ISSN 1810-2328, Journal of Engineering Thermophysics, 2018, Vol. 27, No. 4, pp. 405–414. © Pleiades Publishing, Ltd., 2018.

Features of Propene Oxidation in Argon, Carbon Dioxide and Water Vapor Media at a High Density of Reagents

O. N. Fedyaeva[*], **D. O. Artamonov**, and **A. A. Vostrikov**

Kutateladze Institute of Thermophysics, Siberian Branch, Russian Academy of Sciences,
pr. Akad. Lavrent'eva 1, Novosibirsk, 630090 Russia

Received May 11, 2018

Abstract—The features of propene oxidation in high-density mixtures of C_3H_6/O_2 ($[C_3H_6]_0 = 0.23–0.25$ mol/dm^3, $[O_2]_0 = 0.76–0.82$ mol/dm^3), diluted with argon, carbon dioxide and water vapor at uniform heating (1 K/min) to $T \leq 620$ K are investigated for the first time. From the time dependences of reaction mixtures temperature it is found that propene self-ignition occurs at 465 K and does not depend on the nature of the diluent. Using mass spectrometry analysis it is demonstrated that in the composition of the products of propene oxidation in the Ar and CO_2 medium predominate methanol, acetaldehyde, acetone, acetic acid and formaldehyde; in the oxidation in the H_2O medium, only small amounts of these substances were registered. Degree of consumption of O_2 in the oxidation of propene increases in the following order: $CO_2 \ll Ar < H_2O$, which is a consequence of the involvement of CO_2 and H_2O molecules in chemical transformations. Mechanisms of the observed processes are discussed.

DOI: `10.1134/S1810232818040045`

INTRODUCTION

Combustion of fuels directly in the heat transfer agents (supercritical water or carbon dioxide) raises ecological cleanliness and efficiency of the production of heat and electrical power [1–4]. Obviously, to develop new technologies based on combustion of various fuels in supercritical water or carbon dioxide, it is necessary to identify the particular features of oxidation of individual compounds in these media. We studied earlier [5–7] the combustion of hydrogen, methane and isobutane in the medium of water vapor and carbon dioxide. The aim of this work is to determine the characteristics of propene oxidation in argon, carbon dioxide and water vapor media at a high density of reactants. Unlike water and carbon dioxide, argon, is chemically inert diluent, which will allow us to reveal the role of H_2O and CO_2 in propene oxidation.

It is of interest to study propene combustion because it is one of the components of liquefied petroleum gas. We pay attention to the study of oxidation of propene, as a simplest hydrocarbon containing single and double carbon–carbon bonds, because alkenes are one of the products of conversion of alkanes in supercritical water [8–10]. Wilk et al. [11] studied the low-temperature propene oxidation in air (autoclave, 580–715 K, 0.1 MPa, fuel equivalence ratio $\varphi = 0.8–3.0$), defined the temperature interval corresponding to the negative temperature coefficient of the reaction rate, and proposed mechanisms of oxidation. It is shown that the initial oxidation stage is the H atom abstraction from propene in the reaction with oxygen:

$$CH_3CH{=}CH_2 + O_2 \rightarrow CH_2CHCH_2 + HO_2, \quad \Delta H^\circ_{298} = +167\,\text{kJ/mol}, \tag{1}$$

the interacting of OH and HO_2 radicals with propene results in the formation of the allyl radical, hydrogen peroxide and water:

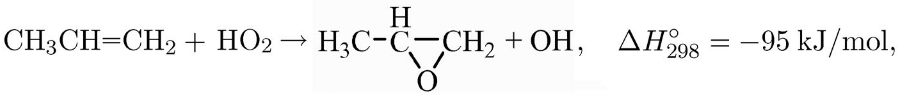
$$CH_3CH{=}CH_2 + HO_2 \rightarrow CH_2CHCH_2 + H_2O_2, \quad \Delta H^\circ_{298} = -3\,\text{kJ/mol}, \tag{2}$$

---

[*] E-mail: `fedyaeva@itp.nsc.ru`

$$CH_3CH{=}CH_2 + OH \rightarrow CH_2CHCH_2 + H_2O, \quad \Delta H^\circ_{298} = -129\ \text{kJ/mol}, \qquad (3)$$

and HO_2 bonding to propene in the reaction:



$$CH_3CH{=}CH_2 + HO_2 \rightarrow H_3C{-}\overset{H}{C}\underset{O}{\diagdown\diagup}CH_2 + OH, \quad \Delta H^\circ_{298} = -95\ \text{kJ/mol}, \qquad (4)$$

results in formation of propylene oxide. Here and below, the heat effect of reaction ΔH°_{298} is calculated using the reference data [12]. Based on analysis of the composition of products, Wilk et al. [11] have concluded that reactions (2) and (3) are dominant at 580–626 K, and chain branching occurs mainly through the decomposition of methyl- and allyl-hydroperoxide. Stark and Waddington [13] in the study of oxidation of propene in the air (autoclave, 505–549 K, 0.01–0.4 MPa) have registered a high yield of propylene oxide and explained this fact by reactions involving HO_2, CH_3O_2, $C_3H_5O_2$, and $C_2H_3CO_3$ radicals. From a comparison of experimental data and the suggested kinetic model, the authors [13] concluded that the lower the oxidation temperature, the higher the yield of propylene oxide; at that, the pressure of the reaction mixture is of minor importance.

