

DOI: 10.1134/S0869864319040115

Propane burning in argon, carbon dioxide, and water vapor at increased pressure^{*}

O.N. Fedyaeva, D.O. Artamonov, M.Ya. Sokol, and A.A. Vostrikov

Kutateladze Institute of Thermophysics SB RAS, Novosibirsk, Russia

E-mail: fedyaeva@itp.nsc.ru

*(Received January 21, 2019; revised February 19, 2019;
accepted for publication February 28, 2019)*

The paper presents investigation results on propane combustion in argon, carbon dioxide, and water vapor under the conditions of O₂ deficiency and high reagent density when they are uniformly heated up to 620 K. Based on time dependences of reaction mixture temperature, the self-ignition temperature of propane was determined. It has been established that the oxidation of propane in an Ar and H₂O medium proceeds according to the mechanism of chain-thermal explosion. The results of mass spectrometric analysis showed that oxidation in a CO₂ medium is characterized by the lowest degree of propane conversion. It was also found that at a low density of water vapor, the oxidation of propane is accompanied by a high yield of H₂. The mechanisms of CO₂ and H₂O molecule participation in the oxidation of propane are discussed in the paper.

Keywords: propane, self-ignition, chain-thermal explosion, carbon dioxide, water vapor.

Introduction

Combustion of fossil fuels and organic waste directly in the heat carrier (supercritical water or carbon dioxide) increases the energy efficiency and environmental friendliness of heat and electricity production [1–5]. Obviously, to develop new technologies based on fuel and waste combustion in CO₂ and H₂O, it is necessary to identify the characteristics of combustion for individual compounds in these media. The combustion of hydrogen, methane, propene, and isobutane in water vapor and carbon dioxide medium was studied by the authors earlier [6–9]. The purpose of this work is to reveal the characteristics of CO₂ and H₂O molecule participation in oxidation based on comparative analysis of propane oxidation in high-density mixtures of C₃H₈/O₂/Ar, C₃H₈/O₂/CO₂, and C₃H₈/O₂/H₂O.

Interest in the study of propane combustion is caused, first of all, by the fact that it is one of natural gas components. Propane is the lightest of alkanes, and the general laws of chain oxidation, characteristic of alkanes, are manifested starting from this compound [10]. According to the mechanisms of the initial stages of low-temperature oxidation of propane (600–800 K, 0.1 MPa) proposed in [11], the process is initiated by separation of a hydrogen atom from propane in reaction

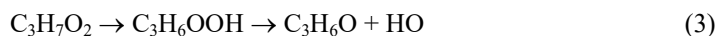


^{*} The work was financially supported by the Russian Foundation for Basic Research (Grant No. 18-29-06005).

The following interaction of C_3H_7 radicals with oxygen leads to the formation of peroxypropyl radicals

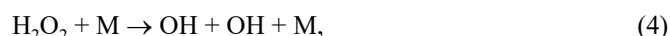


whose accumulation and subsequent decay proceeding through rearrangement into hydroperoxypropyl radicals



determine the time of ignition delay [11]. In [12], the ignition of propane–air mixtures (500–1000 K, 0.1 MPa) was studied using numerical methods, and the mechanisms of two-stage ignition and behavior of the negative temperature coefficient of the reaction rate were considered. From the comparison of results of numerical simulation and experimental data, the authors of [12] concluded that the proposed kinetic model is consistent with the results obtained using the rapid compression machine, but is at variance with the results obtained in the autoclave due to the approximate consideration of radical death on its wall. In [13], when studying the combustion of propane–air mixtures in an autoclave (523–573 K, 0.1–1.5 MPa, $C_3H_8 = 10$ –70 mol %) it was found that at constant concentration of propane, the self-ignition temperature decreases with increasing pressure. For example, when burning a mixture containing 40 mol % propane, the self-ignition temperature decreases from 573 K (0.1 MPa) to 523 K (1.5 MPa).

In [14], when studying the ignition of propane–air–steam mixtures (0.1 MPa, $[H_2O] \leq 20$ wt %), initiated by a nichrome wire heated by electric current, it was found that the presence of steam increases the minimal ignition energy (MIE) for lean fuel mixtures; while for enriched mixtures, this factor becomes less significant. The authors of [14] explained this effect by high heat capacity of water and participation of H_2O molecules as a third body in the chain termination reactions at the stage of fuel ignition. In [15], it was shown by numerical methods that at $T = 353$ K, $P \leq 0.1$ MPa, and $[H_2O] \leq 15$ wt %, the MIE is proportional to the back pressure and increases exponentially with increasing dilution of air–fuel mixtures with steam. In addition, it was found that participation of H_2O molecules in the chain termination reactions increases the MIE value significantly and reduces the limit of mixture dilution with water vapor, at which fuel ignition occurs. In [16], when studying the effect of water vapor on propane combustion in nitrogen medium (the jet stirred reactor was used; the temperature was 720–1100 K, the pressure was 0.11 MPa, fuel equivalence ratio was $\varphi = 0.5$ –1.5, $[H_2O] \leq 40.5$ wt %), it was found that in the low temperature region, water as a third body is actively involved in the decomposition of hydrogen peroxide:



and this accelerates oxidation.

