

Relative Conversion of Lower Alkanes in Their Simultaneous Partial Gas-Phase Oxidation

V. S. Arutyunov*, V. M. Rudakov**, V. I. Savchenko**, and E. V. Sheverdenkin**

* *Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow, 119991 Russia*
e-mail: arutyunov@center.chph.ras.ru

** *Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*

Received February 7, 2005

Abstract—Experimental and theoretical studies are undertaken to analyze the relative conversions of methane and ethane in their simultaneous partial oxidation and also the conversions of C₁–C₄ hydrocarbons in the oxidation of more complex mixtures that model real natural and associated gases. It is shown that, under the conditions at which C₁–C₄ hydrocarbons are oxidized to oxygenates and at an initial oxygen concentration of 4–16%, the rapid burnout of higher hydrocarbons is accompanied by an increase in the concentration of methane produced by their oxidative reforming.

Partial oxidation along with steam and carbon dioxide reforming are the main processes of chemical reforming of natural gas. Depending on the process conditions, the products of partial oxidation can be oxygenates, ethylene, or synthesis gas [1]. The most attractive aspect of gas-phase partial oxidation is the exothermicity of the reaction (which, therefore, requires no energy supply from external sources) and the relative compactness of equipment in comparison with catalytic processes. Although steam reforming remains the main and most economical industrial process of synthesis gas production, processes combining partial oxidation with steam and carbon dioxide reforming are widely used to reduce energy consumption, cut equipment cost, and obtain the optimal (for further processing) ratio between CO and H₂ [2].

Among serious problems in catalytic steam reforming is the complexity of processing of gases with a noticeable concentration of higher hydrocarbons. They cause sooting and coking of a catalyst. Currently, the problem of processing of gases with a high concentration of higher hydrocarbons is solved by their preliminary partial catalytic steam reforming in adiabatic reactors (adiabatic prereforming) [2, 3]. However, this causes a 5–6% increase in the total energy consumption [2]. At the same time, in the partial oxidation of methane and its nearest homologues to oxygenates [1], it is these admixtures that have a beneficial effect on the process. In this case, there is preferred oxidation of heavier hydrocarbons, especially in mixtures with their high concentration. This property can be used to design a step of preliminary oxidative reforming of natural gas, which would precede the step of natural gas reforming to synthesis gas. Thus, the concentration of heavier homologues of methane can be decreased by their partial conversion to the end products of reforming (carbon oxides and hydrogen) and also to additional

amounts of valuable oxygen-containing products (methanol, formaldehyde, etc.).

The purpose of this work was to study the relative conversion of lower alkanes in their simultaneous gas-phase partial oxidation.

EXPERIMENTAL

Experiments on the oxidation of hydrocarbon mixtures of different composition were carried out on a pilot high-pressure setup [4, 5] intended for studying the kinetics of oxidation of hydrocarbon gases at pressures up to 100 atm. A stainless steel reactor with a 250-mm working part and quartz inserts 7 mm i.d. was used. A low (0.2–1 m³/h) gas flow rate allowed us to perform studies of preliminarily prepared gas mixtures of almost any composition. In the experiments, both commercial methane (used as a gas motor fuel) and natural gas from a gas line (containing no less than 98% methane, no more than 1% higher hydrocarbons, small amounts of CO₂ and N₂, and also about 30 µg/m³ odorants) were used without additional purification, in particular, without desulfurization. Commercial ethane we used contained 91.2% ethane, 8.3% methane, and 0.5% propane–butane fraction. In the experiments with addition of the propane–butane fraction, household liquefied gas was used.

