrography [24] for studying the atmospheric two-stage diethyl ether flame.

R.Del-Burgo and C.Wovel [25.36] studied one- and two-stage diethyl ether flames under pressures 46.6 - 101.3 kPa. The drop of the pressure was accompanied by visible increase of a distance between two flame stages and growth of flame thikness. The qualitative composition of cool flame products was shown to be identical [36] independently of number of stages.

Stabilized in the vertical tube reactor cool flame of acetaldehyde which was one of the general intermediate compound of cool flames of hydrocarbones [1,3] and diethyl ether [24,25] was studied. Experiments on the stabilization and investigation IR-spectrum of two-stage acetaldehyde cool flame were described in Ref.[37].

Bradly [37,38] and then Griffith [39] used the zond sampling procedure combined with the mass-spectrometer analysis in order to obtain concentration profiles of the stage acetaldehyde, propionaldehyde and propene flames stabilized in the vertical tube reactor.The exothermicity of cool and two stage flames was found to be enough for the support of combustion without heating during half an hour.

The stabilization of cool flames of hydrocarbons, particularly lower hydrocarbons, is possible at preliminary heating of the fuel mixture, heating value being increased at transition from butane to metane [26].

Bollinger and Raison [26] stabilized one- and two-stage cool flames of n-butane, n-pentane and n-heptane. It was shown that stationary cool flames are very convenient models for testing the effectivness of inhibition and promotor additions. In addition, the two-stage flames were found to be stabilized better in a glass burner than in a rustless steel burner. This fact indicates the sensitivity of the cool flames to experiment conditions (features of heat and mass transfer).

G.I. Ksandopulo and his co-workers [40] have investigated concentration and temperature profiles in low temperature part of the hexane flame by using of mass-spectrometer and thermocouple probe. It has been found that hydrocarbon radicals, are formed and accumulated more rapidly at flame conditions than at those of spontaneous ignition [40], the presence of unburned oxygen leading to the formation of peroxy radicals. The regularities of hexane combustion have been found to be the same for that of lower paraphines (propane) [42]. G.I. Ksandopulo and R.A. Zubtsova [41] have studied the distribution of the peroxy compounds in the hexane flame front.

Polarographic analysis of samples selected from various points of the

flame front allowed three types of peroxides to be identified: alkylhydroperoxides ($E_{1/2}$=-0.32V), dialkylhydroperoxides ($E_{1/2}$=-0.87 V) and hydrogen peroxide ($E_{1/2}$= -1.05 V) [43].
The authors [41] considered obtained peroxide concentration profiles to the results of radical concentration distribution in the pre-flame region.

The cool flames of n-heptane stabilized in conic-cylindric reactors made of pyrex and rustless steel have been studied [44-46]. It has been found that growth of reactor temperature leads to the displacement of maximums of temperature and radical concentrations towards the reactor inlet, the distance between these maximums decreasing. It should be noted that if the rise of reactor temperature causes increasing RO_2-concentration then the maximum flame temperature decreases.

A.A. Mantashyan and his co-workers [27,47-50] have developed the method of cool flame stabilization in heated reactor consisting of two sections linked with a thin tube. The residence time of the reaction mixture in the first secction was equal to an induction period of cool flame at a current temperature. Passing throw the thin tube the fuel mixture ignited and cool flame was stabilized in the second reactor section. This method is very convenient for the investigation of cool flame since separated heating of two sections allowes to study the influence of temperature and different additions on the cool flame. In the course of investigation of stabilized cool flames of n-butane, propane and propene [27,30,50] peroxy radicals have been found, their concentrations were over $10^{14}cm^{-3}$ that was more in 10-20 times than those in the first section.

It has been found that complicated temperature profiles having asymmetrical form with the maximum at the upper part of the reactor arised, as it was in the experiments at the static conditions [50]. Temperature gradients gained 70 C and even exeeded this value. The total temperature profile obtained in a cross-section in the form of isotherms over each 10 C in the stabilized n-butane cool flame built on the base of temperature profiles taken from two axes is of great interest.[51].

Complex forms of heating profiles observed in n-butane cool flame apparently were connected with the increase of heat release rate and the possible effects of the gasdynamic factors as it was noted in [51]. However the estimation of the role of gasdynamic factors has shown the turbulence of the gas stream to be very low that indicated the possible existence of the sharp gradient of the temperature leading to asymmetrical heating profiles.

Analysis of the above works on the invvestigation of the stationary cool flames enables the works to be conditionaly separated into two groups.

The first group includes cool flames stabilized in the heating reactors. They are characterized by light heating (20 -80 C), and the fuel conversion carries out with the formation of olephynes and oxide compounds. They are of great interest from the viewpoint of the technological combustion.

The second group is stage flames where cool flame is the first stage and the second one can be blue or hot flame. In this case, as it seen from [26], the influence of hot region on the cool flame is essential. The hot flame front, as it was shown in [52], is a source of diffusion of H-,O-atoms and hydroxyl radicals which lead to the chain branching and continuation reactions in fresh mixture with the following crashing of the fuel molecules to deep stages.

In case when the second stage is the blue flame its front generates hydrocarbon radicals which are less active in comparison with the H-atoms diffusing towards the side of cool flame, total fuel conversion being more complete.

Analysing the above considered works one can note that there are two important problems in the investigation of the stationary cool flame structure. One of them concerns the stabilization of one dimensional cool flames convenient for zond sampling of the flame front, and the second one is to obtain profiles of the active particle distribution.

One should indicate that in heated reactors cool flames are possible for superrich fuel mixtures. These flames cannot be stabilized on the flat burner due to insufficient heat release for the support of chemical reactions occuring in the cool flame. Therefor to solve the first problem the heated burners and reactors are used.

The solving of the second problem is complicated by that there is no opportunity at present to make a full identification of all active particles that is connected with the limited possibilities of the ESR method. Apparentelly, it is purposefull to apply ESR method combined with other original methods to be developed for the determination and identification of both stable and labile intermediates, then one should to make a joint data analysis on their distribution in the flame front.

EXPERIMENTAL

The flat flame burner

The general experimental scheme is shown in Fig.1,and Fig.2 represents the flat flame burner. Diethyl ether in the cylinder was heated to 50 C, then it was flowed into the mixer and the fuel-air mixture was transported into the burner where it was ignited with the Rumford coil. The flow

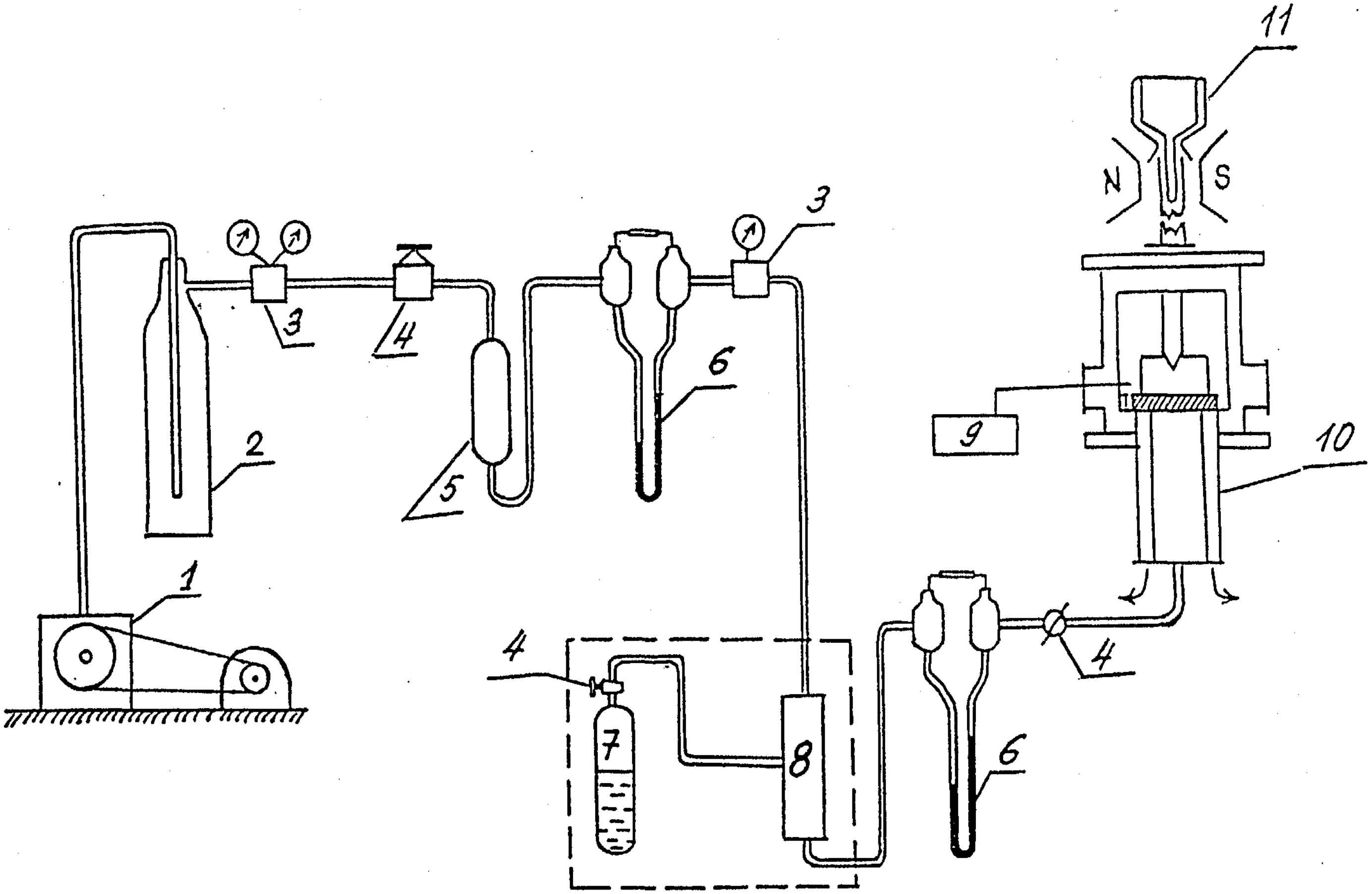


Fig. 1 . General scheme of a set-up for study of the cool flame of diethil ether. 1. compressor 2. receiver 3. manometer 4. tap 5. filter with silicagel and silicate cotton 6. reomether 7. cylinder with ether 8. mixer 9.Rumford's coil 10. flat flame burner 11. Dewar vessel