Davis et al. [14] investigated composition of the products of high-temperature oxidation and pyrolysis of propene in a flow reactor (≈ 1200 K, 0.1 MPa) and proposed a detailed kinetic mechanism of the process, which comprises reaction of propene, propyne, allene and propane transformations. Burke et al. [15] studied by the experimental and numerical methods propene combustion using a jet stirred-reactor (800–1100 K, ≈ 0.1 MPa, $\varphi = 0.6{-}2.2$) and a flow reactor (843–1020 K, 0.6–1.2 MPa, $\varphi = 0.7{-}1.3$). Using analysis of the sensitivity coefficients, the authors [15] isolated the main reactions that determine the combustion rate of propene: hydrogen atom abstraction from propene in reaction with O_2, OH or HO_2; recombination of allyl radicals; the reaction between allyl- and hydroxyperoxiradicals; reactions of 1- and 2-propenyl radicals with oxygen. Le Cong et al. [16] studied the effect of H_2O (10% mol) and CO_2 (30% mol) on ethylene and propene combustion in a jet-stirred reactor (950–1450 K, 0.1 MPa, $\varphi = 0.5{-}2$). It was found that water inhibits oxidation of ethylene, especially in the case of lean fuel mixtures, whereas carbon dioxide slightly accelerates its oxidation. The influence of H_2O and CO_2 on propene oxidation in the conditions [16] has not been reported.

From the above analysis it follows that the data on the effect of H_2O and CO_2 on the ignition of propene at elevated pressures, as well as on the composition of its oxidation products are fragmented. In this study we investigated for the first time the peculiarities of propene oxidation in high-density $C_3H_6/O_2/Ar$, $C_3H_6/O_2/CO_2$, and $C_3H_6/O_2/H_2O$ mixtures under their uniform slow heating.

EXPERIMENTAL PROCEDURE

The experimental setup is described in detail in [5–7]. The main element of the setup is a tubular reactor (internal diameter 30 mm, volume 65.0 cm^3), made of stainless steel 12X18H10T (AISI 321 analog). The reactor was placed in an oven whose temperature was controlled by a thermoprogrammer connected to a thermocouple (T_{out}) mounted on the outer wall of the reactor. An internal thermocouple (T_{in}) entered into the center of the reaction space through the reactor face measured temperature of the reactants. The temperature measurement accuracy is ± 0.5 K. A diaphragm strain gauge measured pressure of the reagents. The pressure measurement accuracy is 0.15% of the measured value. Time dependences of the temperature and pressure were recorded digitally with a frequency of 10 Hz using an analog-to-digital converter. The reactants were fed into the pre-evacuated reactor through a capillary tube welded into the central part of the reactor sidewall through a control valve. The volume of the reactor inside the oven is 64.1 cm^3, and that of the cold volumes outside the furnace is 0.9 cm^3. Before each experiment, the reactor's inner surface was passivated (oxidized) with a mixture of H_2O/O_2 at 873 K.

We conducted four experiments corresponding to different composition of the reaction mixture (Table 1). In experiment 1 the diluent of the C_3H_6/O_2 mixture was argon, in experiment 2—carbon dioxide, and in experiments 3 and 4—water vapor. In experiments 1 and 2 the components of the reaction mixture were charged into the reactor at 303 K as follows: diluent (up to ≈ 0.3 MPa pressure), fuel, diluent and oxygen to a predetermined pressure. Such a sequence of reactor charging is caused, on

Table 1. Conditions and results of the experiments

Experiment	Partial pressure, MPa			Amount of reagents, mmol			φ	x_{d}, % mol	α_{f}, % mol	α_{O}, % mol
(Diluent)	C_3H_6	O_2	Diluent	$[C_3H_6]_0$	$[O_2]_0$	$[\mathrm{Diluent}]_0$				
1 (Ar)	0.55	1.95	4.06	15.4	50.8	107	1.36	62	88.2	87.8
2 (CO_2)	0.54	1.94	3.32	15.0	50.5	101 (15.8)	1.34	61	70.6	57.1
3 (H_2O)	0.55	1.96	–	14.9	49.0	103	1.36	62	–	–
4 (H_2O)	0.59	2.15	–	15.8	52.8	172	1.34	73	87.5	98.5

The amount of CO_2 condensed in the cold volumes of the reactor is given in brackets.

the one hand, by the need to fill the cold volumes with diluent to reduce the error in determining the amount of fuel in the heated part of the reactor, and, on the other hand, by the low pressure of saturated vapor of propene in a standard vessel (1.02 MPa at 293 K [17]). In experiments 3 and 4 the reactor was charged through the separation membrane at room temperature with 2.8 and 4.0 cm^3 of distilled water. The reactor was then heated to $T_{\mathrm{out}} = 403$ K and thermostatically controlled for 45 min. The unheated the reactor' volumes were filled with water during this time. After thermostatic control of the reactor, 103 mmol of water (experiment 3) and 172 mmol of water (experiment 4), respectively, remained in its heated part. After cooling the reactor to 303 K it was consecutively charged with propene and oxygen.

Values of the partial pressure of the reactants and diluents charged into the reactor (into its heated part), their amount ($[C_3H_6]_0$, $[O_2]_0$, and $[\mathrm{Diluent}]_0$), the fuel equivalence ratio φ, the fraction of diluent x_{d} in the mixture, the degree of conversion of propene α_{f} and oxygen α_{O} are shown in Table 1. The amounts of the reagents and diluents were determined based on the values of their temperature and partial pressure, as well as the reactor volume, using the reference P–v–T data [17].