KINETIC MODELING OF GAS-PHASE PARTIAL OXIDATION OF METHANE–ETHANE MIXTURES

For kinetic analysis of the partial oxidation of methane–ethane mixtures on the basis of published models of partial kinetic methane oxidation [1, 6, 7], we developed a kinetic model of the partial gas-phase oxidation

Table 1. Experimental data on the oxidative reforming of methane–ethane mixtures

Exp. no.	<i>P</i> , MPa	<i>T</i> , °C	Composition of mixture at reactor inlet, vol %					Composition of mixture at reactor outlet, vol %												α	β , %		
			CH ₄	C ₂ H ₆	N ₂	O ₂	CO ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	H ₂	N ₂	O ₂	CO ₂	CO	CH ₃ OH	CH ₂ O	C ₂ H ₅ OH	CHOOH		H ₂ O	CH ₄	C ₂ H ₆
1	3.0	500	10.0	62.0	21.3	7.2	0.07	12.9	50.5	1.0	2.1	21.8	0.5	0.35	4.23	1.90	0.53	0.31	0.02	4.0	1.58	-29.0	18.5
2	2.7	550	10.2	52.0	30.0	8.2	0.03	12.4	37.0	2.7	3.0	29.6	0.0	0.37	5.74	1.92	0.52	0.24	0.01	6.6	1.71	-21.6	28.8
3	3.0	519	10.6	57.6	25.2	7.3	0.03	11.8	45.6	1.2	3.7	25.0	0.2	0.30	4.91	1.88	0.53	0.29	0.02	4.5	1.41	-11.3	20.8
4	2.5	472	12.0	64.0	18.5	5.8	0.03	12.5	56.6	0.5	1.7	18.5	0.3	0.18	4.48	1.65	0.58	0.25	0.01	2.7	1.18	-4.2	11.6
5	2.5	450	13.4	69.1	13.6	3.8	0.03	13.9	64.0	0.3	1.2	13.7	0.2	0.19	2.28	1.36	0.66	0.21	0.005	2.0	1.12	-3.7	7.4
6	3.0	413	83.4	3.4	10.2	2.3	0.0	82.0	3.1	0.01	0.0	10.0	0.6	0.0	0.0	0.70	0.3	0.02	-	2.2	1.08	1.7	8.8
7	3.5	450	73.6	12.4	8.5	3.1	0.0	74.3	9.0	0.1	0.7	8.7	0.1	0.10	1.10	-	-	-	-	1.39	-0.95	27.4	
8	3.0	510	60.9	7.7	22.4	7.0	0.0	63.8	2.6	0.1	2.3	19.8	0.1	0.03	1.07	2.60	1.1	0.07	-	7.9	3.10	-4.8	66.2
9	4.0	620	44.3	8.5	32.9	11.4	0.0	46.6	3.1	0.7	1.9	31.0	0.1	0.43	3.80	1.40	0.6	0.11	-	5.5	2.88	-5.2	63.5
10	3.0	740	44.8	1.3	39.6	13.8	0.0	39.3	1.0	1.6	3.1	41.5	0.0	1.20	4.60	0.32	0.12	0.02	-	6.9	1.14	12.3	23.1

Note: “-” means that the concentration of this component of a mixture was not determined.

of C₁–C₂ hydrocarbons at high (up to 100 atm) pressures and moderate (600–1200 K) temperatures. The model consists of 417 elementary chemical reactions and is intended for modeling the oxidative processes in mixtures rich with methane and ethane, first of all, their partial oxidation to methanol and other oxygenates and also the oxidative dimerization of methane to ethane and ethylene. Calculations in terms of the model were performed using the kinetic program Kintecus-V3 both for isothermal and for adiabatic reaction conditions. In the calculations, no fitting of kinetic parameters of the model was performed.

PARTIAL OXIDATION OF METHANE–ETHANE MIXTURES

The conditions and results of the performed experiments on the partial oxidation of methane–ethane mixtures are presented in Table 1. As a measure of relative burnout of methane and ethane in this process, we took the ratio between these gases at the inlet and the outlet of the reactor:

$$\alpha = (\text{CH}_4/\text{C}_2\text{H}_6)_f / (\text{CH}_4/\text{C}_2\text{H}_6)_0.$$

Moreover, we calculated the percentage change in the concentration of each of the hydrocarbons in the oxidation:

$$\beta = (C_0 - C_f)/C_0;$$

a negative value of β means that the concentration of a given hydrocarbon in the mixture is higher than the initial concentration.