In [17] (under the conditions of a flow reactor, at a temperature of 850–1250 K and pressure of 0.1 MPa), the effect of H_2O and CO_2 on self-ignition of propane — air mixtures was studied using experimental and numerical methods. It was found that H_2O and CO_2 have both thermal and chemical effects on mixture reactivity. This was explained by high heat capacity of H_2O and CO_2 , which causes a decrease in the temperature of adiabatic flame, which leads to a change in the reaction mechanisms. According to publications [18, 19], one of the main ways of chemical participation of carbon dioxide in fuel oxidation is the reaction



In the present work, oxidation of propane in the medium of argon, carbon dioxide, and water vapor is studied for the first time under conditions of a high density of reagents during their uniform slow heating. In contrast to water and carbon dioxide, argon is a chemically inert diluent, which makes it possible to reveal the role of H_2O and CO_2 molecules in oxidation.

Experimental setup

The scheme of experimental setup, described in detail in [6, 7], is shown in Fig. 1. The main element of setup is a tubular reactor with an external diameter of 60 mm, internal diameter of 30 mm, and volume of 65.0 cm³, made of stainless steel AISI 321H. The reactor was placed in a furnace whose heating was regulated by a thermal programmer coupled to a thermocouple (T_{out}) mounted on the outer wall of reactor. The temperature of the reaction mixture was measured with a thermocouple (T_{in}) introduced into the center of the reaction volume through the end of the reactor. In the experiment, the chromel-alumel thermocouples with open junction obtained through welding were used. The temperature measurement error was ± 0.5 K. The pressure of reagents was measured with a membrane strain gauge with an accuracy of 0.15 % of the measured value. Temporal temperature dependences were recorded in digital form with a frequency of 10 Hz using an analog-to-digital converter. Reagents were fed through a control valve to a previously evacuated reactor through a capillary welded into the central part of the reactor side wall. The volume of reactor inside the furnace (reaction volume) was 64.1 cm³, and the volume of reactor outside the furnace, including a channel for introducing thermocouples into the reactor (0.75 cm³) and capillaries connecting the reactor with a shut-off (0.1 cm³) and control (0.1 cm³) reagent supply valves, was equal to 0.95 cm³, which amounted to 1.5 % of the total reactor volume. Before each experiment, the inner surface of reactor was passivated by a H₂O/O₂ mixture at 873 K.

There were four experiments corresponding to different composition of the reaction mixture (see Table 1). Each experiment was reproduced 2-3 times, while the time dependences of temperature change $T_{\text{in}}(t)$ were completely repeated. In experiment 1, argon was used as a diluent for the C₃H₈/O₂ mixture; in experiment 2, it was carbon dioxide; and in experiments 3 and 4, it was water vapor.

In experiments 1 and 2, the components of the reaction mixture were charged into the reactor at room temperature in the following sequence. Initially, a diluent was charged into

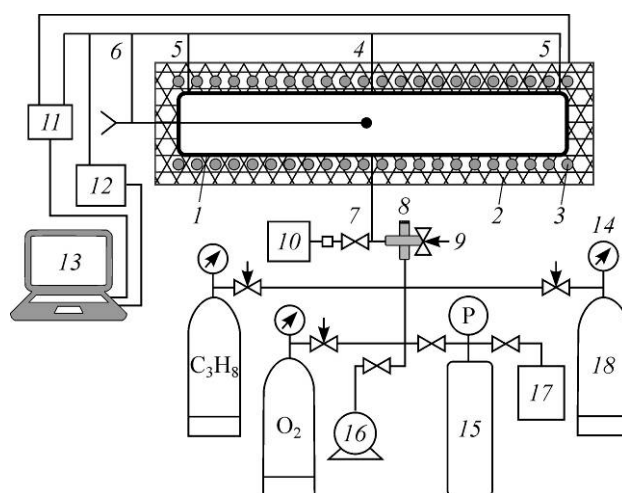


Fig. 1. Scheme of experimental setup.

- 1 — reactor, 2 — furnace, 3 — ohmic heater, 4 — control thermocouple on the reactor wall (T_{out}),
 5 — measuring thermocouples, 6 — thermocouple introduced into the reactor (T_{in}), 7 — shutoff valve,
 8 — rubber membrane, 9 — control valve, 10 — membrane tenzosensor,
 11 — thermal programmer, 12 — analogue-digital converter, 13 — PC,
 14 — manometer, 15 — product collector, 16 — forepump,
 17 — unit of mass-spectrometric diagnosis, 18 — tank with Ar or CO₂.