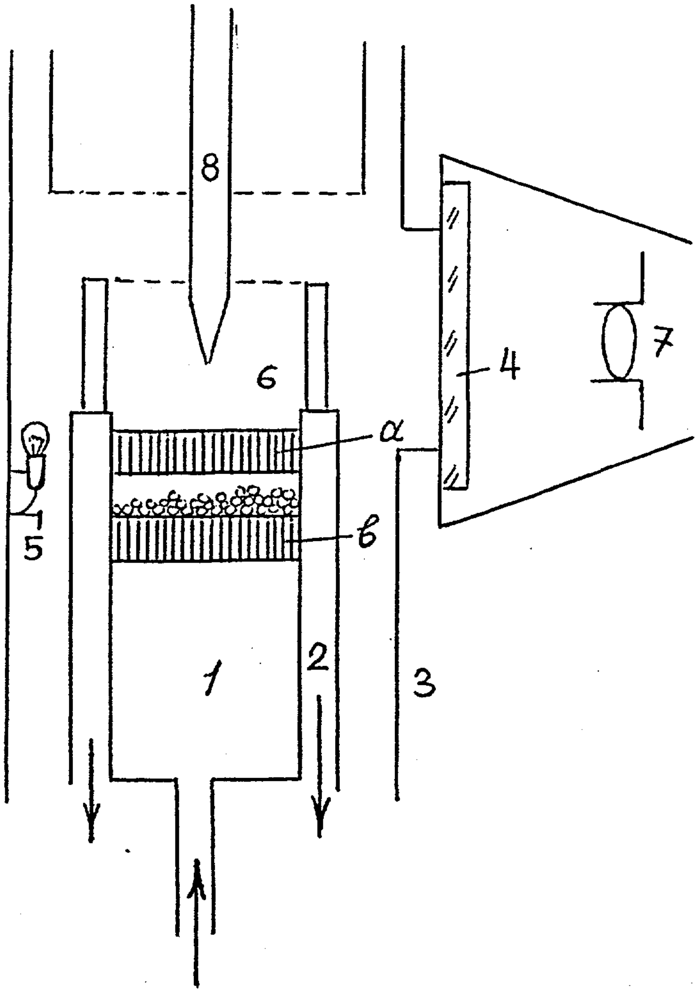


Fig. 2. Sheme of the burner
1.burner, 2. cooling water jacket
3. jacket, 4. incpection window
5. flash lamp for illumination
6. reaction volum 7. camera
8. sampler (probe)

rate of diethyl ether was determined by a difference between readings taken from two reometers. The flame process and probe position were observed through a special window. The probe and thermocouple zond positions relatively to the flame location and burner surface were defined with the KM-8 kathetometer.

The flame temperature was measured with chromel-alumel thermocouple (d=100 mmn). The working surface of thethermocouple was covered with a thin layer of silicon oxide. The flame temperature was registered by a K-121 loop oscillographan КСП-4 potentiometer.

Experimental set-up for studying the stabilized cool flame of hexane.

The experimental set-up is shown in Fig.3. The main part of the arrangement is two-section reactor developed by A.A. Mantashyan for stabilizing cool flame. The reactor sections are cylindrical vessels of pyrex glass linked with a thin tube (L=20 mm, d=8 mm). Temperatures of stoves were controlled by a thermostatic regulator BT-1, then they were measured by chromel-alumel thermocouple and registered by the potentiometer КСП-4. In all experiments pure hexane was used. Vacuum pump HBP-5Д was used to deacrese pressure.

Experiments were carried out in both vertical and horizontal reactors. The horizontal reactor consisted of two cylinders (d=50 mm, L_1 =300 mm, L_2 =120 mm), while the vertical one had two cylinders with other parameters (d=50 mm, L_1=660 mm, L_2=130 mm).

A thermocouple prob to detect radicals in the reaction zone consisted of three chromel-alumel thermocouples (d = 0,005 mm) installed at the same level. One of the thermocouples was used to control temperature, the two others, switched on differentelly, were used to detect radicals. A thermocouple probe was moved along the axis of the second section. The surface of all thermocouples were pre-passivated by diethyl ether of orthocilicic acid [62]. After passivation, one of the differential thermocouples was covered with LiCl solution in ethyl alcohol. Signals from the thermocouple probe were recorded on an H-117 multi-channel light beam oscilloscope having low sluggishness.

The temperature gradients along axes of both reactor sections produced by electrical stoves without reagent flows were about 10 C in the first section and 15 C in the second one.

The modified flat flame reactor

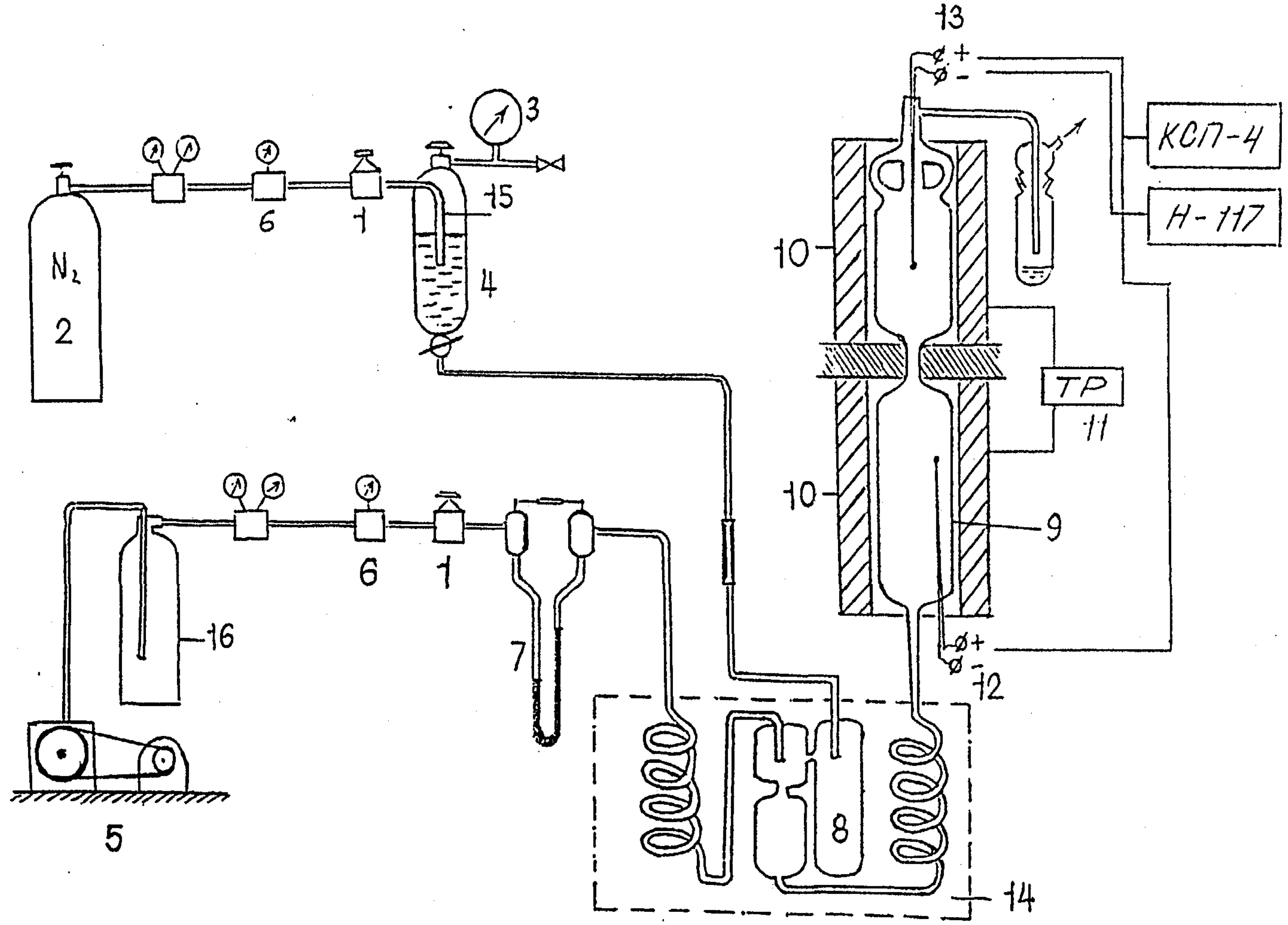


Fig. 3. Scheme of the experimental set-up for study pentane- and hexane cool flames

1. tap 2. cylinder 3. control manometer 4. cylinder with pentane (hexane) 5. compressor 6. manometer 7. reometer 8. mixer 9. two-section reactor 10. stove 11. thermoregulator 12, 13. thermocouples 14. water thermostat

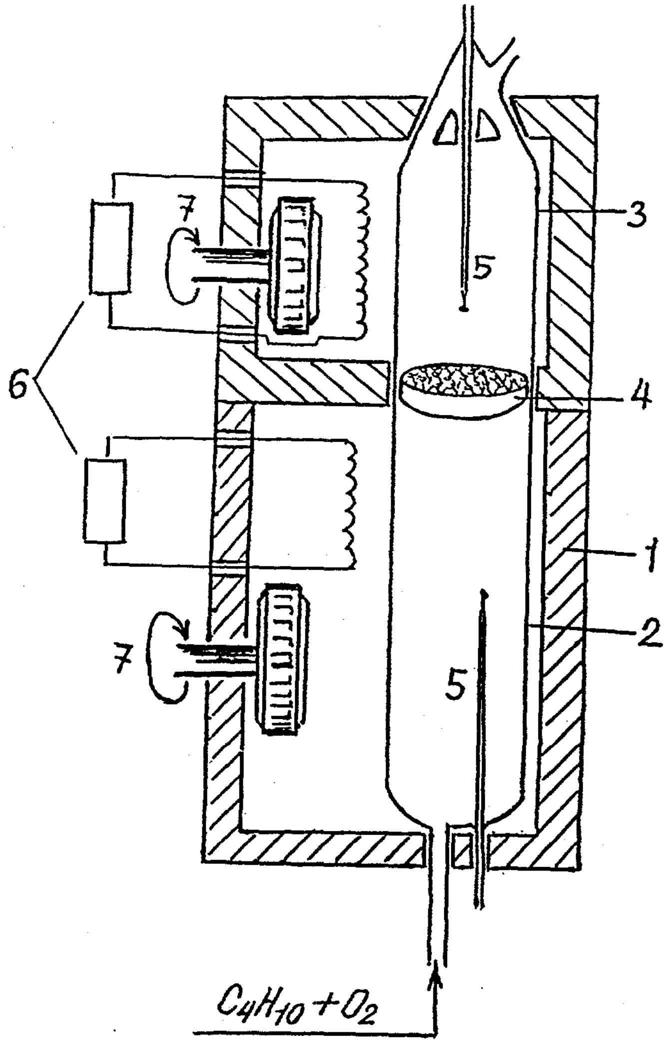


Fig. 4. Heated flat flame reactor
1. thermostat 2. firsts sectio 3. second section
4. perforated pyrex plate 5. thermocouple
6. electric heater 7. ventilator