The experiments performed can be conditionally divided into three groups. In the first group of experiments, we studied the oxidation of mixtures with a significant excess of ethane (52–69%) over methane (10–13%) in the range of oxygen concentrations in a mix-

ture of 3.8–8.2% (experiments 1–5). In the second group, we investigated the oxidation of mixtures in which, conversely, the concentration of ethane was much lower than that of methane (experiments 6–8). In the third group, mixtures were oxidized at high (11–14%) initial oxygen concentration and, correspondingly, much higher temperature of self-heating of a mixture (experiments 9 and 10).

For the first group of experiments, Figs. 1–4 present the experimental and calculated data on the dependence of α on the main experimental parameters, namely, the oxygen concentration, the pressure in the reactor, the reaction temperature, and the ethane concentration in the reaction mixture.

Figure 1 compares the experimental and calculated plots of the burnout α as a function of the initial oxygen concentration. For mixtures with high (52–69%) ethane concentration, α rapidly increases with an increase in the initial oxygen concentration. Up to an initial oxygen concentration of $[\text{O}_2]_0 \sim 5\text{--}6\%$, when the heating of the mixture in the oxidation is relatively low (the adiabatic heating in the partial oxidation of methane to methanol is 40°C per percent of oxygen in the mixture; in the ethane oxidation, this heating is much lower), the results of the calculations for the isothermal conditions virtually coincide with the experimental data. At higher oxygen concentrations, the experimental α values increase noticeably more rapidly, which is nearly adequately taken into account by the calculations for the adiabatic conditions. Indeed, estimates show that, under our experimental conditions, the characteristic heat-transfer time and the reaction time are close and the reaction heating is near-adiabatic. The calculations for the adiabatic conditions virtually accurately described the experimental dependence at all the studied initial oxygen concentrations.

An interesting result of the kinetic modeling is the striking difference in the dependence of the relative burnout α on the initial oxygen concentration between mixtures with low and high initial ethane concentration (Fig. 1). At a high (52–69%) ethane concentration and an initial oxygen concentration below 5%, the calculations for the isothermal and the adiabatic conditions give virtually identical results, whereas, at a low (3%) ethane concentration, their results not only differ strongly but also have opposite behavior as functions of the oxygen concentration.

One can assume two main causes of this difference. First, the thermal conductivity of mixtures with low ethane concentrations is significantly lower, which leads to markedly higher heating under the adiabatic conditions. Second, at a very low concentration of ethane, which is one of the main gas-phase products of oxidative methane reforming [1, 4], ethane actually remains unconsumed since its concentration, beginning with a certain value, is maintained at a quasi-steady-state level. With an increase in the oxygen concentration and at adiabatic heating of the mixture above 200°C, the process already enters the temperature range of oxidative methane dimerization, in which ethane and ethylene are primarily formed. This is confirmed by experiment 10 (Table 1), at a low initial ethane concentration of 1.3% and a high initial oxygen concentration of 13.8%. Under these conditions and on adiabatic heating of the mixture to 740°C, the ethane concentration remains virtually constant (~1%), which is natural from the standpoint of the process kinetics.

The kinetic modeling results show that a change in pressure within the range 25–70 atm slightly affects the relative burnout α at any initial ethane concentrations from 3 to 65% (Fig. 2). Only an insignificant decrease in α with an increase in the ethane concentration is observed, and the modeling results agree well with available experimental data.