Table 1

Experimental conditions

Experiment No.	Partial pressure, MPa			Amount, mmol			φ_F	x_d , mol %
	C ₃ H ₈	O ₂	Diluent	[C ₃ H ₈] ₀	[O ₂] ₀	[Diluent] ₀		
1 (Ar)	0.51	2.19	3.82	14.2	56.6	101	1.25	59
2 (CO ₂)	0.56	2.18	3.35	15.7	56.5	101 (15.8)	1.39	58
3 (H ₂ O)	0.57	2.16	–	15.2	52.9	103	1.44	60
4 (H ₂ O)	0.56	2.27	–	15.2	56.8	172	1.34	70

The amount of carbon dioxide, condensed in cold volumes of the reactor, is given in parentheses.

the reactor (to a pressure of ≈ 0.3 MPa), which ensured the filling of the cold parts of reactor and thereby the reduction of the error in determining the amount of propane in the reaction volume. Then propane and again a diluent were supplied to a predetermined partial pressure. The filling of reactor was completed with the oxygen supply. This sequence of reactor filling was due to the low pressure of saturated propane vapor in a standard tank (0.83 MPa at 293 K [20]). In experiments 3 and 4, the order of reactor filling was as follows. Initially, at room temperature, distilled water in the volume of 2.8 and 4.0 cm³ was charged into the reactor through a rubber membrane (Fig. 1) using a syringe. Then the reactor was heated to $T_{\text{out}} = 403$ K and thermostated for 45 minutes. At that, water was partially condensed in the unheated parts of the reactor. The estimated amount of water remaining in the reaction volume was 103 (experiment 3) and 172 (experiment 4) mmol (Table 1). After the reactor was cooled to 373 K, propane and oxygen were successively charged into it to a given partial pressure. After charging, the reactor was heated to $T_{\text{out}} \leq 620$ K at rate $q = 1$ K/min. The partial pressure of components charged into the reactor ($[C_3H_8]_0$, $[O_2]_0$ and $[Diluent]_0$), their amount in the reaction volume, as well as fuel equivalence ratio φ_F and diluent fraction x_d in the mixture, calculated according to formulas

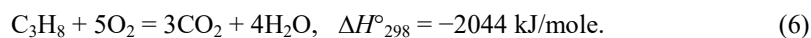
$$x_d = 100 \cdot [Diluent]_0 / \{[C_3H_8]_0 + [O_2]_0 + [Diluent]_0\}, \quad \varphi_F = 5[C_3H_8]_0 / [O_2]_0,$$

are shown in Table 1. The amount of components in the reaction mixture was determined based on the volume of reactor, values of temperature and partial pressure using the reference P - v - T data [20].

After the completion of experiment at $T_{\text{out}} \leq 620$ K, the reactor was cooled at a rate of ≈ 6 K/min to room temperature, and then the pressure of reactants in the reactor was measured. The composition and amount of volatiles obtained at propane oxidation were determined using a MS-7303 quadrupole mass spectrometer in accordance with the procedure of [21]. The amount of carbon formed during propane oxidation and deposited on the reactor wall in experiments 1 and 2 was calculated based on mass spectrometric measurements of the amount of CO₂ obtained as a result of oxidation of carbon by a H₂O/O₂ mixture at 873 K. During oxidation of propane in a H₂O medium (experiments 3 and 4), no carbon coating was detected.

Results and discussion

According to Table 1, the experiments were carried out with a high proportion of diluent ($x_d = 58$ –70 mol %) and fuel excess ($\varphi_F = 1.25$ –1.44), i.e., the amount of $[O_2]_0$ in the reaction mixture was less than the stoichiometric one, corresponding to total propane oxidation in reaction



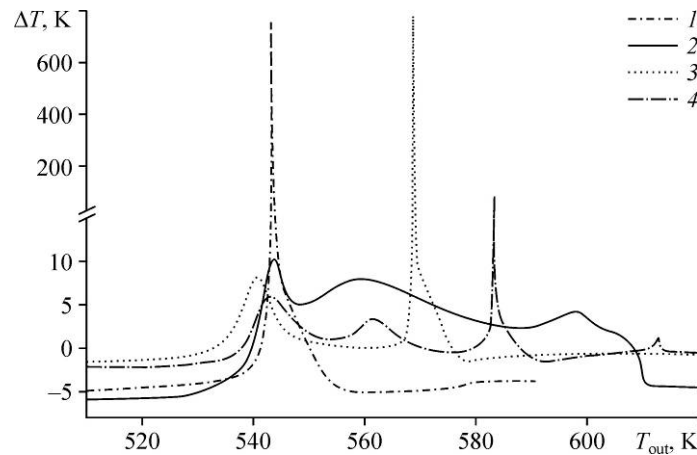


Fig. 2. Temperature dependences of temperature difference $\Delta T = T_{in} - T_{out}$ of reactants in the central part of reactor (T_{in}) and temperature of the outer wall of reactor (T_{out}) during propane oxidation in the medium of argon (1), carbon dioxide (2), and water vapor (3, 4). The numbers of curves correspond to the numbers of experiments in Table 1.