After reaching the desired temperature the reactor was cooled at a rate of ≈ 6 K/min to room temperature and the residual pressure of reactants in the reactor was measured. The composition and amount of reactants were determined using an MS-7303 quadrupole mass spectrometer according to [18]. The amount of carbon in the low-boiling liquid products formed in experiments 1 and 2 was calculated from the results of measurement of the amount of $(CO_2)_{\mathrm{R}}$ formed during their oxidation by the H_2O/O_2 mixture at 873 K. At oxidation of propene in the H_2O medium (experiments 3 and 4) no liquid products were found.

RESULTS AND DISCUSSION

In this work we investigated peculiarities of oxidation of high-density mixtures C_3H_6/O_2 diluted with argon, carbon dioxide and water vapor. As seen in Table 1, the experiments were conducted with fuel-enriched mixtures ($\varphi = 1.34$–1.36), i.e., the amount of $[O_2]_0$ in the reaction mixture is less than stoichiometric amount corresponding to complete oxidation of propene in the reaction:

$$\mathrm{C_3H_6} + 4.5\mathrm{O_2} = 3\mathrm{H_2O} + 3\mathrm{SO_2}, \quad \Delta H^{\circ}_{298} = -1886\ \mathrm{kJ/mol}, \tag{5}$$

this reveals the influence of diluents on the composition of the products of its partial oxidation.

Oxidation of Argon and Carbon Dioxide

Results of measurements of T_{in} and T_{out} versus time, which were obtained in the oxidation of propene in Ar and CO_2 medium are shown in Fig. 1 as dependences $\Delta T = T_{\mathrm{in}} - T_{\mathrm{out}}$ on T_{out}. Here T_{out} corresponds to a predetermined increase in the temperature of the reactor at a rate $q = 1$ K/min, and T_{in} is the reaction mixture temperature measured by the internal thermocouple. It is seen that, with increased $T_{\mathrm{out}}(t)$, in all the experiments we observed the rise of temperature $\Delta T(t)$, caused by self-ignition of the C_3H_6/O_2 mixture (by self-acceleration of exothermic reaction (5)). Table 2 presents the following parameters of the curves $\Delta T(T_{\mathrm{out}})$ and the reaction mixture: T^*_{out} and T^*_{in} are

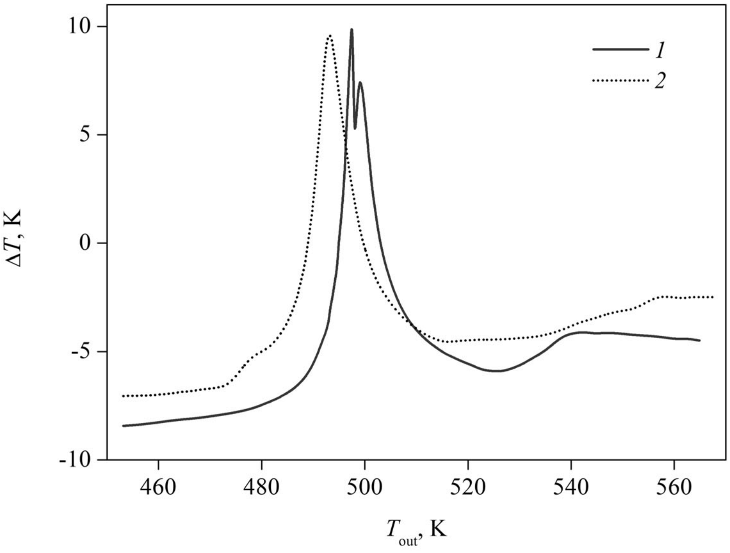


Fig. 1. Temperature dependence of the temperature difference ($\Delta T = T_{\rm in} - T_{\rm out}$) of reactants in the central part of the reactor $T_{\rm in}$ and at the outer wall of the reactor $T_{\rm out}$ in the oxidation of propene in Ar (*1*) and CO_2 (*2*). The numbers of curves correspond to the numbers of experiments in Table 1.

Table 2. Characteristic points of the curves in Figs. 1, 2 and thermodynamic parameters of reaction mixture

Experiment (Diluent)	$T^*_{\rm out}$, K	$T^*_{\rm in}$, K	$T^{\rm min}_{\rm out}$, K	$T^{\rm min}_{\rm in}$, K	$t_{\rm ox}$, min	S, K·min	$T^{\rm max}_{\rm out}$, K	$T^{\rm max}_{\rm in}$, K	$\Delta T^{\rm max}$, K	C^*_v, J/K	$\Delta T^*_{\rm ad}$, K
1 (Ar)	473 526	465 520	526 565	520 560	53 39	161 24	497 542	507 528	18 2	3.8	5605
2 (CO_2)	472	466	516	512	44	166	493	503	16	6.0	3528
3 (H_2O)	471 563	465 558	563 603	558 600	92 40	313 45	504 590	508 595	10 11	3.2	6418
4 (H_2O)	471 576	465 572	576 596	572 593	105 20	252 27	504 591	507 581	9 1	3.1	7138