Table 1

Dimensions, diapason and measuring error (%)

N	Measured magnitute	Dimensions	Diapason	Measuring error,%
1	Flow rate of hydrocarbon fuel	cm/min	100-3000	2.0
2	Flow rate of oxygen	cm/min	100-2000	2.0
3	Reactor wall temperature	K	373-1223	2.5
4	Evaporator temperature	K	350	1.0
5	Fractional conversion of initial hydrocarbon fuel	weight %	0.1-80	2.5
6	Time of a process	min	5.0-600	2.5
7	Temperature inside the reactor	K	273-1473	2.5
8	Concentration of main gaseous products of combustion	vol. %	0.1-90	2.0

To study the front structure of the stabilized flat butane flames we modified the two-section reactor developed by A.A. Mantashyan. It was the two-section separately heated pyrex reactor with inner diameter of 62 mm. Reactor sections were separated with a sieved pyrex plate. The plate had 50 holes with a total area of 50 mm. The section lengths were L_1=300 mm and L_2 =100 mm. The reactor was vertically oriented and the reaction mixture was injected into the first section from beneath. The reactor temperature was thermostated by mixing hot air flows. The temperature control was accurate to 1+ C according to the temperature regulater BT-1.(Fig. 4).

Identification of paramagnetic centres in the flame front and their detection were carried out by a radiospectrometer PЭ-1301. And see table 1.

RESULTS AND DISCUSSION

Stabilized hexane- and pentane-air cool flames [58 - 63,76 - 80]

There are a few works devoted to investigations of hexane cool flames in stream conditions [71-74]. At present it has been established that the main intermediates in low temperature hydrocarbon oxidation are peroxy RO_2 and HO_2 radicals. Unfortunately, there are no data on tracing of free radicals as well as their distribution in the reaction zone of hexane flames in current literature. At the same time, alcyl radicals formed in reactions are known to be frozed out lightly at the temperature of liquid nitrogen,giving a character ESR spectrum [64,75].

So it can be considered that at low temperature hexane oxidation the ESR spectra represent spectrum of mixture of long chain alcyl and light peroxy radicals. In this connection, the investigation of low temperature oxidation of hexane-air mixtures is of practical interest for discovering ESR spectra of alcyl and peroxy radicals and studying the influence of experimental conditions on their concentrations and forms of these spectra. Results of ESR studies of hexane-air cool flame stabilized in the horizontal two-section reactor at atmospheric and lower pressures an T_1=420-540K(firstssection),T_2=480-770(second sectionare presented here. The component ratios were C_6H_{14}: O_2 = 3:1, 2:1, 1:1 and 1:2, and the residence time of the mixture in the second section was τ_c = 6-39 s. [76 - 78].

Temperature profiles of the stabilized cool flames registered at T_1 = 573 K and T_2 =630 K (τ_c =21.6 s., C_6H_{14}:O_2 =2:1) and p=36.6, 50 and 63 kPa are represented in Fig.5. As it is seen, the maximum flame heating up

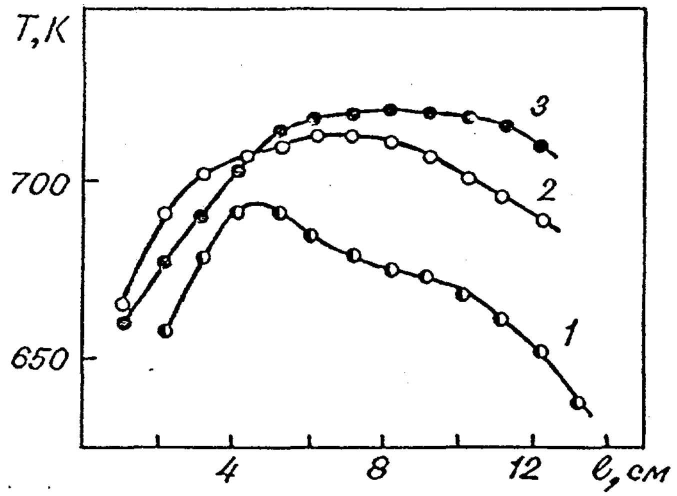


Fig. 5. Profiles of temperatures by T_2=630 K and
P: 1-36.6 kPa; 2-50 kPa; 3-63 kPa

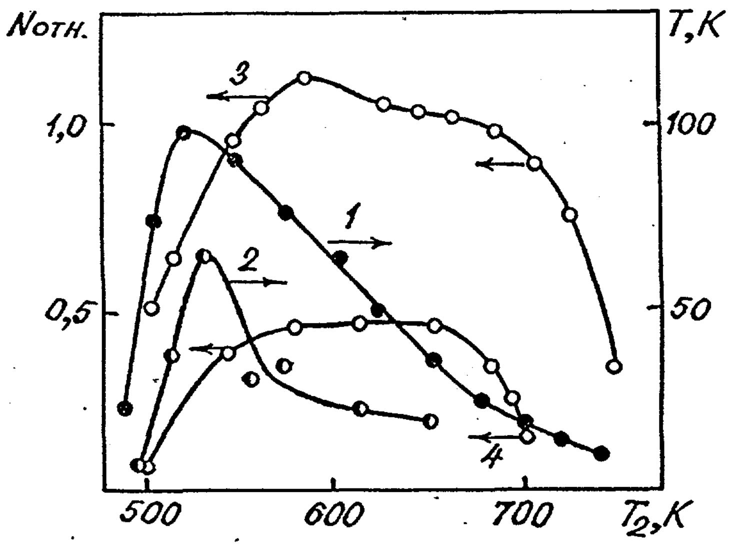


Fig. 6. Dependence of maximum flame temperature on T_2 at
P = 36,6 kPa and τ_c = 21,6s (1) and 39,6s (2)
Dependence of maximum concentrations of peroxy radicals on
T_2 at P = 36,6 kPa and τ_c = 21,6 s (3) and 39,6 s (4)

at p=36.6 kPa is 64 K (the curve 1) and its location is near to the reactor inlet. The further pressure increasing up to 50 kPa (the curve 2) and 63 kPa (the curve 3) induces growth of the maximum temperature and its location shifts to the reactor outlet. At the same time, the value of the maximum flame heating up falls with pressure increasing.

The phenomenon of negative temperature effect of the fuel mixture combustion has been found. As it can be seen in Fig.6. at p=36.6 kPa and T_1 = 490 K the maximum difference of the flame temperature from $T_2$is 95 K, the futher temperature rise leads to the considerable decreasing of flame heating up (the curve 1, Fig.6.). Under the same conditions, but at τ_x= 39.6 s the maximum temperature difference from T(T_2=553 K)is 63 K (the curve 2, Fig.). The residence time of the mixture in the second section increases, the maxumum T value decreases. However in both cases the maximum T_{max} value is observed at the same temperature of the second section.

An analysis of the hexane-air flame products was made by IR-spectroscopy, a low temperature vessel containing a small botton plate of KBr cooled with liquid nitrogen was being used [76].The IR-spectrum of a part of cool flame products is shown in Fig.7.(T_1=433 K, T_2=594 K, p=36.6 kPa,τ_c=21.6 s.,ratio hexane:air=2:1).The following flame products such as formaldehyde,acetaaldehyde and alcohols are defined strictly from the IR-spectra. The intensity of strips corresponding to these products allow top redict their relative content in the mixture. Besides, there are a few strips in the IR-spectrum, which is not defined.

The IR-spectrum analysis of samples taken from the various zones of the second section shows that the relative concentration of acetaldehyde (ν=520 cm^{-1}) increases slowly up to its maximum value in the middle of the reactor and then falls, while those of formaldehyde (ν =1495 cm^{-1}) and alcohols (ν =1050 cm^{-1}) increase constantly and gain their maximum values at the reactor outlet.(Fig.8.)

The determination of organic peroxy radical concentrations was carried out by Banerdzy and Budke method [56]. Fig.9. showed the dependence of organic peroxide concentrations on T_2 value. One can note that maximum concentration of organic peroxides isachieved at temperatures 553-563 K where maximum flame heating up is observed. The futher growth of T_2 caused lowering of the content of organic peroxides in flame products.

To find peroxy radicals a sampling probe was applied in combination with the ESR method.(Fig.9.)9During the reaction a small sample of the reacting gases was taken from the reaction zone and at p=10 kPa was directed onto a nitrogen-cooled finger of the Dewar vessel inserted into

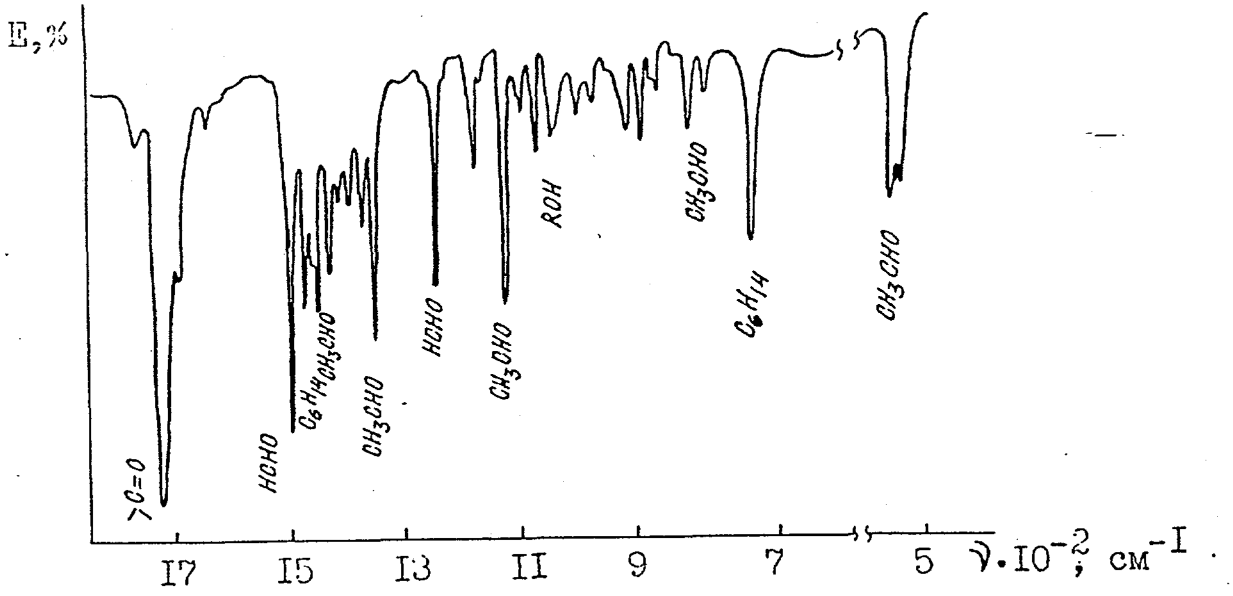


Fig. 7. IR-spectra products of cool hexane flame.