The time dependences of T_{out} and T_{in} measurements obtained during propane oxidation in Ar, CO₂, and H₂O medium are shown in Fig. 2 in the form of dependences of $\Delta T = T_{in} - T_{out}$ on T_{out} . It is seen that against the background of an increase in $T_{out}(t)$, an increase in temperature $\Delta T(t)$ caused by self-ignition of the C₃H₈/O₂ mixture (self-acceleration of the exothermic reaction (6)) was registered in all experiments. The negative value of ΔT on the $\Delta T(T_{out})$ curves before and after oxidation is due to the fact that the temperature of the outer surface of the reactor wall T_{out} is higher than the temperature of the reaction mixture T_{in} . Table 2 shows the following parameters of the $\Delta T(T_{out})$ curves and reaction mixture: T_{out}^* and T_{in}^* are, respectively, the temperatures of the reactor wall and reaction mixture, at which self-ignition occurs (they are determined from condition $|\Delta T_i(T_{out}) - \Delta T_i'(T_{out})| > 3\sigma$, where $\sigma = \{[\sum(\Delta T_i(T_{out}) - \Delta T_i'(T_{out}))^2]/(n-1)\}^{0.5}$ is the standard deviation of experimental values on the linear region of curve $\Delta T(T_{out})$); T_{out}^{min} and T_{in}^{min} are the temperatures corresponding to completion of propane oxidation (correspond to the minimum of curve $\Delta T(T_{out})$); $t_{ox} = (T_{out}^{min} - T_{out}^*)/q$ is the duration of oxidation, S is the area under curve $\Delta T(T_{out})$ limited by the base line (the baseline is a straight line connecting the straight sections of $\Delta T(T_{out})$ dependence before and after oxidation), during time period t_{ox} ; T_{out}^{max} and T_{in}^{max} are the temperatures

Table 2

The values of characteristic points of curves in Fig. 2 and thermodynamic parameters of reaction mixtures

Experiment No.	T_{out}^* , K	T_{in}^* , K	T_{out}^{min} , K	T_{in}^{min} , K	t_{ox} , min	S , K·min	T_{out}^{max} , K	T_{in}^{max} , K	ΔT^{max} , K	C_p^* , J/K	ΔT_{ad}^* , K
1 (Ar)	522	518	562	557	40	202	543	1290	751	4.1	5634
2 (CO ₂)	524	519	626	622	102	692	544	554	16	6.8	3397
3 (H ₂ O)	524	522	580	578	56	219	569	1345	778	5.8	3729
4 (H ₂ O)	525	523	616	616	91	202	583	674	93	6.0	3870

corresponding to the maximum of curve $\Delta T(T_{\text{out}})$; $\Delta T^{\text{max}} = (T_{\text{in}}^{\text{max}} - T_{\text{in}}^*) - (T_{\text{out}}^{\text{max}} - T_{\text{out}}^*)$ is the maximum increase in temperature of the reaction mixture obtained due to heat release at combustion; $C_v^* = \sum c_{v,i} x_i$ are the values of heat capacity of the reaction mixture at temperature calculated using the reference data [20] (here x_i is the mole fraction of the i th component in the gas phase); $\Delta T_{\text{ad}}^* = Q/C_v^*$ are the values of an increase in the reaction mixture temperature under the adiabatic conditions due to heat release in reaction (6).

Based on the results of [6], it can be assumed that under conditions of the present work, heat release during propane oxidation occurs due to both heterogeneous (on the reactor wall) and homogeneous (in the volume of the reaction mixture) processes. Heterogeneous exothermic reactions have almost no effect on the thermocouple readings T_{in} due to high heat capacity ($C = 548 \text{ J/(kg K)}$) and thermal conductivity ($\lambda = 21 \text{ W/(m K)}$) of stainless steel [22], as well as the stabilizing effect of thermal programmer, which regulates reactor heating by reducing the power of the heater. Under the adiabatic conditions, heat release at complete consumption of O_2 in experiments 1, 2, and 3 ($Q = 23.1, 23.1, \text{ and } 21.6 \text{ kJ}$, respectively) can lead to the $\approx 11 \text{ K}$ increase in the temperature of reactor, whose mass is 3.6 kg , and the temperature of gas contained in the reactor ($C_v^* = 4.1, 6.8 \text{ and } 5.8 \text{ J/K}$) at homogeneous combustion can be increased by the value $\Delta T_{\text{ad}}^* = 5634, 3397, \text{ and } 3729 \text{ K}$ (see Table 2). In fact, due to heat removal, an increase in the temperature of the reaction mixture ΔT^{max} was significantly lower than ΔT_{ad}^* .

Oxidation in argon

The self-ignition temperature of propane $T_{\text{in}}^* = 518 \text{ K}$ in the Ar medium (experiment 1, Table 2), recorded in the present work, turned out to be close to the similar value obtained at combustion of propane-air mixtures [13]. As can be seen in Fig. 2, when propane is oxidized in the Ar medium (curve 1), the chain-thermal explosion occurred. According to the studies of [23] and [24], such a regime takes place at avalanche-like multiplication of atoms and radicals if heat release during the chemical reaction prevails over the heat removal; in this case, with increasing temperature, heat release accelerates to a greater extent than heat removal. Due to chain-thermal explosion at propane oxidation in experiment 1, the temperature increase ΔT^{max} was 751 K , and the temperature of the reaction mixture $T_{\text{in}}^{\text{max}}$ reached 1290 K (Table 2).