According to the calculations, α in the oxidation of mixtures with a low ethane concentration of 3% and a relatively low initial oxygen concentration of 5% under the isothermal conditions somewhat decreases with an increase in temperature (Fig. 3). At higher initial oxygen concentrations, when the self-heating of a mixture in the oxidation cannot be ignored, the relative ethane burnout abruptly increases (Table 1, experiments 8 and 9). However, at a lower initial ethane concentration of 1% (Table 1, experiment 10), α is close to 1 again since this concentration of ethane is close to its quasi-steady-state concentration determined by the kinetics of consumption and formation of ethane in the methane oxidation.

Figure 4 presents α as a function of the ethane concentration in a mixture. Naturally, the quantity α at zero concentration of ethane or methane is meaningless, all the more so as they are products of oxidative transformation to each other. This fact has a particularly strong effect as a zero concentration of either of them is

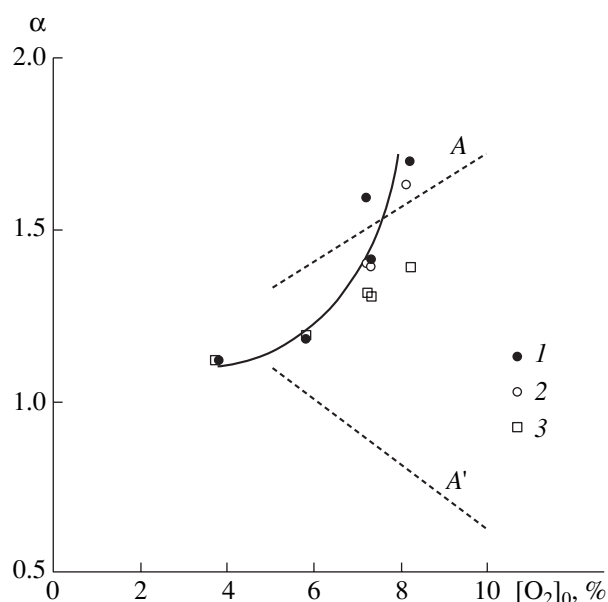


Fig. 1. Relative burnout α versus initial oxygen concentration. The solid line and points 1 represent the results of experiments 1–5; points 2 and 3, the results of calculations for (2) adiabatic and (3) isothermal conditions; and the dashed lines A and A', the results of calculations at $[C_2H_6]_0 = 3\%$, $T = 673$ K, and $P = 70$ atm for isothermal and adiabatic conditions, respectively.

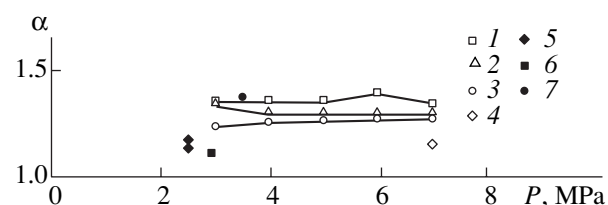


Fig. 2. Relative burnout α versus pressure at various initial ethane concentrations $[C_2H_6]_0$ in a mixture. The lines and points 1–4 represent the results of calculations at $T = 673$ K; $[O_2]_0 = 5\%$; and $[C_2H_6]_0 = (1) 3, (2) 5, (3) 10,$ and (4) 65%. Points 5–7 represent the results of experiments (5) 4 and 5, (6) 6, and (7) 7 at $[C_2H_6]_0 = (5) 64$ and 69.1, (6) 3.4, and (7) 12.4%.

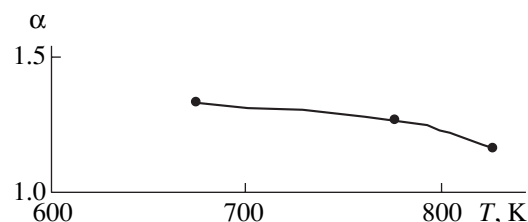


Fig. 3. Relative burnout α versus temperature as calculated for isothermal conditions at $[O_2]_0 = 5\%$, $[C_2H_6]_0 = 3\%$, and $P = 70$ atm.