temperatures of the reactor wall and the reaction mixture, respectively, at which the self-ignition occurs (they were determined from the condition $|\Delta T_i(T_{\rm out}) - \Delta T'_i(T_{\rm out})| > 3\sigma$, where σ is standard deviation of the experimentally measured values on the linear portion of the curve $\Delta T(T_{\rm out})$); $T^{\rm min}_{\rm out}$ and $T^{\rm min}_{\rm in}$ are temperatures corresponding to termination of noticeable oxidation of propene (corresponding to a minimum of the curve $\Delta T(T_{\rm out})$); $t_{\rm ox} = (T^{\rm min}_{\rm out} - T^*_{\rm out})/q$ is duration of oxidation; S is the area under the curve $\Delta T(T_{\rm out})$ bounded by the baseline and corresponding to the time $t_{\rm ox}$; $T^{\rm max}_{\rm out}$ and $T^{\rm max}_{\rm in}$ are temperatures corresponding to the maximum of $\Delta T(T_{\rm out})$; $\Delta T_{\rm max} = (T^{\rm max}_{\rm in} - T^*_{\rm in}) - (T^{\rm max}_{\rm out} - T^*_{\rm out})$ is the maximum growth of temperature of the reaction mixture as a result of heat release during combustion; values of the specific heat $C^*_v = \Sigma C_{v,i} x_i$ of the reaction mixture at a temperature $T^*_{\rm in}$, calculated using the reference data [17] (here x_i is mole fraction of the ith component in the gas phase); values of the growth of the reaction mixture temperature $\Delta T^*_{\rm ad} = Q/C^*_v$ under adiabatic conditions due to heat release in reaction (5).

As follows from the data in Table 2, the temperature of propene self-ignition $T^*_{\rm in}$ in Ar and CO_2 media is almost the same (465 and 466 K, respectively), indicating the same mechanism of onset of oxidation. The maximum temperature increase $\Delta T^{\rm max}$ in the Ar medium proved to be slightly larger than in the

CO_2 medium, which can be caused by greater heat capacity of the $C_3H_6/O_2/CO_2$ mixture. The values of the area S, which characterizes the heat release, in the Ar and CO_2 medium appeared approximately equal.

Figure 1 shows that in the CO_2 medium (curve *2*) a marked increase in the oxidation rate $d\Delta T/dT_{out}$ started at a lower temperature than that in the Ar medium (curve *1*). This may be due to shielding the inner surface of the reactor by adsorbed CO_2 molecules, promoting a reduction of the contribution of heterogeneous exothermic reactions, and as a consequence, a reduction of heat removal from the reaction system. We considered earlier in detail in [5] the effect of adsorbed molecules of diluent on the contribution of homogeneous and heterogeneous reactions to the recorded heat emission, using hydrogen oxidation as an example. Note that the heterogeneous exothermic reactions almost have no influence on indications of the thermocouple T_{in} due to the high specific heat $C = 548$ J/kg·K and thermal conductivity $\lambda = 21$ W/m·K of stainless steel [19], as well as the stabilizing effect of the thermoprogrammer that controls heating of the reactor by decreasing the heater power. Under adiabatic conditions, heat release with complete O_2 consumption in experiments 1 and 2 ($Q = 21.3$ and 21.2 kJ) could lead to an increase in temperature of the reactor whose weight is 3.6 kg, by ≈ 11 K, or gas contained in the reactor ($C_v^* = 3.8$ and 6.1 J/K), at homogeneous combustion by $\Delta T_{ad}^* = 5605$ and 3528 K (Table 2). In fact, due to the heat removal, the increase of the reaction mixture temperature ΔT^{max} is considerably lower than ΔT_{ad}^*.

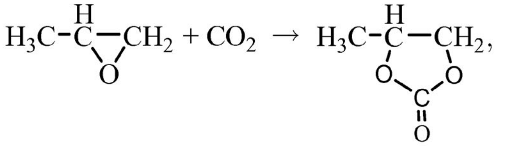
The results of the mass spectrometric analysis of the products of propene oxidation in CO_2 and Ar are listed in Table 3. It is seen that in addition to CO_2 and CO, in the oxidation products predominate methanol, acetaldehyde, acetone, acetic acid and formaldehyde; lower alkanes and alkenes, ethanol, and propylene oxide are present in minor amounts. Overall, these data agree well with the results obtained in the low-temperature oxidation of propene in the air medium [11, 13].

The main distinctions in the composition of the propene oxidation products obtained in Ar and CO_2 medium are as follows. Firstly, there is a higher yield of CO in the CO_2 medium (Table 3). Taking into account the results of Zhang et al. [20], one can assume that the oxide layer on the inner surface of the reactor, whose principal ingredient is magnetite Fe_3O_4 [21], exerted catalytic effect on the decomposition of CO_2. Secondly, in the CO_2 medium the degree of conversion of propene and oxygen was minimal (see values of α_f and α_O in Table 1). One reason for this may be the formation of propylene carbonate (Table 3) in the reaction of propylene oxide formed by the reaction (4) with carbon dioxide [22–24]:

Table 3. Composition and amount of the oxidation products of propene in argon, carbon dioxide and water vapor (mmol)

Substance	Experiment (Diluent)			Substance	Experiment (Diluent)		
	1 (Ar)	2 (CO_2)	4 (H_2O)		1 (Ar)	2 (CO_2)	4 (H_2O)
Ar	106.6	–	–	Ethanol	0.13	0.24	0.01
H_2	0.71	0.77	1.12	Acetaldehyde	0.56	0.93	0.05
O_2	6.11	21.65	0.78	Acetic acid	0.44	0.50	0.01
CO	3.66	5.67	3.66	Propane	0.13	0.08	0
CO_2	18.05	117.5	31.84	Propene	1.82	4.41	1.98
Methane	0.27	0.12	0	Acetone	0.82	0.65	0.02
Methanol	2.12	1.82	0.19	Propylene oxide	0.01	0.02	0
Formaldehyde	0.22	0.41	0	Propylene carbonate	–	0.03	–
Formic acid	0.01	0	0	Butadiene	0.02	0.03	0.01
Ethane	0.12	0.12	0	$(CO_2)_R$	7.45	8.26	–
Ethylene	0	0.01	0	Carbon balance, % mol	94.2	94.7	88.3