Table 3 shows the results of mass-spectrometric analysis of propane oxidation products and degrees of propane and oxygen conversion α_F and α_O , calculated from these data by the following formulas:

$$\alpha_F = \{1 - ([\text{C}_3\text{H}_8] / [\text{C}_3\text{H}_8]_0)\} \cdot 100, \quad \alpha_O = \{1 - ([\text{O}_2] / [\text{O}_2]_0)\} \cdot 100,$$

where $[\text{C}_3\text{H}_8]$ and $[\text{O}_2]$ are the amounts of propane and oxygen in oxidation products. The value of α_F with an excess of fuel ($\varphi_F > 1$, Table 1) in experiments 1–4 is obviously determined not only by oxidation of propane in reaction (6), but also by its thermolysis. It follows from the amount of CO_2 in the products that the bulk of O_2 in experiments 1–4 was spent on propane oxidation in reaction (6). The degree of propane conversion due to oxidation is easily estimated by formula $\alpha_{FO} = 100 - \alpha_O / \varphi_F$; thus, the difference $\alpha_T = \alpha_F - \alpha_{FO}$ characterizes the degree of propane conversion during thermolysis.

Table 3

Composition of products and degree of propane conversion at its partial oxidation in the medium of argon, carbon dioxide, and water vapor (mmol)

Products	Experiment No.			
	1 (Ar)	2 (CO ₂)	3 (H ₂ O)	4 (H ₂ O)
Ar	100.4	—	—	—
H ₂	15.06	0.86	31.1	3.09
O ₂	0.56	1.45	0.45	3.07
CO	8.22	5.38	2.36	0.83
CO ₂	28.22	127.9	39.3	40.1
Methane	0.05	0.58	0.33	0.50
Methanol	0	1.70	0.03	0.13
Formaldehyde	0.05	0.20	0.16	0.02
Formic acid	0	0.02	0.16	0.02
Ethane	0.02	0.12	0.06	0.13
Ethylene	0	0.11	0.13	0.03
Ethanol	0	0.06	0	0.02
Acetaldehyde	0	0.73	0.05	0.13
Acetic acid	0.03	0.05	0.16	0.04
Propane	0.38	3.98	0.31	0.79
Propene	0	0	0	0.07
Acetone	0	0.53	0	0.03
Propylene oxide	0.03	0	0	0
Butadiene	0.05	0.01	0	0
(CO ₂) _R	2.02	3.36	—	—
Carbon balance (mol%)	94.1	94.5*	96.7	98.7
α_O (mol%)	99.0	97.4	99.1	94.6
α_F (mol%)	97.3	74.6	98.0	94.8
α_{FO} (mol%)	20.8	29.9	31.2	29.4
α_T (mol%)	76.5	44.7	66.8	65.4

* The carbon balance takes into account the amount of carbon dioxide condensed in cold volumes of the reactor.

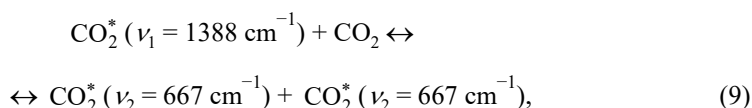
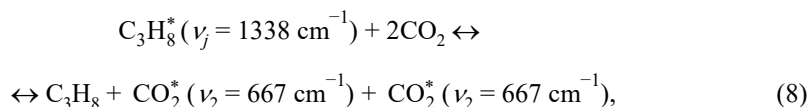
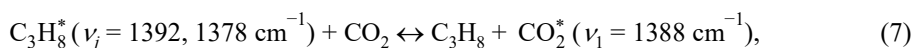
It can be seen from Table 3 that during propane oxidation in the Ar medium (experiment 1), CO₂, CO, and H₂ prevail in the composition of the conversion products, and α_F and α_O are close to 100%. At that, the α_T value turned out to be maximal in comparison with the values from other experiments, and this is an obvious consequence of high temperature T_{in}^{max} achieved at explosion (Table 2). We should note that one of the CO sources under the conditions of this study may be the decomposition of CO₂. Taking into account the results of [25], it can be assumed that the oxide layer on the inner surface of reactor, whose main component is magnetite Fe₃O₄ [26], could have a catalytic effect on decomposition of CO₂. In general, data on the composition of the products of partial oxidation of propane are consistent with the results of [11, 12].

Oxidation in carbon dioxide

Oxidation of propane in the CO₂ medium (curve 2, Fig. 2) corresponds to degenerate explosion [23]. The self-ignition temperature of propane in the CO₂ medium turned out to be close to the value T_{in}^* obtained in the Ar medium, despite high heat capacity C_v^* of the C₃H₈/O₂/CO₂ mixture (Table 2). It can be seen in Fig. 2 that propane oxidation in a CO₂ medium is characterized by a wide temperature (time, $t_{ox} = 102$ min) range of the process and

the presence of three maxima on the $\Delta T(T_{\text{out}})$ curve at $T_{\text{out}} = 543, 560$, and 598 K. At that, the first maximum coincided with temperature $T_{\text{out}}^{\text{max}}$, recorded at propane oxidation in the Ar medium (experiment 1, Table 2). The duration of oxidation t_{ox} and area S , characterizing heat release, in the CO_2 medium were, respectively, 2.5 and 3.4 times longer than in the Ar medium, and the maximum temperature increase ΔT^{max} in the CO_2 medium was only 16 K. It follows from comparison of α_{O} , α_{F} , α_{FO} , and α_{T} values (experiment 2, Table 3) that with almost complete consumption of O_2 ($\alpha_{\text{O}} = 97.4\%$), the degrees of propane conversion α_{F} and α_{T} in CO_2 medium turned out to be minimal. This is explained by a small increase in temperature ΔT^{max} (Table 2) and, as a consequence, weak thermolysis of propane. As a result, the content of H_2 and CO in the propane conversion products decreased, but the amount of partial oxidation products (methanol, acetaldehyde, and acetone) increased (Table 3).