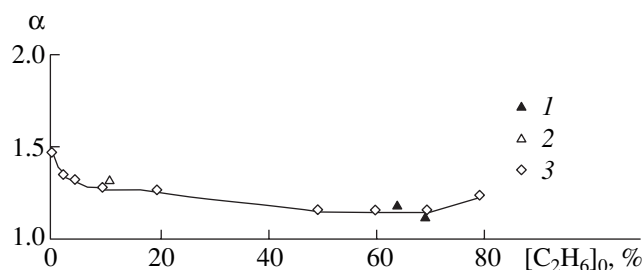


Fig. 4. Relative burnout α versus initial ethane concentration in a mixture. Points 1 and 2 represent the results of experiments (1) 4 and 5 and (2) 7; the line and points 3, the results of calculations at $T = 673$ K, $P = 70$ atm, and $[O_2]_0 = 5\%$ for isothermal conditions.

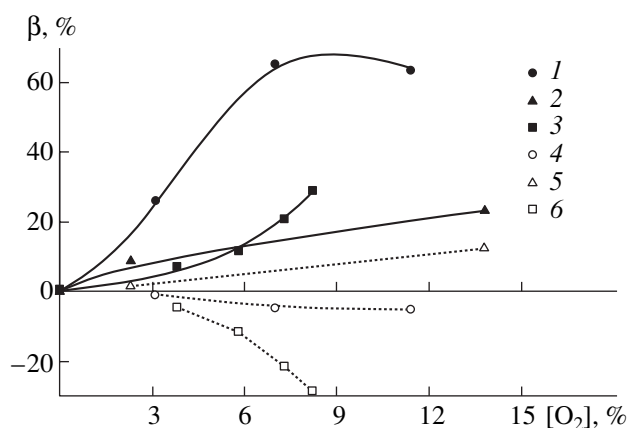


Fig. 5. Relative change β in the concentration of (1–3; solid lines) ethane and (4–6; dashed lines) methane versus initial oxygen concentration at an initial ethane concentration of (2, 4) 7–12, (2, 5) 1–3, and (3, 6) 52–69%.

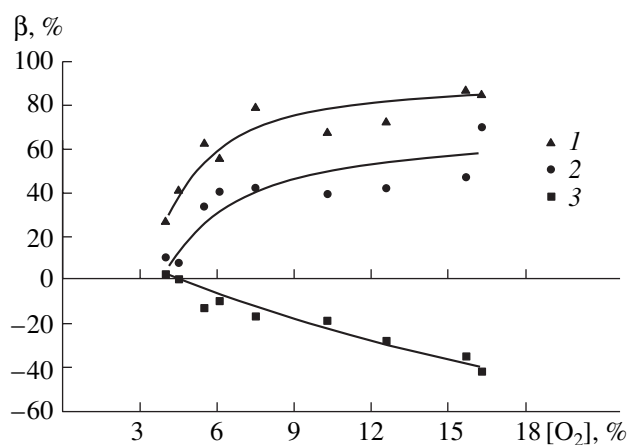


Fig. 6. Relative change β in the concentration of (1) butanes, (2) propane, and (3) methane versus initial oxygen concentration.

approached; this is the reason why the calculations were performed in the ethane concentration range 1–80%. For the isothermal conditions, α depends very slightly on the ethane concentration over much of the range and increases only a little as the limits of the range are approached. Bearing in mind the weak effect of pressure on α , the calculation results can be compared to the results of experiments 4, 5, and 7, with close initial oxygen concentrations. This comparison shows a good agreement between them, which allows one to perform a forecasting calculation of the relative burnout α for conditions for which experimental data are unavailable.