Balance on carbon in experiment 2 is shown with the amount of CO_2 condensed in the cold reactor volumes.



$$\Delta H^\circ_{298} = -76\ \mathrm{kJ/mol}. \qquad (6)$$

Based on the fact that propylene carbonate, as opposed to propylene oxide, has a lower saturated vapor pressure (the boiling temperatures are 513 and 308 K, respectively, [25]), and the rate of the liquid-phase oxidation is lower than that of the gas-phase oxidation, it can be concluded that the formation of propylene carbonate in reaction (6) prevented further oxidation of fuel in the CO_2 medium. Furthermore, we previously established [26] that under uniform heating (1 K/min) propene is subject to oligomerization at $T \geq 587$ K with the formation of aromatic hydrocarbons. Apparently, under conditions of the present work the above processes also occurred, as evidenced by the high values of $(CO_2)_R$, particularly in the CO_2 medium (Table 3).

In addition, note that we also observed a low degree of O_2 conversion in the oxidation of isobutane in the CO_2 medium and explain this fact by the high density of CO_2 and the presence of the resonant vibrational energy exchange in the CO_2/i-C_4H_{10} system [7]. Since the frequencies of deformation oscillations of CH_3 and CH_2 groups in isobutane and propene are close [27], we may assume that the resonant vibrational energy exchange in the CO_2/C_3H_6 system also affects the oxidation of propene.

Oxidation in Water Vapor

The measurements of temperature and pressure of the reaction mixture, obtained in the oxidation of propene in the H_2O medium (experiments 3 and 4), are shown in Fig. 2 as dependencies $\Delta T(T_{\mathrm{out}})$ and $P(T_{\mathrm{out}})$. Compared with experiment 3, in experiment 4 the amount of water increased 1.7 times and the amount of reactants filled into the reactor increased by 6–7% (Table 1). According to the reference data [17], the complete evaporation of water in the reaction system in experiments 3 and 4 occurred at $T_{\mathrm{ev}} = 545$ and 576 K, respectively, (in Fig. 2 it is indicated by vertical arrows). Based on the fact that the temperature of propene self-ignition in experiments 3 and 4 is 465 K (Table 2) it follows that

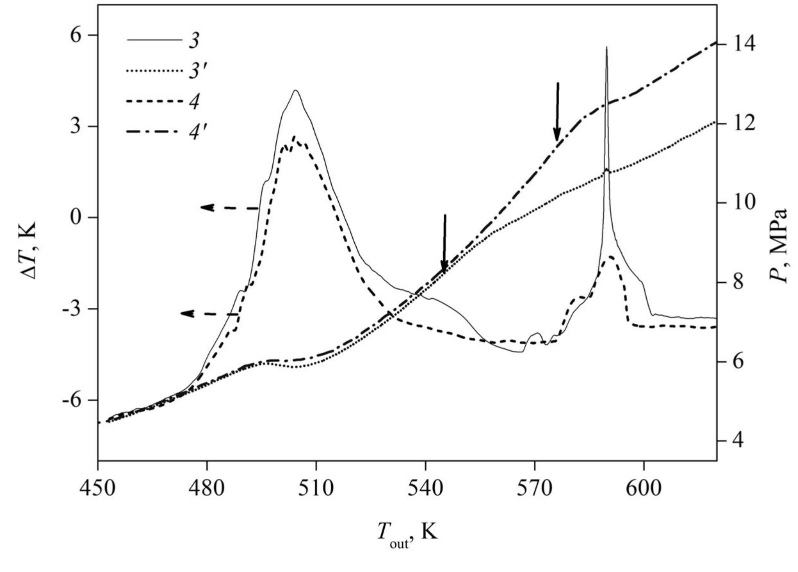


Fig. 2. Temperature dependence of the temperature difference ($\Delta T = T_{\mathrm{in}} - T_{\mathrm{out}}$) of reactants in the central part of the reactor T_{in} and the outer wall of the reactor T_{out} in the oxidation of propene in H_2O medium at dilution $x_{\mathrm{d}} = 62$ (*3*) and 73% mol (*4*); temperature dependence of reactants of pressure variation in experiments 3 (3′) and 4 (4′). The vertical arrows denote the temperature of complete evaporation of water, as determined by the reference data [17]. The numbers of curves correspond to the numbers of experiments in Table 1.