The low degree of propane conversion at such a long duration of the process ($t_{\text{ox}} = 102$ min, Table 2) in CO_2 can be a result of combination of high CO_2 density in the reaction mixture and resonant exchange of vibrational energy (V–V exchange) [27] between the C_3H_8 and CO_2 molecules in reactions



where ν_1 and ν_2 are frequencies of valent symmetric and deformation vibrations of a CO_2 molecule [28], $\nu_j = 1392, 1378$, and 1338 cm^{-1} correspond to deformation vibrations of CH_3 and CH_2 groups. The sink of energy of vibration excitation of CO_2^* molecules ($\nu_2 = 667 \text{ cm}^{-1}$) occurred during their collision with the reactor wall. The high rate of vibration energy transport to the reactor wall as a result of the V–V exchange is ensured by a high CO_2 density, and a high rate of subsequent deactivation of CO_2^* molecules ($\nu_2 = 667 \text{ cm}^{-1}$) is ensured by the presence of an adsorbed layer of CO_2 molecules on the reactor wall [6]. The mechanisms for increasing the rate of deactivation of CO_2^* molecules upon their collision with the condensed phase were described in [29]. We should note that a similar effect was recorded by the authors when studying isobutane oxidation in the CO_2 medium [9].

Oxidation in water vapor

In experiments 3 and 4, propane was oxidized in the H_2O medium with different initial amounts of water (Table 1). It can be seen in Fig. 2 that curves 3 and 4 differ significantly from curves 1 and 2. It turned out that the self-ignition temperature of propane T_{in}^* in experiment 3 was higher than in experiments 1 and 2 by 4 and 3 K, respectively, and in experiment 4, it was 1 K higher than in experiment 3. According to reference data [20], complete evaporation of water in the reaction system in experiments 3 and 4 occurred at $T_{\text{ev}} = 545$ and 576 K, respectively. Since the temperature of propane self-ignition $T_{\text{in}}^* < T_{\text{ev}}$, it follows that its

oxidation was accompanied by evaporation water, and, as a consequence, an increase in the heat capacity of water vapor with increasing temperature [20]. At that, a part of heat released during oxidation was spent on evaporation of water. The heat expenses for water evaporation with increasing temperature from T_{in}^* to T_{ev} in experiments 3 and 4 were 1.7 and 5.0 kJ [20], which corresponds to the amount of heat released at oxidation of 0.8 and 2.4 mmol of propane, respectively (see reaction (6)).

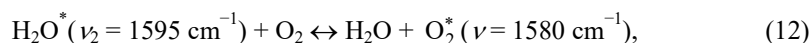
It can be seen in Fig. 2 that propane oxidation in the H_2O medium (curves 3 and 4) proceeds according to the chain-thermal explosion mechanism similar to oxidation in the Ar medium (curve 1). The difference is that in the H_2O medium, oxidation proceeds in several stages. At a dilution degree $x_d = 60$ mol % (experiment 3, Table 1), the explosion is preceded by a heat release peak with a maximum at $T_{out}^{max} = 541$ K, which almost coincides with the temperature T_{out}^{max} recorded in the Ar medium (experiment 1, Table 2) and the first maximum in curve 2 (Fig. 2), obtained in a CO_2 medium. Obviously, the chain-thermal explosion at this temperature was hindered, first of all, by the heat loss associated with evaporation of water. As a result, the maximum intensity of the chain-thermal explosion in the H_2O medium ($x_d = 60$ mol %) occurred at $T_{out}^{max} = 569$ K (Table 2). Temperature increase $\Delta T^{max} = 778$ K and reaction mixture temperature $T_{in}^{max} = 1345$ K correspond to this maximum (Table 2). These values turned out to be higher than in the Ar medium, despite a smaller amount of $[O_2]_0$ in experiment 3 than in experiment 1, as well as the higher heat capacity of the $C_3H_8/O_2/H_2O$ mixture than the $C_3H_8/O_2/Ar$ mixture (Tables 1 and 2). With an increase in the degree of dilution x_d to 70 mol % (experiment 4), the explosion is preceded by two heat release peaks with maxima at $T_{out}^{max} = 543$ and 602 K, however, these maxima have a smaller temperature increase ΔT than the first maximum in curve 3 (Fig. 2). An increase in the amount of water also led to a decrease in the maximum increase in temperature ΔT^{max} to 93 K and temperature of reaction mixture T_{in}^{max} to 674 K, despite a 7 % increase in the amount of $[O_2]_0$ in experiment 4 as compared to experiment 3 (Table 1).

It follows from data given in Table 3 that during propane oxidation in a H_2O medium, the α_F and α_O values are close to 100 %, as well as at oxidation in the Ar medium. The composition of oxidation products contains only a small amount of alkanes, alkenes, alcohols, aldehydes and acids. It is noteworthy that in experiment 3, the yield of H_2 is 10 times greater than in experiment 4. Apparently, this is caused by the higher rate of steam reforming and water gas shift reactions



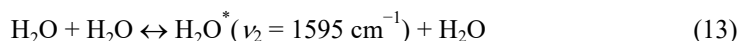
because of the higher ΔT^{max} in experiment 3 (Table 2). We should note that a similar effect was detected during isobutane oxidation under the conditions of low water vapor density [9]. Thus, the partial oxidation of alkanes in the water vapor medium can be considered as an effective method for generating hydrogen.