Figure 5 shows the experimental plots of the relative change β in the concentrations of methane and ethane in their simultaneous oxidation as a function of the initial oxygen concentration, whose behavior is governed by the ratio between the initial concentrations of ethane and methane. At an ethane concentration above several percent, not only does preferred ethane burnout take place but also the concentration of methane formed as a product of the oxidative degradation of ethane increases. However, at an initial ethane concentration of about 1%, ethane formally remains almost unconsumed since its concentration is maintained at a quasi-steady-state level determined by the processes of its formation as a product of the oxidative reforming of methane and the subsequent oxidative reforming of ethane itself. Thus, in the partial oxidation of methane–ethane mixtures, it is fundamentally impossible to achieve the complete conversion of only one of these hydrocarbons.

OXIDATION OF MIXTURES CONTAINING THE PROPANE–BUTANE FRACTION OF HYDROCARBONS

The next group of experiments was performed with hydrocarbon gases of more complex composition, which contain all saturated C_1 – C_4 hydrocarbons at noticeable concentrations. The experimental conditions and the composition of the initial reactants and products are given in Table 2.

Table 3 presents the relative change β in the initial concentration of each of the hydrocarbons, and Fig. 6 illustrates the dependence of β on the most strongly influencing factor, namely, the initial oxygen concentration in the mixture.

It is well seen that, whereas the burnout of propane and butane rapidly increases with an increase in the initial oxygen concentration, the methane burnout at initial oxygen concentrations above 5% is negative; i.e., the methane concentration in the mixture increases. Obviously, the formation of methane, much as in the case of ethane oxidation, is a consequence of the oxidative degradation of higher alkanes. But, at oxygen concentrations below 5%, the relative burnout of C_3 – C_4 hydrocarbons abruptly decreases and the methane con-

Table 2. Composition (vol %) of the initial reactants and products of the partial oxidation of a multicomponent mixture of C₁–C₄ hydrocarbons

Exp. no.	Composition	T, °C	P, atm	H ₂	CH ₄	O ₂	N ₂	CO	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	Σ, %
1	Reactants	453	35	0.0	57.5	4.0	16.0	0.0	0.0	0.0	2.0	0.0	18.0	1.0	1.5	100.0
	Products			1.1	56.1	0.0	18.0	2.0	0.2	0.2	0.6	0.1	16.0	0.8	1.0	96.1
2	Reactants	461	35	0.0	56.0	4.5	17.5	0.0	0.0	0.0	2.0	0.0	17.7	1.0	1.3	100.0
	Products			0.8	56.0	0.0	21.4	2.5	0.2	0.2	0.7	0.1	16.2	0.8	0.5	99.4
3	Reactants	469	35	0.0	53.0	5.5	20.0	0.0	0.0	0.0	1.9	0.0	17.5	0.9	1.2	100.0
	Products			0.8	60.0	0.0	21.0	5.0	0.2	0.2	0.5	0.0	11.5	0.3	0.5	100.0
4	Reactants	488	35	0.0	50.0	6.1	23.0	0.0	0.0	0.0	1.8	0.0	17.0	0.9	1.2	100.0
	Products			1.8	55.0	0.0	24.0	5.8	0.2	0.4	0.8	0.6	10.0	0.5	0.4	99.5
5	Reactants	523	30	0.0	47.5	7.5	25.0	0.0	0.0	0.0	1.7	0.0	16.5	0.8	1.0	100.0
	Products			1.0	55.6	0.0	26.0	6.4	0.3	0.2	0.5	0.2	9.4	0.1	0.3	100.0
6	Reactants	564	25	0.0	42.0	10.3	30.0	0.0	0.0	0.0	1.5	0.0	15.0	0.7	0.9	100.4
	Products			1.3	50.0	0.0	31.0	7.0	0.5	0.1	0.2	0.5	9.0	0.3	0.2	100.1
7	Reactants	592	25	0.0	36.0	12.6	33.5	0.0	0.0	0.0	1.4	0.0	14.7	0.8	1.0	100.0
	Products			1.8	46.2	0.0	34.0	6.9	1.0	0.5	0.3	0.4	8.4	0.2	0.3	100.0
8	Reactants	623	25	0.0	32.5	15.7	35.0	0.0	0.0	0.0	1.3	0.0	14.0	0.7	0.8	100.0
	Products			2.1	44.0	0.0	36.0	7.2	1.8	0.9	0.1	0.5	7.3	0.1	0.1	100.1
9	Reactants	640	25	0.0	29.4	16.3	40.0	0.0	0.0	0.0	1.0	0.0	12.0	0.6	0.7	100.0
	Products			2.5	41.8	0.0	41.0	7.3	2.1	1.1	0.2	0.3	3.5	0.1	0.1	100.0