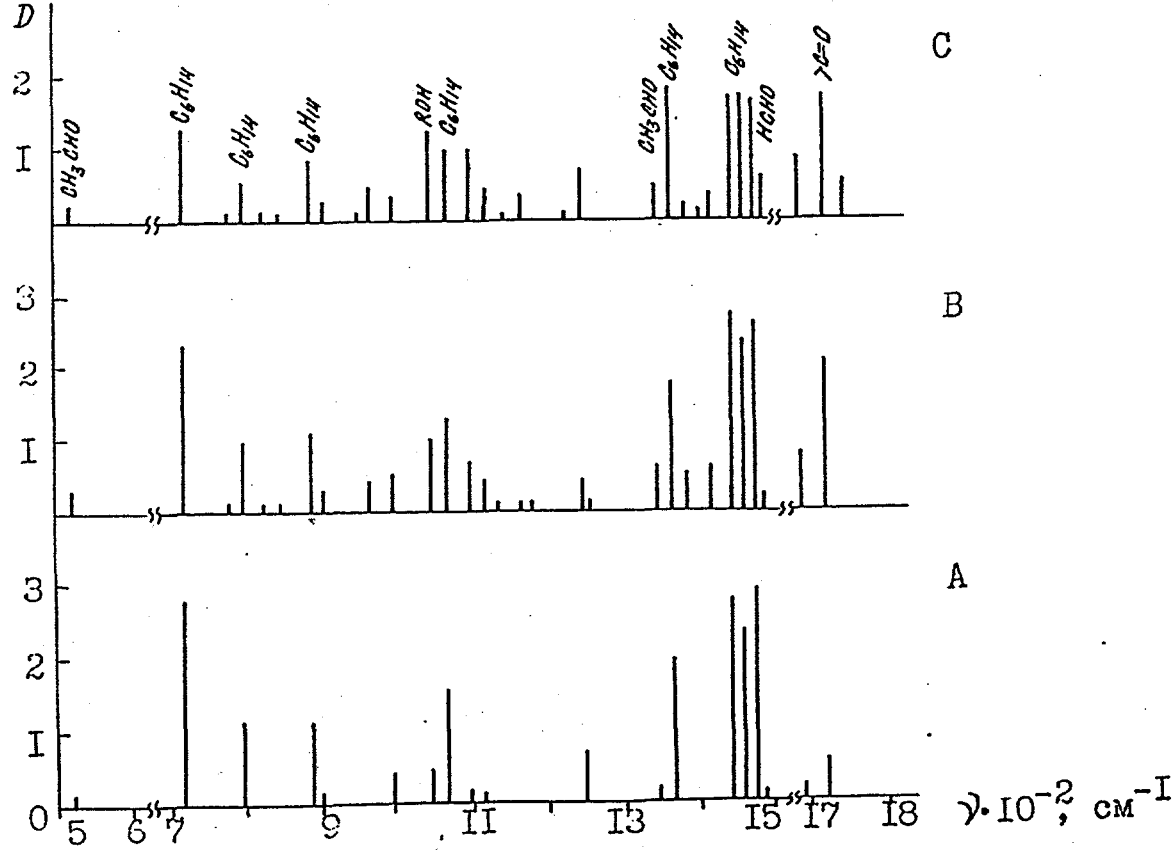


Fig. 8. IR-spectra probe selected from various zones of the reactor

A in the point=3 sm

B in the point=7 sm

C in the point=11 sm

the ESR spectrometer where taken gases were frozen up and radicals accumulated. The dependence of peroxy radical concentrations on T_2 a τ_c =21.6 s (curve 1) and τ_c=39.6 s (curve 2) and p=36.6 kPa, and dependence of the organic peroxy radical concentrations on T_2 at p=36.6 kPa are illustrated in Fig.9.As is seen with increasing residense time radical concentrations fell and their temperature zone narrowed. As well with a rising temperature over 670 K negative temperature motion of the curves of peroxy radical concentrations was observed. The ESR spectra of the samples recorded at T_2 =540 K and 670 K are represented in Fig.10 .At low temperatures RO_2 radicals type (1) accumulated and with increasing temperatures the spectrum splits. This can be due to the fact that in these conditions, besides alkyl peroxy radicals, HO_2 is formed (2). For comparison, the ESR (RO_2 -HO_2) spectrum recorded in the course of butane cool flame oxidation is presented on the Fig.10.[64].

A comparison of the spectra for peroxy radicals recorded at p=36.6 kPa and at different temperatures T_2 ,indicates that already at T_2=620 K the splitting of the ESR spectrum equals value of 3.2 Oe. With increasing temperature, this splitting gradually grows and at T_2=750 K it is equal to 14.5 Oe. The splitting of peroxy radicals also rises with increasing pressure which means that with increasing temperature and pressure the portion of HO_2 radicals in the total amount of radicals grows.

We also studied pentane-air flames stabilized in the two-section reactor at T_1=453-523 K, T_2=623-763 K, τ_c=5-20 s [79,80]. The temperature profiles detected along the axis of the second reactor section are represented in Fig. 11. As seen from Fig.11 increasing the temperature of the second section to 100 K led to increasing flame temperature, and the form of the adjacent curve changes imperceptibly. The second section temperature increases to 773 K, the flame temperature grows sharply and gaines its maximum value equaled 860 K.

It should be noted that the flame kernel is concentrated at the middle part of the reactor, while in two previous cases (curves 1 and 2) the flame engages all volume of the second section. See also Fig. 12.

Data of the chromatography analysis are represented in table 2 . Increasing of oxidizer fraction and residence time lead to growth of oxycompounds in the combustion products. Especially it affects on increasing of the yield of methyl alcohol, acetaldehyde and ethyl alcohol.

Together with these compounds one can observe considerable rise of concentrations of water and carbon dioxide. The yield of ethylene compounds increases with the growth of the second section temperature, the propene concentration falls and that of ethylene increases.

The principal possibility to alterate ratio of products depending on

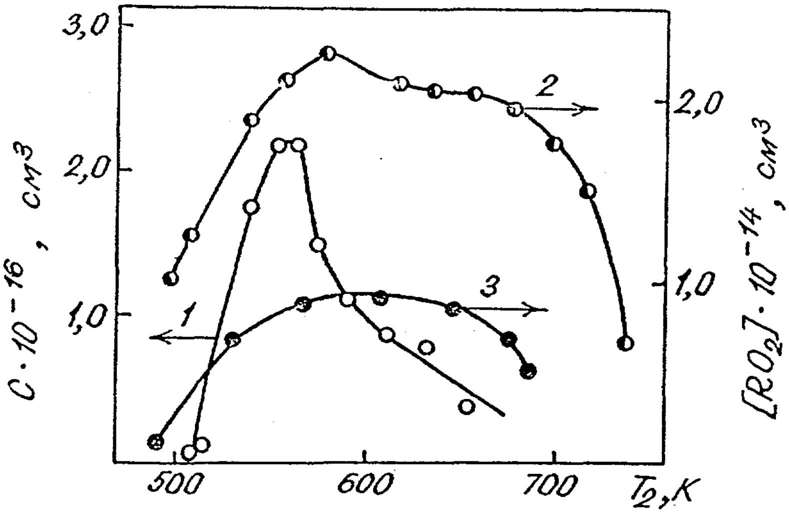


Fig. 9. Dependence of organic peroxyd's concentration from T_2 at P=36.6 kPa (curve1). Dependence maximum concentrations of peroxyl radicals from T_2 at P=36.6 kPa and τ_c 1). 21.6 s (curve2) 2). 39.6 s (curve 3)

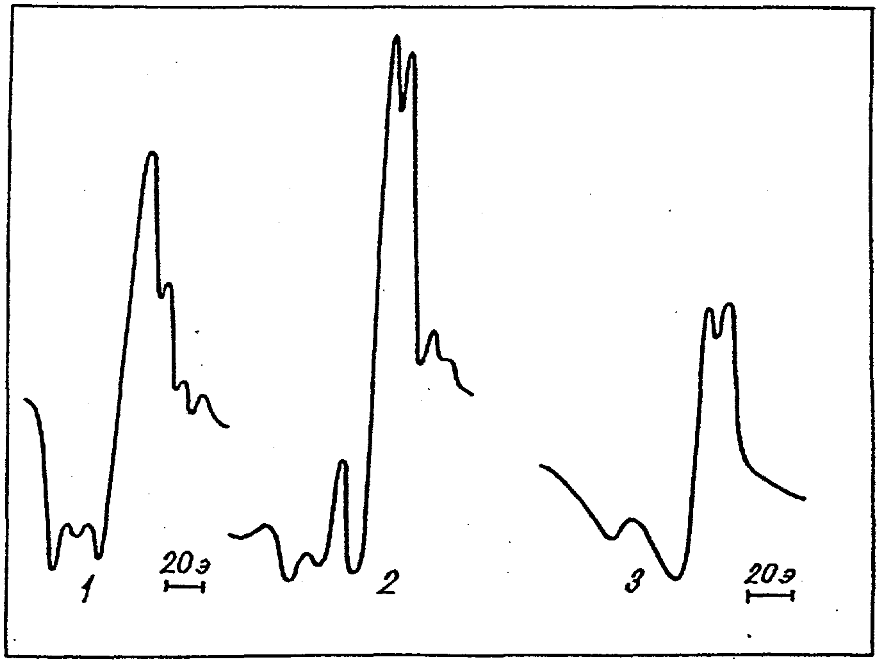


Fig. 10. ESR spectra of peroxyl radicals by P=36.6 kPa and T_2: 1- 540 K, 2- 670 K, 3- from ref. [ ]

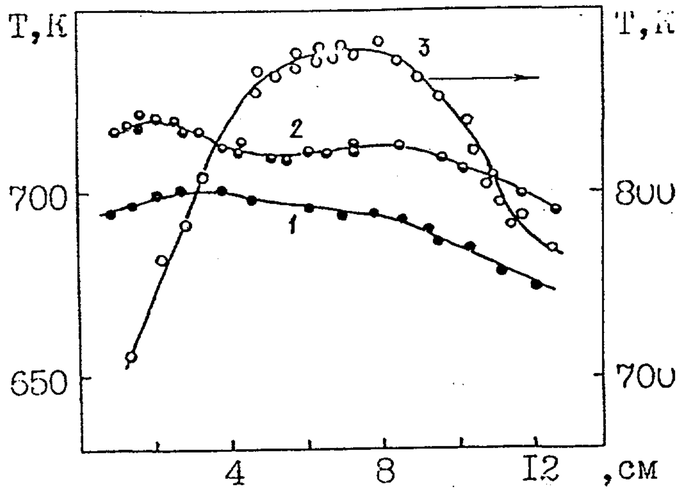


Fig. 11. Profiles of temperatures of pentan-air flame in dependence from from second section's temperature of the reactor (T_2) at T_1 = 453 K and τ_c = 5s 1- T_2 =523 K: 2- T_2 = 708 K: 3- T_2 = 773 K.