Based on the results obtained, it can be assumed that along with the chemical participation of H_2O molecules in elementary reactions of propane oxidation [14–16], the processes of resonant exchange of vibration energy between the H_2O^* and O_2 molecules during the reaction play an important role [27, 30]:



where ν_2 is frequency of deformation vibrations. Since the rate of oxidation by vibrationally excited molecules of O_2^* is higher than by unexcited molecules of O_2 [31, 32], in the general case, this leads to an increase in the specific oxidation rate (per a mole of O_2) in the H_2O medium. We should note that the equilibrium fraction of H_2O^* molecules ($\nu_2 = 1595 \text{ cm}^{-1}$) at 550 K in accordance with the Boltzmann distribution is 1.5 % of the amount of H_2O molecules in the vapor phase.

According to [30], the reaction rate constant (12) at 300 K is $5.5 \cdot 10^{-13} \text{ cm}^3/\text{s}$, and the reaction rate constant of the translational-vibrational exchange



is two orders higher ($5.5 \cdot 10^{-11} \text{ cm}^3/\text{s}$). This means that the amount of H_2O^* molecules deactivated in reaction (12) is continuously replenished in the reaction system during reaction (13). In general, under the conditions of high water density, this can contribute to intensification of fuel oxidation.

Conclusion

In the present work, propane oxidation at a high density of reagents and dilution of the reaction mixture with argon, carbon dioxide, and water vapor under conditions of excess fuel was studied for the first time. Excess fuel made it possible to identify the intermediate oxidation products and mechanisms of their formation. It has been established that oxidation of propane in the Ar and H_2O medium proceeds according to the chain-thermal explosion mechanism. At propane oxidation in the CO_2 medium, a minimum degree of fuel conversion was recorded. In the H_2O medium, oxidation proceeds in several stages, which is associated with the presence of liquid water in the reactor until the beginning of the chain-thermal explosion.

References

1. J.P.S. Queiroz, M.D. Bermejo, F. Mato, and M.J. Cocero, Supercritical water oxidation with hydrothermal flame as internal heat source: Efficient and clean energy production from waste, *J. Supercrit. Fluids*, 2015, Vol. 96, P. 103–113.
2. Z. Chen, X. Zhang, S. Li, and L. Gao, Novel power generation models integrated supercritical water gasification of coal and parallel partial chemical recovery, *Energy*, 2017, Vol. 134, P. 933–942.
3. R. Allam, S. Martin, B. Forrest, J. Fetverdt, X. Lu, D. Freed, Jr. G.W. Brown, T. Sasaki, M. Itoh, and J. Manning, Demonstration of the Allam Cycle: an update on the development status of a high efficiency supercritical carbon dioxide power process employing full carbon capture, *Energy Procedia*, 2017, Vol. 114, P. 5948–5966.
4. K.J. Borgert and E.S. Rubin, Oxy-combustion carbon capture for pulverized coal in the integrated environmental control model, *Energy Procedia*, 2017, Vol. 114, P. 522–529.
5. F. Crespi, G. Gavagnin, D. Sanchez, and G.S. Martinez, Supercritical carbon dioxide cycles for power generation: a review, *Applied Energy*, 2017, Vol. 195, P. 152–183.
6. A.A. Vostrikov, O.N. Fedyaeva, A.V. Shishkin, D.S. Tretyakov, and M.Y. Sokol, Features of low temperature oxidation of hydrogen in the medium of nitrogen, carbon dioxide, and water vapor at elevated pressures, *Int. J. Hydrogen Energy*, 2018, Vol. 43, P. 10469–10480.
7. A.A. Vostrikov, O.N. Fedyaeva, A.V. Shishkin, M.Y. Sokol, F.I. Kolobov, and V.I. Kolobov, Partial and complete methane oxidation in supercritical water, *J. Engng Thermophysics*, 2016, Vol. 25, No. 4, P. 474–484.
8. O.N. Fedyaeva, D.O. Artamonov, and A.A. Vostrikov, Features of propene oxidation in argon, carbon dioxide and water vapor media at a high density of reagents, *J. Engng Thermophysics*, 2018, Vol. 27, No. 4, P. 405–414.