centration also reduces. This is likely to be related to the preferred participation of methane in chain branching reactions early in the oxidation. We previously observed that, in the oxidation of propane–butane mixtures, the absence of methane from the mixtures leads to a decrease in the oxidation rate. The same phenomenon is demonstrated by the kinetic modeling of the oxidation of methane–ethane mixtures. Our previous experiments on the oxidation of methane–ethane mixtures showed [5] a decrease in the reaction temperature and an increase in the methanol yield with an increase in the methane concentration to 30–40%, which can be interpreted as a manifestation of promotion of ethane oxidation by methane additives.

Thus, in the partial oxidation of complex mixtures of C₁–C₄ hydrocarbons at an initial oxygen concentration above 5%, there are an effective decrease in the concentration of C₂–C₄ hydrocarbons and a simultaneous increase in the methane concentration in the mixture, with carbon oxides and hydrogen being formed up to noticeable concentrations. However, in the oxidation of methane–ethane mixtures, as shown by our experimental and theoretical results, which agree well, there is mutual transformation of both hydrocarbons; therefore, their concentrations are coupled more strongly and it is difficult to achieve the preferred ethane burnout.

Thermodynamic calculations of the equilibrium composition of the products showed [8] that, in this

process, which is performed without catalysis at relatively low temperatures, the composition of the products is generally far from the thermodynamically equilibrium composition and is governed by the kinetics of the processes occurring. This is particularly obvious for the oxidation of methane–ethane mixtures with low oxygen concentration (Table 1) and, correspondingly, low heating. The products of these reactions contain noticeable concentrations of such thermally unstable

Table 3. Relative change β (%) in the concentration of individual hydrocarbons in the partial oxidation of a multicomponent mixture

Exp. no.	[O ₂] ₀ , %	Relative change β in concentration of hydrocarbons, %				
		CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	iso-C ₄ H ₁₀
1	4.0	2.4	70.0	11.1	33.3	20.0
2	4.5	0.0	65.0	8.5	61.5	20.0
3	5.5	–13.2	74.0	34.3	58.3	66.7
4	6.1	–10.0	55.5	41.2	66.7	44.4
5	7.5	–17.0	70.6	43.0	70.0	87.5
6	10.3	–19.0	86.7	40.0	77.8	57.1
7	12.6	–28.3	78.6	42.8	70.0	75.0
8	15.7	–35.4	92.3	47.8	87.5	85.7
9	16.3	–42.2	80.0	70.8	85.7	83.3

(under these conditions) oxygen-containing compounds as alcohols and aldehydes. For the oxidation of mixtures of C₁–C₄ hydrocarbons with higher oxygen concentration and heating to 640°C (Table 2), the thermodynamic calculation for the gas phase (without considering the formation of solid products) already approximately describes the yield of the main products—methane and CO. The fact that the experimental concentrations of CO₂ and hydrogen are much lower than those found by the thermodynamic calculations is mainly related to the extremely low reactivity of the water formed. At typical process temperatures in the absence of heterogeneous catalysts, the time it takes for the equilibrium concentrations of water, hydrogen, and carbon oxides to be attained is many orders of magnitude longer than the reaction time.

The beneficial effect of the formed partial oxidation products (carbon oxides, hydrogen, and oxygenates) on catalytic reforming can be an additional factor in favor of using this process as a preliminary step of steam reforming. However, this question requires further investigations.