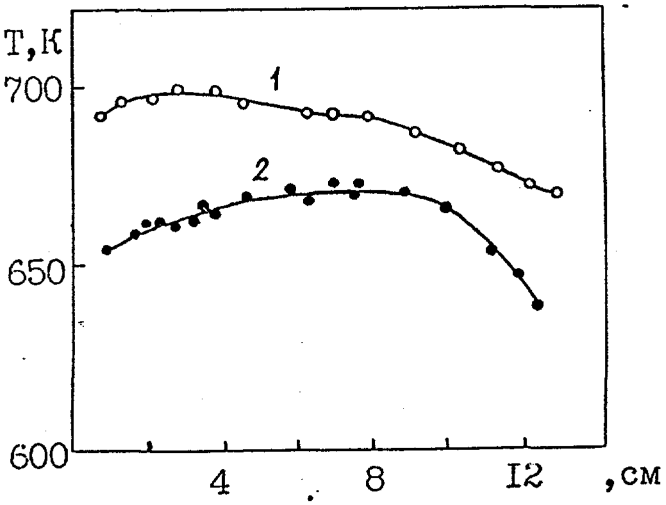


Fig. 12. Profiles of temperatures pentan-air flame in dependence from temperature of the first section of the reactor (T_1) at T_2=623 K and τ_c=5 s 1). T_1=453 K 2). T_1= 523 K

Table 2

General results of the cool flame oxidation pentane

Experrimental conditions

1. T_1=523 K T_2=623 K C_5H_{12}=19.5 %
2. T_1=413 K T_2=823 K C_5H_{12}=29.5 %
3. T_1=438 K T_2= 723 K C_5H_{12}= 9.5 %

$Q_{1\text{-}3}$= 514 sm ^{3}/min

substance	final products contents, V % by oxidation of pentan in various conditions		
	1	2	3
H_2	0.9	1.8	traike
O_2	0.5	5.7	2.3
CH_4	0.3	4.2	2.0
CO	3.0	4.8	3.6
CO_2	2.1	0.3	1.8
C_2H_4	1.4	4.0	1.7
C_3H_6	6.6	5.7	4.3
H_2O	11.4	14.0	13.2
CH_3OH	6.2	3.1	1.4
CH_3CHO	2.0	0.6	0.9
n-C_5H_{10}	1.0	0.6	0.6
n-C_5H_{12}	12.3	8.5	3.4

the conditions of the pentane cool flame oxidation has been shown.

The study of propane-oxygen flames at low pressures [84]

The stabilization of propane-oxygen flames was studied at 2.66 - 13.3 kPa. Temperature profiles obtained at 2.66, 7.98 and 13.3 kPa are presented in Fig.13. At 2.66 kPa and propane-oxygen ratio 1:2.74 the flame has a stretched luminous zone, which diameter is small relatively (28-30 mm).

The flame front differs slightly from the flat one because its boaders are bent to the side opposite to the matrix. The thikness of the flame front is 11.6 mm. The flame temperature rise gradually the further it gets from the matrix and gaines its maximum value at the front part of the flame.

Apparently, at 2.66 kPa the scatter of experimental points is rather large in comparison with that at other pressures. It can be interpreted by that the stability of the reaction zone rises with the increase of pressure. At 5.32 kPa the flame of fuel ratio 1:2.75 was obtained.

The flame front was at a distance of 5.5 mm from the matrix, its thikness and diameter were 5 mm and 40 mm correspondingly. The flame form looked like a flat disk and was lightly blue. At 7.98 kPa the flame had the same color and the fuel ratio was 1:2.6. The final distance between the flame and matrix was 4.3 mm.,its thikness was 4.2 mm. and its form was also like a disk.

The pressure growth to 10.6 kPa changed the flame color, the latter became turquoise. The fuel ratio in the initial mixture was 1:2.85, the flame thikness was 4.6 mm and its distance from the matrix was 2.8 mm. At p=13.3 mm the flame had light green color. In addition the considerable soot yield was observed.The fuel ratio was 1:2.87,the flame thikness was 2.9 mm and the distance betwwen flame and matrix was 2.3 mm.

Thus, it can be concluded that the pressure growth lead to narrowing of pre-flame zone and the flame thikness. Therefor, the heat transfer to the burner matrix rises, so the formation of intermediates starts not only in the volume but on the matrix surface.

The concentration profiles taken from the propane-oxygen flame at 7.98 kPa are shown in Figures 14 ,15. As Fig 14. showes the fuel consumes in the pre-flame region. The generation of flame products such as propene, butylene, iso-butylene startes near the burner matrix. Their concentrations gain maximum values in the region 2.3 - 2.7 mm, then they fall. The appearance of carbon oxide is noticable on

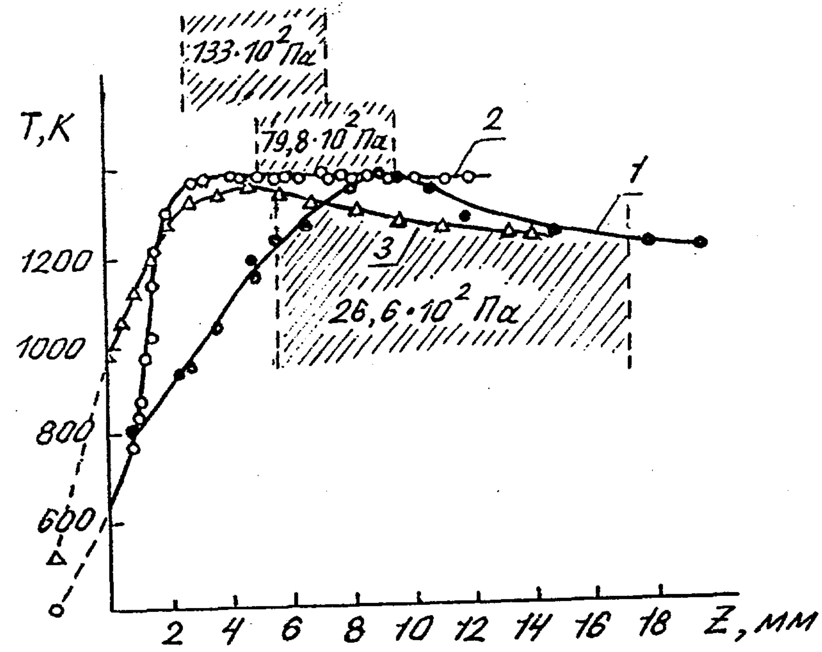


Fig. 13. Temperature profiles of front flame for various pressures in the burner 1- 26,6 • 10² Pa, 2 - 79,8•10² Pa, 3 - 133•10² Pa

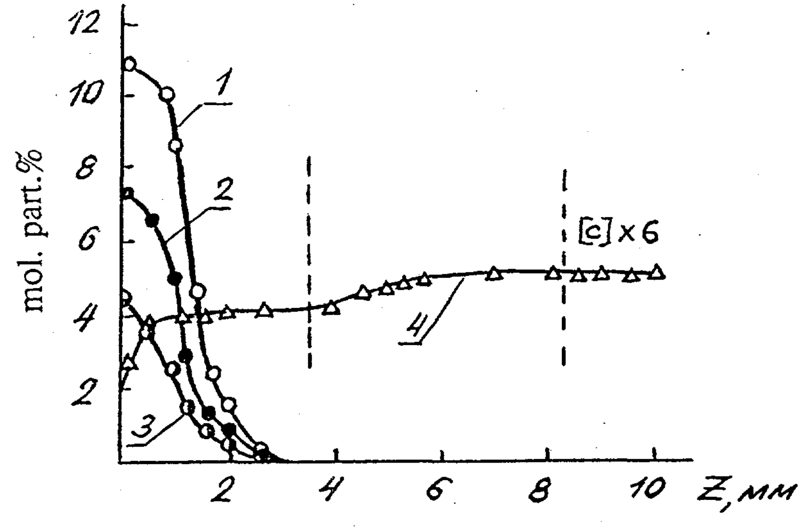


Fig. 14. Concentration profiles of initial and final combution products: 1 - propane, 2 - iso-butane, 3 - butane, 4 - water

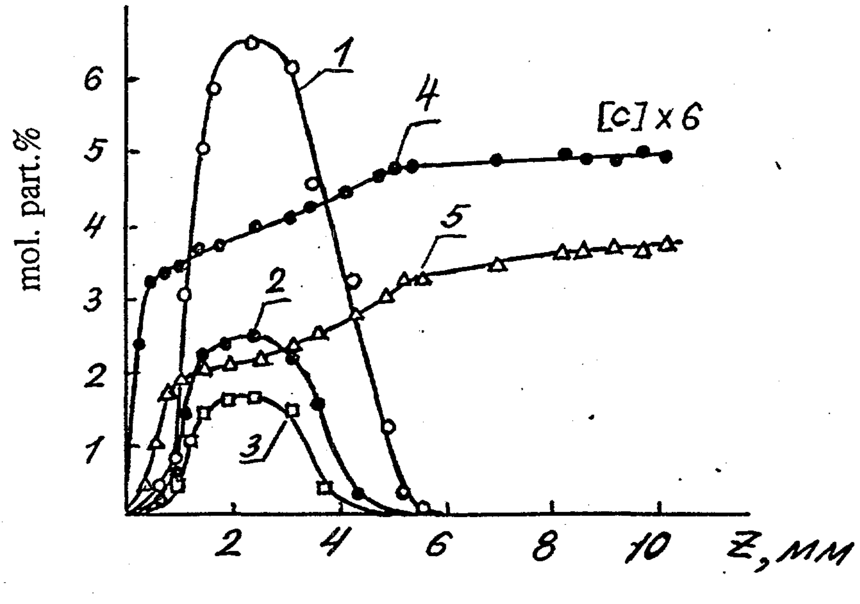


Fig. 15. Concentration profiles of intermediate and final combustion products: 1 - propilene, 2 - iso-butilene, 3 - butilene, 4 - oxide carbon, 5 - dioxide carbon

the burner matrix. Their concentrations gain maximum values in the region 2.3-2.7 mm, then they fall. The appearance of carbon oxide is noticable on the burner matrix, then its concentration sharply increases and gains the maximum at the point 5.5 mm.