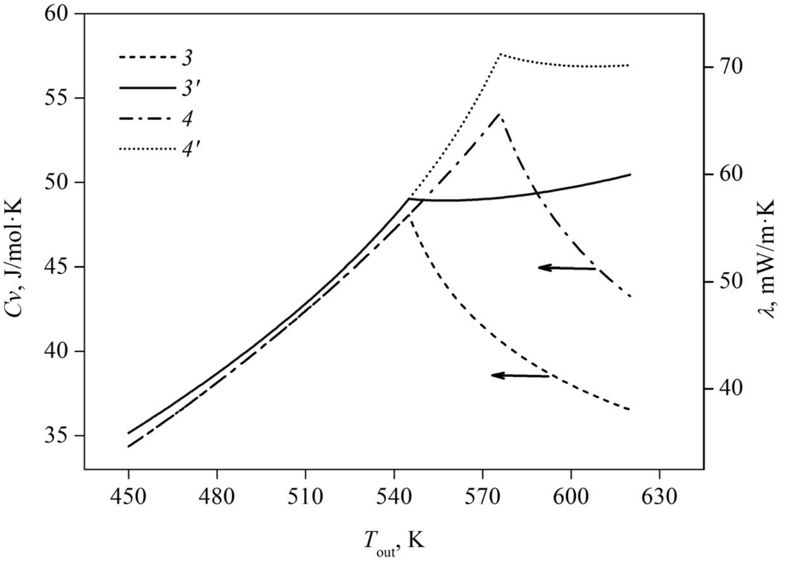


Fig. 3. Temperature dependence of the change in heat capacity (*3*, *4*) and thermal conductivity (3′, 4’) of saturated and superheated vapor, corresponding to amount of water loaded into the reactor in experiments 3 and 4 and determined by reference data [17]. The kinks in the curves correspond to complete water evaporation. The numbers of curves correspond to the numbers of experiments in Table 1.

its oxidation was accompanied by evaporation of water, i.e., by an increase in the heat capacity and thermal conductivity of the reaction medium with increasing temperature (Fig. 3). At that, part of the heat released during propene oxidation was spent on water evaporation. For example, in experiment 3 the thermal expenditures for water evaporation with temperature increasing from to $T_{\rm ev}$ are 4 kJ [17]; this corresponds to the amount of heat released in the oxidation of 3.4 mmol of propene (see reaction (5)).

Behavior of the curves $P(T_{\rm out})$ in Fig. 2 corresponds to the change in pressure associated with the evaporation of water with increasing temperature, the heat generation in the oxidation of propene, and the reaction mixture cooling to a predetermined temperature $T_{\rm out}$. The difference between curves 3′ and 4′ is caused by the following factors: at $T_{\rm out} > 495$ K—by greater reduction of the ohmic heater power due to the greater growth of temperature $\Delta T^{\rm max}$ in experiment 3; at $T_{\rm out} > 515$ K—by fewer components in the gas phase in experiment 3; at $T_{\rm out} > 545$ K—by complete evaporation of liquid water in experiment 3.

Table 2 shows that the ignition temperature of propene $T^*_{\rm in}$ in the Ar, CO_2, and H_2O medium is the same, i.e., does not depend on the nature of the diluent. However, in the H_2O medium (experiment 3) the oxidation time $t_{\rm ox}$ is greater, whereas the maximum temperature increase $\Delta T^{\rm max}$ is less than in the Ar and CO_2 medium (first peaks in Figs. 1 and 2). This means that the consumption of heat released during the oxidation of propene for evaporation of water and increase of the specific heat and thermal conductivity of the medium as the temperature increased (Fig. 3) prevented the increase in the oxidation rate. Another evidence is the decrease of $\Delta T^{\rm max}$ with increasing $[H_2O]_0$ in experiment 4 as compared with experiment 3, even despite the greater amount of reactants filled into the reactor in experiment 4 (Tables 1 and 2). The presence of more water in experiment 4 resulted in that $\Delta T^{\rm max}$ of the second peak (at $T^{\rm max}_{\rm out} = 504$ K) has dropped from 11 to 1 K in comparison with experiment 3. From the comparison of the areas S, characterizing the heat release in experiments 1–3 (Table 2) it follows that in the H_2O medium the area S is ≈ 2 times greater than in the Ar and CO_2 media. This indicates that the contribution of homogeneous reactions in the H_2O medium was decisive probably due to the presence of the layer of adsorbed H_2O molecules on the inner surface of the reactor, which reduces heat removal from the reaction system [5].

Analysis of the results of mass spectrometry of the oxidation products (Tables 1 and 3) shows that in the oxidation of propene in the H_2O medium (experiment 4), there occurred almost complete consumption of O_2 ($\alpha_O = 98.5\%$ mol), and the products contain only small amounts of methanol, ethanol, acetaldehyde, acetone, and acetic acid. From the comparison of the data on the composition and yield of products in experiments 1, 2, and 4 (Table 3), we can assume that the more complete oxidation of propene in the H_2O medium is due not only to the greater oxidation time t_{ox} in test 4 (see Table 2), but also due to involving water molecules in the elementary reactions. Holgate and Tester [28] in the study of the kinetics of hydrogen oxidation in supercritical water (flow reactor, 678–873 K, 24.6 MPa) have found that the rate of the reaction of chain branching

$$\mathrm{HO_2 + H_2O \rightarrow H_2O_2 + OH}, \quad \Delta H^{\circ}_{298} = +63\ \mathrm{kJ/mol}, \tag{7}$$

increases along with increasing density of water. Lubrano Lavadera et al. [29] in the study of the influence of water vapor on combustion of propane in nitrogen (a jet stirring flow reactor, 720–1100 K, 0.11 MPa, $\varphi = 0.5$–1.5, $[H_2O] \leq 40.5\%$ mol) have found that in the range of low temperatures the H_2O molecules, as a third body, are actively involved in the reaction of decomposition of hydrogen peroxide:

$$\mathrm{H_2O_2 + M \rightarrow OH + OH + M}, \tag{8}$$

which accelerates the oxidation. Moreover, we have previously shown [26] that water vapor suppresses oligomerization of propene due to existence of “cage effect.” This means that in the H_2O medium, oxidation of propene does not lead to formation of high-boiling substances in contrast, for example, to oxidation in the CO_2 medium (see the reaction (6)), i.e., the oxidation processes take place mainly in the gas phase.