9. A.A. Vostrikov, O.N. Fedyaeva, A.V. Shishkin, D.O. Artamonov, and M.Y. Sokol, Features of low-temperature oxidation of isobutane in water vapor and carbon dioxide with increased density of reagents, *J. Eng. Thermophysics*, 2017, Vol. 26, No. 4, P. 466–475.
10. N.S. Titova, P.S. Kuleshov, and A.M. Starik, Kinetic mechanism of propane ignition and combustion in air, *Combustion, Explosion and Shock Waves*, 2011, Vol. 47, No. 3, P. 249–264.
11. S.S. Merchant, C.F. Goldsmith, A.G. Vandeputte, M.P. Burke, S.J. Klippenstein, and W.H. Green, Understanding low-temperature first-stage ignition delay: propane, *Combust. Flame*, 2015, Vol. 162, P. 3658–3673.
12. J.C. Prince and F.A. Williams, Short chemical-kinetics mechanisms for low-temperature ignition of propane and ethane, *Combust. Flame*, 2012, Vol. 159, P. 2336–2344.
13. F. Norman, F. Van den Schoor, and F. Verplaetsen, Auto-ignition and upper limit of rich propane-air mixtures at elevated pressures, *J. Hazard. Mater.*, 2006, Vol. 137, No. 2, P. 666–671.
14. W. Ebina, C. Liao, H. Naito, and A. Yoshida, Effect of water mist on minimum ignition energy of propane/air mixture, *Proc. Combust. Institute*, 2017, Vol. 36, P. 3271–3278.
15. W. Zhang, X. Gou, and Z. Chen, Effect of water vapor dilution on the minimum ignition energy of methane, n-butane and n-decane at normal and reduced pressures, *Fuel*, 2017, Vol. 187, P. 111–116.
16. M. Lubrano Lavadera, P. Sabia, M. De Joannon, A. Cavaliere, and R. Raggi, Propane oxidation in a jet stirred flow reactor. The effect of H₂O as diluent species, *Exp. Thermal Fluid Sci.*, 2018, Vol. 95, P. 35–43.
17. P. Sabia, M. Lubrano Lavadera, P. Guidicianni, G. Sorrentino, R. Raggi, and M. De Joannon, CO₂ and H₂O effect on propane auto-ignition delay times under mild combustion operative conditions, *Combust. Flame*, 2015, Vol. 162, P. 533–543.
18. F. Liu, H. Guo, and G.J. Smallwood, The chemical effect of CO₂ replacement N₂ in air on burning velocity of CH₄ and H₂ premixed flame, *Combust. Flame*, 2003, Vol. 133, P. 495–497.
19. A.E. Masunov, E.E. Wait, A.A. Atlanov, and S.S. Vasu, Quantum chemical study of supercritical carbon dioxide effects on combustion kinetics, *J. Phys. Chem. A*, 2017, Vol. 121, No. 19, P. 3728–3735.
20. E.W. Lemmon, M.O. McLinden, and D.G. Freid, Thermophysical properties of fluid systems. NIST chemistry WebBook, in: P.J. Linstrom and W.G. Mallard (Eds.), NIST standard reference database No. 69, National Institute of Standards and Technology, Gaithersburg MD, 2018, 20899, <http://webbook.nist.gov/chemistry/fluid/>.
21. O.N. Fedyaeva, A.A. Vostrikov, A.V. Shishkin, M.Y. Sokol, N.I. Fedorova, and V.A. Kashirtsev, Hydrothermolysis of brown coal in cyclic pressurization-depressurization mode, *J. Supercrit. Fluids*, 2012, Vol. 62, P. 155–164.
22. A.Ya. Guva, Brief Thermal-Physical Reference Book, Sibvuzizdat, Novosibirsk, 2002.
23. N.N. Semenov, About Some Problems of Chemical Kinetics and Reactivity, AS USSR, Moscow, 1958.
24. D.A. Frank-Kamenetskiy, Diffusion and Heat Transfer in Chemical Kinetics, Nauka, Moscow, 1987.
25. C. Zhang, S. Li, L. Wang, T. Wu, and S. Peng, Studies on the decomposing carbon dioxide into carbon with oxygen-deficient magnetite. II. The effects of properties of magnetite on activity of decomposition CO₂ and mechanism of the reaction, *Mater. Chem. Physics*, 2000, Vol. 62, P. 52–61.
26. A.A. Vostrikov, O.N. Fedyaeva, A.V. Shishkin, M.Y. Sokol, and A.V. Zaikovskiy, Synthesis of Fe_xO_y nanoparticles during iron oxidation by supercritical water, *Techn. Phys. Lett.*, 2012, Vol. 38, Iss. 10, P. 955–958.
27. V.N. Konradiev and E.E. Nikitin, Kinetics and Mechanisms of Gas-Phase Reactions, Nauka, Moscow, 1974.
28. Computational chemistry comparison and benchmark data base, Release 18, Standard reference database 101, Ed. R.D. Johnson III. National Institute of Standards and Technology, 2018, <http://cccbdb.nist.gov/>.
29. A.A. Vostrikov and S.G. Mironov, The role of van der Waals molecules in vibrational relaxation kinetics, *Chem. Phys. Lett.*, 1983, Vol. 101, No. 6, P. 583–587.
30. D.L. Huestis, Vibrational energy transfer and relaxation in O₂ and H₂O, *J. Phys. Chem. A*, 2006, Vol. 110, P. 6638–6642.
31. A.M. Starik, N.S. Titova, and B.I. Lukhovitsky, Kinetics of low-temperature initiation of H₂/O₂/H₂O mixture combustion upon the excitation of molecular vibrations in H₂O molecules by laser radiation, *Tech. Phys.*, 2004, Vol. 74, No. 1, P. 76–82.
32. N.A. Popov, The effect of nonequilibrium excitation on the ignition of hydrogen-oxygen mixtures, *High Temperature*, 2007, Vol. 45, No. 2, P. 261–279.