The noticable concentrations of intermediate and final products observed near the buner matrix testify the beginning of fuel conversion on the matrix surface and even inside the matrix that confirms the assumption proposed in Ref. [53]. As it known [54], the soot formation from the thermodynamic viewpoint initiates when in the equation

$$C_mH_n + yO_2 \longrightarrow 2yCO + n/2H_2 + (m\text{-}2y)C \qquad (1)$$

m becomes greater than 2y, i.e. when the C/O ratio exeeds the unit. Experimentally the limits of soot formation are equated to the appearance of luminescence that is observed not at C/O = 1 but usually at C/O = 0.5. Considerable amounts of CO_2 and H_2O are observed in the region of the limiting C/O ratio, although their concentrations, it would seem, are to be slight in the presence of soot. This result can be explained by the nature of the process occuring in the flame zone. OH radical reacts with the initial fuel,H and CO that leads to the formation of H_2O and CO_2 .

$$CO + OH \longrightarrow CO_2 + H \qquad (2)$$
$$H_2 + OH \longrightarrow H_2O + H \qquad (3)$$
$$R + OH \longrightarrow HO + R \qquad (4)$$

At the same time H- and O-atoms interact with initial fuel generating various hydrocarbon radicals which participate additional reactions preceding soot formation.

Ch.K. Westbrook has shown [54] that mechanism of hydrocarbon conversion changes at the transition from lean to stochiometric and rich mixtures. This transition is defined by the expression:

$$\alpha = K_6 / K_7 [O_2] \qquad (5)$$

For the rejime of lean mixtures $\alpha = 2.2$, for stochiomefric and rich mixtures $\alpha > 5.5$. K_6 and K_7 are rate constants of reactions (6) and (7)

$$C_3H_7 \longrightarrow C_3H_6 + H \qquad (6)$$

$$C_3H_7 + O_2 \longrightarrow C_3H_6 + HO_2 \qquad (7)$$

Estimation of the relation of reactions (6) and (7) for the flame studied at T=1300 K gives:

$$\alpha = \frac{2{,}0\ \ 10^{14}\exp(\ -40\ 000\ /\ RT\ )}{10^{12}\exp(\ -5\ 100\ \ 10^{-4}\ /\ RT\ )} = 30$$

confirming the surplus fuel content and indicates that soot forming reactions are possible.

Radical distribution in front of the cool flames of diethyl ether [57, 82]

Results of the investigation by the ESR method in conjuction with the prob technique [81,82] of stationary two- stage (12,5 and 18% ether) and one-stage (32% ether) cool flames of preliminary mixture of ether and air stabilizated on the burner of a flame are shown below The mixture was lid by a sparc over the stabilizing gaus, thereby a continuouss torch flame could be observed. One or two minutes later, whil the gauze and part of the pirex tube near it grew hotter, a pale blue front of a cool, then of a brighter blue flame slipped down into it against the stream. As the temperature of the flame rose, the cool flame approached the matrix and then stabilzed. It was found by experimnt that, if after the formation of a one or two-stage flame in the region of the pirex tube, the supply of a combustion mixtur is stopped for a short time, and then resumed a flame is formed in the pirex tube, which doas not burn like a torch,outside the gauze. The flame in the pirex tube has a “memory” effect. The flame appears at the same distance from the stabilizing gause were it was put out. The otained “clean” flames are stable and convenient for study. To stubilize the one-stage cool flame rich in ether (32,0 %), a poore mixture had to be set alight. After that the requered consentration of ether was reached.

Fig.16. shows the profile of temperature and consentration of peroxyl

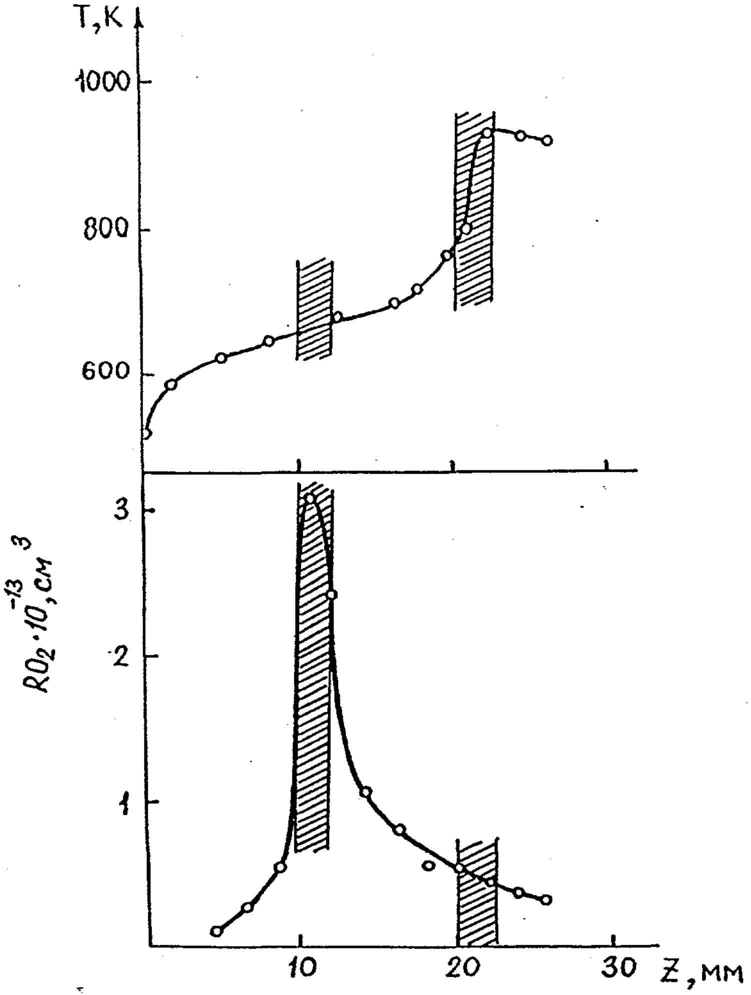


Fig. 16. Profile of temperature and concentration of peroxyl radicals (18.0 % ether). The shoded parts are the front of cool and blue flame.

radicals along the stream beginning from the surface of the matrix for a two-stage flame (18,0% ether). The maximum of peroxyl radcals concentration in the region of a cool flame is 3,0 $10^{13}sm^{-3}$, while in the zone of a blue flame it is 4,0 10^{12} sm^{-3}. In the flame front peroxyl radicals are formed and spent, which is indicated by the maximum of peroxyl radicals concentration in the zone of a cool flame and a glow which is characteristic in a two-stage flame poor in ether (12,5% Fig.17) and Fig.18. shows profiles of temperature and concentration of peroxyl radicals in the zone of one-stage flame rich in ether (32,0%).The comparison of Figures16-18 indicates that between cool and blue flame zones the temperature is rather stable, wich can be explained by a high speed of chemical reaction in the zone of the flame in contrast to the region outside the zones, where heat release goes down correspondingly. It is seen that the growth of fuel concentration leads to the increase of the maximum concentrations of peroxyl radicals, the letter amounts to 8,1 10^{13} sm^{-3} in a one-stage flame.

Fig.19. shows the ESR spectra of peroxyl radicals, selected from a cool flame when the latter is stabilized 5 mm away from the burner matrix (a) and 12 mm from (b).Signals of the srectra is very sharp.The observed splitting in (a) can be explained by the overlapping of the spectra of two types of radicals. The matrix greatly influences the conversion of fuel when the flame is closer to it and the matrix is hot.

After being exposed for two minutes flame was extinguished by interrupting of the ether flow to the fuel mixture. So the value of the ESR signal during these 2-4 minutes grew and after was stable.