As seen in Table 3, the largest amount of H_2 was formed in the H_2O medium, which is an obvious consequence of the water gas shift reaction

$$\mathrm{CO + H_2O \leftrightarrow CO_2 + H_2}, \quad \Delta H^{\circ}_{298} = -41\ \mathrm{kJ/mol}. \tag{9}$$

However, the amount of CO in the products obtained in H_2O and Ar is the same and is determined, apparently, by a lack of oxygen (Table 1) and by the steam reforming reaction in the H_2O medium:

$$\mathrm{C}_i\mathrm{H}_j + i\mathrm{H_2O} = (i + 0.5j)\mathrm{H_2} + i\mathrm{CO}. \tag{10}$$

In general, the balance for carbon in the H_2O medium is less than in Ar and CO_2, which is explained by the high solubility of propene partial oxidation products (alcohols, aldehydes and acids) in water after cooling the reactor and the applied analysis technique [18].

CONCLUSIONS

In this paper we investigated for the first time the propene oxidation at high density of reagents and with diluting the reaction mixture with argon, carbon dioxide and water vapor in the conditions of oxygen deficiency. Based on the time dependences of reaction mixtures temperature it has been found that propene self-ignition occurs at 465 K and does not depend on the nature of the diluent. Lack of O_2 and the limited temperature range ($T \leq 620$ K) made it possible to reveal the oxidation intermediate products and the mechanisms for their formation. It was shown that the degree of consumption of O_2 in the oxidation of propene in diluents increases in the following order: $CO_2 \ll Ar < H_2O$. Implementation of intensive oxidation of propene in a CO_2 medium is prevented by high heat capacity of the $C_3H_6/O_2/CO_2$ mixture and chemical interaction between its components. In the H_2O medium, propene oxidation proceeds until complete depletion of O_2 in the reaction mixture, presumably due to the participation of H_2O molecules in the elementary reactions and the suppression of formation of low-boiling compounds.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant no. 18-29-06005). The authors thank M.Ya. Sokol for assistance in the experiments.

REFERENCES

1. Queiroz, J.P.S., Bermejo, M.D., Mato, F., and Cocero, M.J., Supercritical Water Oxidation with Hydrothermal Flame as Internal Heat Source: Efficient and Clean Energy Production from Waste, *J. Supercrit. Fluids*, 2015, vol. 96, pp. 103–113.
2. Yan, Q., Hou, Y., Luo, J., Miao, H., and Zhang, H., The Exergy Release Mechanism and Exergy Analysis for Coal Oxidation in Supercritical Water Atmosphere and a Power Generation System Based on the New Technology, *Energy Conv. Manag.*, 2016, vol. 129, pp. 122–130.
3. Borgert, K.J. and Rubin, E.S., Oxy-Combustion Carbon Capture for Pulverized Coal in the Integrated Environmental Control Model, *Energy Procedia*, 2017, vol. 114, pp. 522–529.
4. Chen, S., Fundamentals of Oxy-Fuel Combustion, *Oxy-Fuel Combustion: Fundamentals, Theory and Practice*, Chuguang, Z. and Zhaohui, L., Eds. 2018, pp. 13–30.
5. Vostrikov, A.A., Fedyaeva, O.N., Shishkin, A.V., Tretyakov, D.S., and Sokol, M.Ya., 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, pp. 10469–10480.
6. Vostrikov, A.A., Fedyaeva, O.N., Shishkin, A.V., Sokol, M.Ya., Kolobov, F.I., and Kolobov, V.I., Partial and Complete Methane Oxidation in Supercritical Water, *J. Eng. Therm.*, 2016, vol. 25, no. 4, pp. 474–484.
7. Vostrikov, A.A., Fedyaeva, O.N., Shishkin, A.V., Artamonov, D.O., and Sokol, M.Ya., Features of Low-Temperature Oxidation of Isobutane in Water Vapor and Carbon Dioxide with Increased Density of Reagents, *J. Eng. Therm.*, 2017, vol. 26, no. 4, pp. 466–475.
8. Fedyeava, O.N., Antipenko, V.R., and Vostrikov, A.A., Conversion of Sulfur-Rich Asphaltite in Supercritical Water and Effect of Metal Additives, *J. Supercrit. Fluids*, 2014, vol. 88, pp. 105–116.
9. Alshammari, Y.M. and Hellgardt, K., Sub- and Supercritical Water Reforming of n-Hexadecane in a Tubular Flow Reactor, *J. Supercrit. Fluids*, 2016, vol. 107, pp. 723–732.
10. Fedyaeva, O.N., Antipenko, V.R., and Vostrikov, A.A., Peculiarities of Composition of Hydrocarbon and Heteroatomic Substances Obtained during Conversion of Kashpir Oil Shale in Supercritical Water, *Russ. J. Phys. Chem. B*, 2017, vol. 11, pp. 1246–1254.
11. Wilk, R.D., Cernansky, N.P., and Conen, R.S., An Experimental Study of Propene Oxidation at Low and Intermediate Temperature, *Comb. Sci. Technol.*, 1987, vol. 52, pp. 39–58.
12. Baulch, D.L., Bowman, C.T., Cobos, C.J., Cox, R.A., Just, T., Kerr, J.A., Pilling M.J., Stoker, D., Troe, J., Tsang, W., Walker, R.W., and Warnatz, J., Evaluated Kinetic Data for Combustion Modeling: Supplement II, *J. Phys. Chem. Ref. Data*, 2005, vol. 34, no. 3, pp. 757–1397.
13. Stark, M.S. and Waddington, D.J., Oxidation of Propene in the Gas Phase, *Int. J. Chem. Kin.*, 1995, vol. 27, pp. 123–151.
14. Davis, S.G., Law, C.K., and Wang, H., Propene Pyrolysis and Oxidation Kinetics in a Flow Reactor and Laminar Flames, *Comb. Flame*, 1999, vol. 119, pp. 375–399.
15. Burke, S.M., Metcalfe, W., Herbinet, O., Battin-Leclerc, F., Haas, F.M., Santner, J., Dryer, F.L., and Curran, H.J., An Experimental and Modeling Study of Propene Oxidation, part 1: Speciation Measurements in Jet-Stirred and Flow Reactors, *Comb. Flame*, 2014, vol. 161, pp. 2765–2784.
16. Le Cong, T., Bedjanian, E., and Dagaut, P., Oxidation of Ethylene and Propene in the Presence of CO_2 and H_2O: Experimental and Detailed Kinetic Modeling Study, *Comb. Sci. Tech.*, 2010, vol. 182, nos. 4–6, pp. 333–349.
17. Fedyaeva, O.N., Vostrikov, A.A., Shishkin, A.V., Sokol, M.Y., Fedorova, N.I., and Kashirtsev, V.A., Hydrothermolysis of Brown Coal in Cyclic Pressurization-Depressurization Mode, *J. Supercrit. Fluids*, 2012, vol. 62, pp. 155–164.
18. Lemmon, E.W., McLinden, M.O., and Freid, D.G., *Thermophysical Properties of Fluid Systems*, NIST Chemistry WebBook, NIST Standard Reference Database no. 69, Linstrom, P.J. and Mallard, W.G., Eds., National Institute of Standards and Technology, Gaithersburg MD, 2017, 20899, http://webbook.nist.gov/chemistry/fluid/.
19. Guva, A.Y., *Kratkii teplofizicheskii spravochnik* (Brief Thermophysical Handbook), Novosibirsk: Sibvuzizdat, 2002.
20. Vostrikov, A.A., Fedyaeva, O.N., Shishkin, A.V., Sokol, M.Ya., and Zaikovskii, A.V., Synthesis of Fe_xO_y Nanoparticles during Iron Oxidation by Supercritical Water, *Tech. Phys. Lett.*, 2012, vol. 38, pp. 955–958.
21. Zhang, C., Li, S., Wang, L., Wu, T., and Peng, S., Studies on the Decomposing Carbon Dioxide into Carbon with Oxygen-Deficient Magnetite, part II: The effects of Properties of Magnetite on Activity of Decomposition CO_2 and Mechanism of the Reaction, *Mater. Chem. Phys.*, 2000, vol. 62, pp. 52–61.
22. Gharnati, L., Musko, N.E., Jensen, A.D., Kontogeorgis, G.M., and Grunwaldt, J.-D., Fluid Phase Equilibria during Propylene Carbonate Synthesis from Propylene Oxide in Carbon Dioxide Medium, *J. Supercrit. Fluids*, 2013, vol. 82, pp. 106–115.