CONCLUSIONS

(1) The simultaneous partial oxidation of C₁–C₄ hydrocarbons leads to a significant decrease in the concentration of C₂–C₄ hydrocarbons and a simultaneous increase in the methane concentration.

(2) The factor that most strongly influences the change in the relative concentrations of hydrocarbons is the initial oxygen concentration in the mixture, whereas a change in temperature has a much less strong effect and a change in pressure in the range 25–70 atm has almost no effect on this parameter.

(3) The modern level of the kinetic modeling of the oxidation of methane–ethane mixtures allows one to adequately describe the reforming of these hydrocarbons in homogeneous partial oxidation.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 03-03-32105.

NOTATION

P—pressure, atm;
T—temperature, °C;

α —ratio between methane and ethane at the inlet and the outlet of the reactor;

β —percentage change in the concentration of each of the hydrocarbons in the oxidation.

SUBSCRIPTS AND SUPERSSCRIPTS

f—final concentration of a substance;

0—inlet concentration of a substance.

REFERENCES

1. Arutyunov, V.S. and Krylov, O.V., *Okislitel'nye prevrashcheniya metana* (Oxidative Conversion of Methane), Moscow: Nauka, 1998.
2. Fal'kevich, G.S., Topchii, V.A., Kakichev, A.P., Rostanin, N.N., Vilenskii, L.M., Nemira, K.B., and Nefedov, B.K., Catalytic Processes of Conversion of Natural and Associated Gases to Motor Fuels, *Katal. Prom-sti*, 2003, no. 3, p. 10.
3. Haldor Topsoe, A.S., *Materialy seminara "Tekhnologiya proizvodstva sintez-gaza"* (Proc. Seminar on Synthesis Gas Production Technology), Moscow, 1991.
4. Arutyunov, V.S., Rudakov, V.M., Savchenko, V.I., Sheverdenkin, E.V., Sheverdenkina, O.G., and Zheltyakov, A.Yu., Partial Alkane Oxidation Kinetics at High Pressures: Methane Oxidation in Stainless Steel and Quartz Reactors, *Teor. Osn. Khim. Tekhnol.*, 2002, vol. 36, no. 5, pp. 518–522 [*Theor. Found. Chem. Eng. (Engl. Transl.)*, vol. 36, no. 5, pp. 472–476].
5. Sheverdenkin, E.V., Arutyunov, V.S., Rudakov, V.M., Savchenko, V.I., and Sokolov, O.V., Kinetics of Partial Oxidation of Alkanes at High Pressures: Oxidation of Ethane and Methane–Ethane Mixtures, *Teor. Osn. Khim. Tekhnol.*, 2004, vol. 38, no. 3, pp. 332–336 [*Theor. Found. Chem. Eng. (Engl. Transl.)*, vol. 38, no. 3, pp. 311–315].
6. Vedenev, V.I., Gol'denberg, M.Ya., Gorban', N.I., and Teitel'boim, M.A., Quantitative Model of Methane Oxidation: I. Model Description, *Kinet. Katal.*, 1988, vol. 29, no. 1, p. 7.
7. Arutyunov, V.S., Basevich, V.Ya., Vedenev, V.I., and Romanovich, L.B., Kinetic Modeling of Direct Gas-Phase Methane Oxidation to Methanol at High Pressures, *Kinet. Katal.*, 1996, vol. 37, no. 1, pp. 20–27 [*Kinet. Catal. (Engl. Transl.)*, vol. 37, no. 3, pp. 16–22].
8. Savchenko, V.I., Didenko, L.P., Sheverdenkin, E.V., *et al.*, Equilibrium Yield of Products of Steam and Oxidative Reforming of Methane Mixtures with C₂–C₃ Hydrocarbons, *Khim. Fiz.*, 2005, vol. 24, no. 8.