Consequently in the course of probe sampling not only peroxy radicals but also aldyl radicals are frozen, which are not found at present conditions. Howevere, thanks to reaction $R + O_2 = RO_2$ can be measure they concentration by change a signal RO_2. It was set up that ether's decrease also started on the matrix. So in the sample selected from the matrix for 2 -4 minutes when cool flame is situated on a distance 10 mm from matrix the ESR signal was not descovered. However, when the flame is being extinguished and air is being injected at the same pressure in the channel of the sampler (1-2 torr) a signal of peroxy radical is generated.As a result on the finger of Dewar vessel radicals C_2H_5,C_2H_5O, $C_2H_5OCH_2$ which formed due to decomposition of diethyl ether catalized by matrix are firstly accumulated.

$$C_2H_5OC_2H_5 \longrightarrow C_2H_5 + C_2H_5O \qquad (a)$$

$$C_2H_5OC_2H_5 \longrightarrow C_2H_5OCH_2 + CH_3 \qquad (b)$$

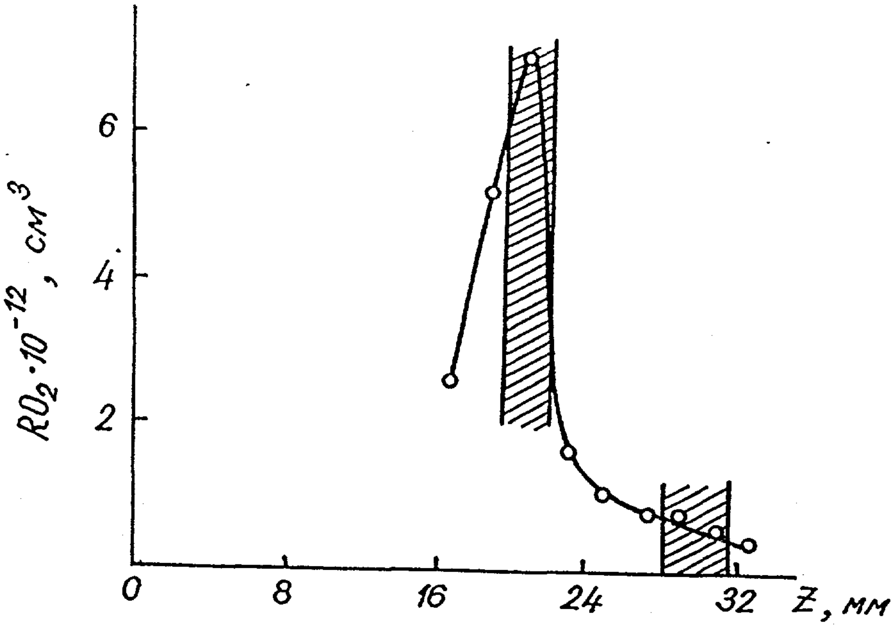


Fig. 17. Profile of concentration of peroxy radicals in poor two-stages flame (12,5% ether). The shaded parts are the front of cool and blue flame

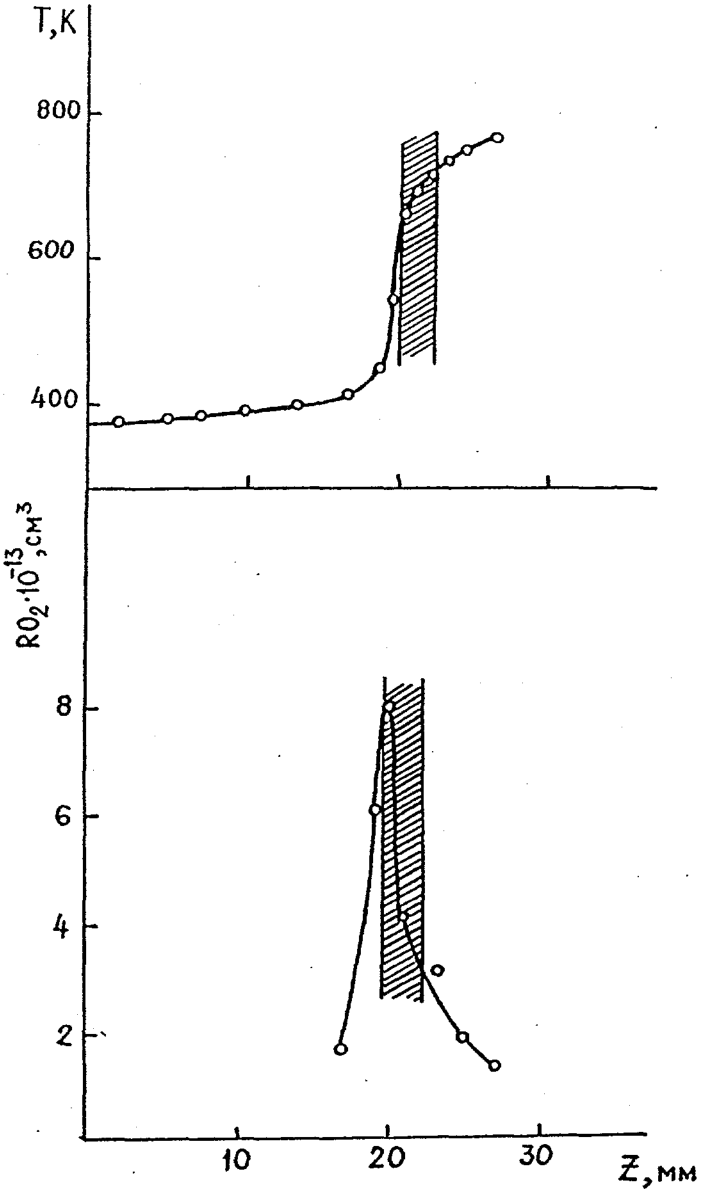


Fig. 18 . Profile of temperature and concentration of peroxyl radicals for one-stage rich flame (32.0 % ether). The shoded part is the front of cool flame.

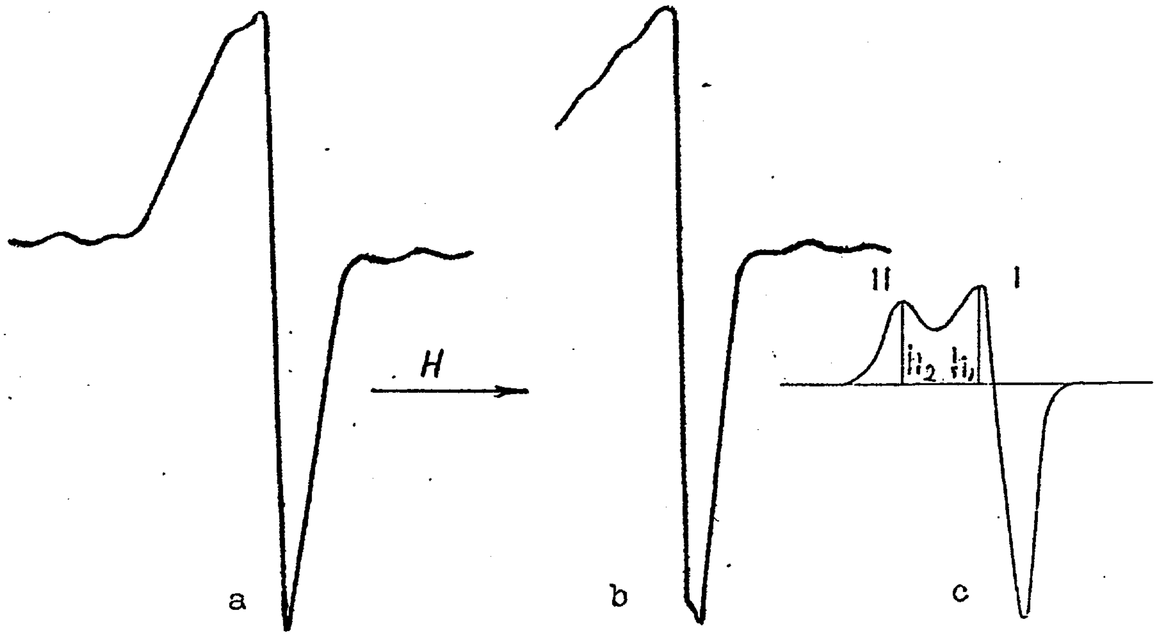


Fig.19. ESR spectra of peroxyl radicals found in the cool flame zone at a distance: a - 12 mm, b - 5 mm away from the matrix of burner

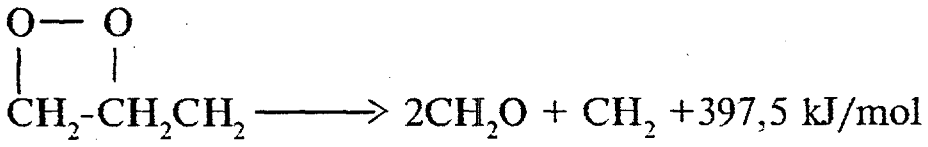
The bond break energy of the reaction (a) is 73.3 + 1.5 kcal/mol,[83] and that of the reaction (b) is the same for the reaction $C_2H_5OCH_3$---CH_3 + CH_2OCH_3 that is considered to equal 78.9 kcal/mol. Further peroxy radicals $C_2H_5O_2$, $C_2H_5O_3$, $C_2H_5OCH_2O_2$ are formed. Ethyl alcohol has been found to be formed from sampler taken on the matrix in the two-stage diethyl ether flame [24] that can be explained by the reaction:

$$RH + RO \longrightarrow ROH + R$$

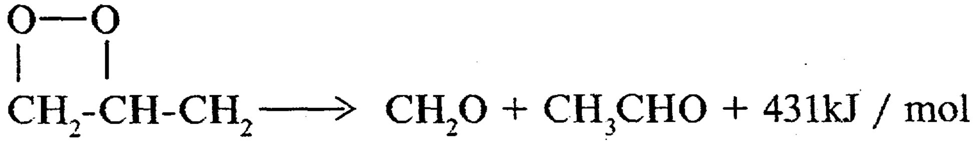
The data obtained confirm the assumption expressed in [9] that in investigation of the flame front structure on the flat burner it is immpossible to estimate the beginning of fuel consuming because the heated matrix can be a centre of chain arising.

It follows from [24,25] that in cool flame the oxidation is incomplete which occures with the formation of CH_3CHO, CO, H_2O and HCHO.

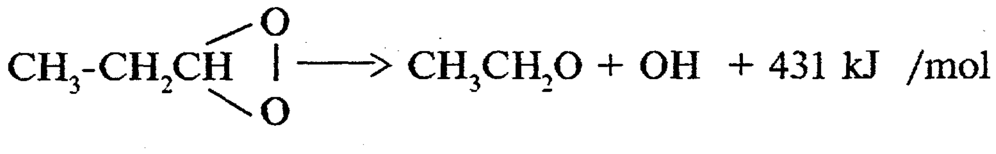
One can believe that according to assumption put forward in [42] peroxy radicals diffusing to the fresh mixture enter reactions of the formation of peroxy biradicals. Differs from the reaction of isomerization of peroxy monoradicals proceeding with the activation energy 83.7 kJ/mol [55] the isomerization of peroxy biradical can carry out without activation. For instance, the desintegration pathes for C_3 - peroxy biradicals may be following :



$$\mathrm{CH_2\text{-}CH_2CH_2} \longrightarrow 2CH_2O + CH_2 + 397{,}5\ \mathrm{kJ/mol}$$



$$\mathrm{CH_2\text{-}CH\text{-}CH_2} \longrightarrow CH_2O + CH_3CHO + 431\mathrm{kJ\ /\ mol}$$



$$\mathrm{CH_3\text{-}CH_2CH} \longrightarrow CH_3CH_2O + OH + 431\ \mathrm{kJ\ /mol}$$

The energetic chain branching is also possible if the large part of energy concentrated on one of the reaction products for which the desintegration energy is enough (about 330-370 kJ/mol).