23. Korosteleva, I.G., Markova, N.A., Kolisnichenko, N.V., Ezhova, N.N., Khadzhiev, S.N., and Trukhmanova, N.I., Catalytic Synthesis of Propylene Carbonate from Propylene Oxide and Carbon Dioxide in the Presence of Rhodium Complexes Modified with Organophosphorus Ligands and Chitosan, *Petrol. Chem.*, 2013, vol. 53, no. 6, pp. 412–417.
24. Lan, D.-H., Yang, F.-M., Luo, S.-L., Au, C.-T., and Yin, S.-F., Water-Tolerant Graphene Oxide as a High-Efficiency Catalyst for the Propylene Carbonate from Propylene Oxide and Carbon Dioxide, *Carbon*, 2014, vol. 73, pp. 351–360.
25. Fizicheskie i khimicheskie svoistva organicheskikh soedinenii: Spravochnik (Physical and Chemical Properties of Organic Substances: Handbook), Bogomolnyi, A.M., Ed., Moscow: Khimiya, 2008.
26. Fedyaeva, O.N., Vostrikov, A.A., Antipenko, V.R., Shishkin, A.V., Kolobov, V.I., and Sokol, M.Ya., Role of Supercritical Water and Pyrite in Transformations of Propylene, *Russ. J. Phys. Chem. B*, 2017, vol. 11, no. 7, pp. 1117–1128.
27. Computational Chemistry Comparison and Benchmark Data Base, Release 18, Standard Reference Database 101, Johnson, R.D., III, Ed., National Institute of Standards and Technology, 2018, http://cccbdb.nist.gov/.
28. Holgate, R.H. and Tester, J.W., Oxidation of Hydrogen and Carbon Monoxide in Sub- and Supercritical Water: Reaction Kinetics, Pathways, and Water-Density Effects, 2: Elementary Reaction Modeling, *J. Phys. Chem.*, 1994, vol. 98, pp. 810–822.
29. Lubrano Lavedera, M., Sabia, P., De Joannon, M., Cavaliere, A., and Ragguci, R., Propane Oxidation in a Jet Stirred Flow Reactor. The Effect of H_2O as Diluent Species, *Exp. Therm. Fluid Sci.*, 2018, vol. 95, pp. 35–43.