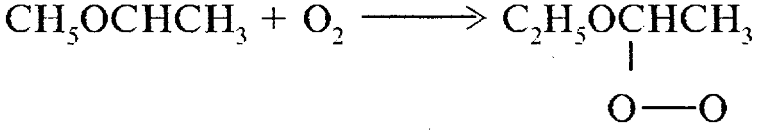
$$CH_2O \longrightarrow CHO + H$$

$$CH_3CHO \longrightarrow CH_3 + CO + H$$

$$CH_3CHO \longrightarrow CH_3CO + H$$

Branching through aldehyds can proceed also in a low-temperatures zone of a hot flame wich represents an incomplete flame cool flame [9,40].The formation of peroxyl radicals near cool flame and into cool flame are possible by reactions of radical interaction wich for receiving by (a) and (b) with oxigen and further oxidation of ether [9]:

$$C_2H_5OC_2H_5 + O_2 \longrightarrow C_2H_5OCHCH_3 + HO_2$$



$$CH_5OCHCH_3 + O_2 \longrightarrow C_2H_5O\underset{\substack{|\\ O-O}}{C}HCH_3$$

When the first stage is over the concentration of peroxy radicals falls noticeably and in the region of the blue flame and over it becomes slight. That distribution is somewhat unexpected as from the chromatographic data it follows that in the region between stadies an area of maximum concentration of acetaldehyde, methyl and ethyl alcohols, CH_3COOH, C_2H_6 is observed. In this region the growth of concentration of CO and CO_2 is initiated, whose maximums lies in the front of blue flame. The observed decrease of the peroxy radical concentrations is probably conditioned by the fact that during the time which elapses between the cool and blue flames radicals with small molecular wheights are formed (CH, CHO, CH_3 , C_2H_5). They do not freeze on the finger of Denwar vessel [64].

The data obtained enable heterogeneous nature of the active centres generation to be assume in cool flames. Obviously this fact is a reason that cool flames are attracted to a surface of heating solids.

Discovery and study of the distribution of hydrogen atoms in hexane- and butane-air cool flame fronts. [65]

To discovery hydrogen atoms we used the thecnique combining method of radical trap~~ping w~~ith additive supply near the sampling point CCl_4 was used as addition which catch of H-atoms in the reaction

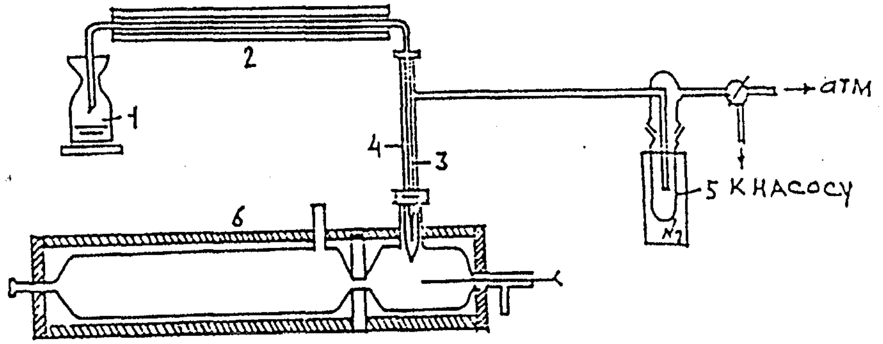


Fig. 20. Scheme of the experimental set-up for study H-atoms in hexan-air cool flame
1.-cylinder with CCl_4, 2-stove, 3.-quartz zond, 4.-capillar for giving CCl_4, 5- trap with liquid N_2, 6.-reactor

$$H + CCl_4 \longrightarrow HCl + CCl_3$$

The first experiments with the addition of CCl_4 on the distance in 40 mm from the place where samples were taken from the flame did not show the presence of H-atoms, but after direct introducing CCl_4 in the place of sampling H-atoms were discovered (Fig.20).

The experiments on the H-atom discovery were carried out in hexane-air cool flame at $T_1 = 470$ K, $\tau_c = 21.6$ s, $C_6H_{14} : O_2 = 2:1$, p=36.6 kPa and at the change of the second section temperature from 500 to 700 K. H-atoms were firstly discovered in hydrocarbon cool flames. Fig.21. shows the dependence of H-atoms concentration on the second section temperature (T_2) which demonstrates that maximum concentration of H-atoms ($1.2\ 10^{12}$ cm^{-3}) is observed at T_2 =610-620 K.

The experiments on the H-atom discovery were also performed in butane-air cool flames stabilized in the heated reactor of flat flame at atmospheric pressure and under conditions: $C_4H_{10} : O_2 = 1:2$, $T_1 = 443$K, $T_2 = 733$ K. The temperature and H-atom cocentration profiles obtained from the front of stabilized cool flame of butane are represented in Fig.22. The maximum H-atom concentration is $1.6\ 10^{11}$ cm^{-3} which anticipates the temperature maximum. It should be noted that maximum concentration of H-atoms in the butane flame is $3\ 10^{13}$ cm^{-3} at T_2=593 K. Results obtained are similiar to data on profiles of peroxy radical concentrations received during the investigation of cool flame of diethyl ether [82], and also to the data obtained by A.A. Mantashyan at the investigation of the propane cool flame oxidation [30].

The profile of H-atom concentration we have obtained firstly in cool hydrocarbon flames proves the assumption on their important role in the pre-flame region of normal flame front put forward by G.I. Ksandopulo who considered this region to be an incomplete cool flame.

CONCLUSIONS

Below we have briefly presented main results obtained in the studies of radical and stable intermediate distribution in the front of cool flames:

- maximum concentrations of H-atoms and peroxy radicals are observed in a luminous zone of the cool flame front;
- analysis of peroxy radical concentration profiles obtained in diethyl ether flame allowes to confirm that peroxy radicals are appeared befor the luminous zone at temperature 430 K due to their diffusion from the luminous zone since the current mixture (32 % ether) does not ignite at this temperature;
- for the first time , hydrogen atoms have been found in cool flames of butane and hexane, their concentration profile has been obtained in the butane flame and essential role of atoms in the cool flame oxidation

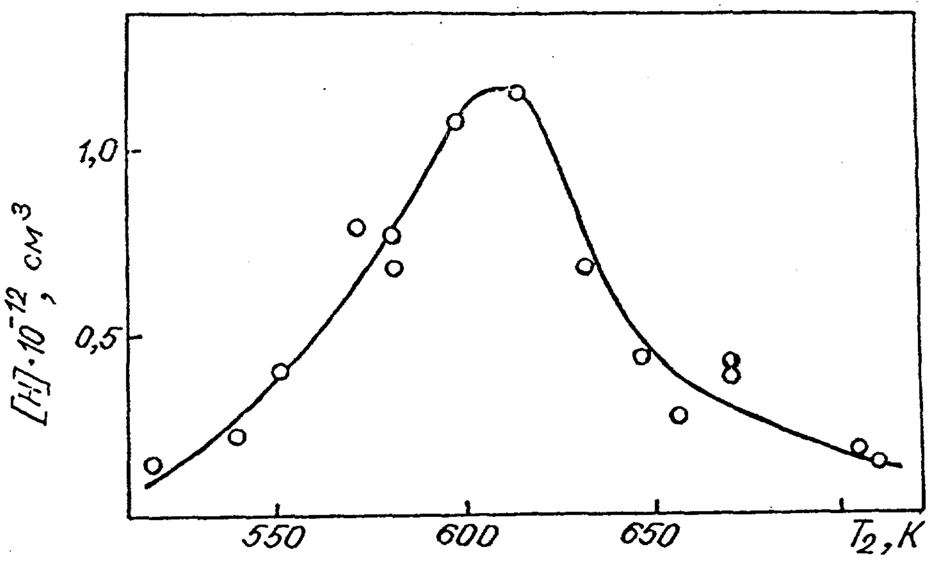


Fig. 21. Hydrogen atoms concentation dependence on the temperature of the reactor second section in the hexane cool flame

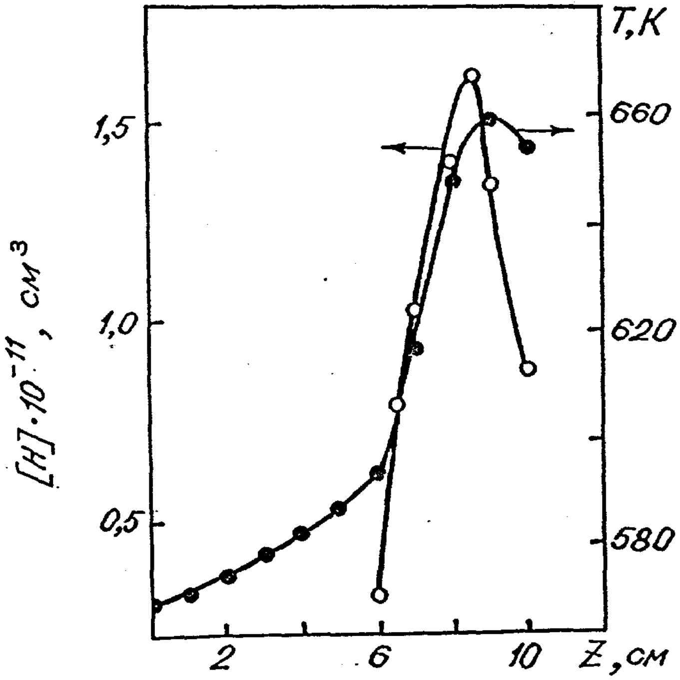


Fig. 22. Profile of temperature and H-atom's concentration
T_1=443 K, T_2=730 K $C_4H_{10} : O_2 = 1 : 2$

- joint analysis of temperature, H-atom and peroxy radical concentration profiles makes it possible to conclude that H-atoms diffuses from the luminous zone to the side of fresh mixture due to their extremal activity. However they penetrates into the fresh mixture on a small depth. At the same time the extension of the action sphear of peroxy radicals in the fresh mixture is much greater than that of H-atoms due to their small activity and high concentrations.

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APPENDIX

Justification of the individual supports:

Prof. Z.A, Mansurov is a well known specialist in the field of investigation of the oxidation and combustion of hydrocarbons

Dr. A.W. Mironenko is a high-skilled specialist in practical gas chromatography and experimental investigation of gas-phase oxidation of hydrocarbons

Dr. D.U. Bodikov is a high-educated specialist in ESR spectroscopy and combustion of hydrocarbons

Engeener K.N. Rachmetkaliev is a specialist in experimental investigation of gas-phase chemical processes