Dependence of the kinetics of gas phase methane oxidation at high pressures on the concentration of oxygen and on temperature

V. S. Arutyunov, V. Ya. Basevich, V. I. Vedeneev, Yu. V. Parfenov, and O. V. Sokolov*

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: +7 (095) 938 2156

A decrease of the rate of high pressure oxidation of very rich methane—oxygen mixtures with increasing oxygen concentration was found. The results were confirmed by kinetic simulation of the process. A very distinct temperature dependence of the rate of oxygen conversion can be explained on the basis of a critical change in the reaction mechanism.

Key words: methane oxidation, kinetic simulation.

Gas phase oxidation of rich methane—oxygen mixtures at high pressures evokes great interest as one of the most promising routes to natural gas conversion into valuable chemicals.[1,2] Apart from merely practical purposes, great theorethical importance attaches to the investigation of the kinetic mechanism of the process, which possesses some specific features.[2,3]

A quantitative model for the oxidation of rich methane—oxygen mixtures at high pressures and moderate temperatures was elaborated previously.[4] A supplemented version of this model was used[5] for elucidation of the process dependence on pressure, temperature, and oxygen concentration. The simulation confirmed the well known fact of a decreasing selectivity of methanol formation with increase of the concentration of oxygen.[2] Moreover, the theoretical conclusion[3,6] that at very low concentrations (≤5 %) oxygen may be regarded in certain sense as an inhibitor of the process was confirmed. The increase of its concentration leads to decrease of the rate of the reaction. Even a significant increase of temperature of the gas mixture with its adiabatic heating does not completely compensate for the inhibiting influence of oxygen. However, except for the data[7] about the lengthening of the self-ignition delay with increase of the concentration of oxygen in rich methane—oxygen mixtures at 70—80 atm, there were no other data confirming this important conclusion.

Among published experimental results on the kinetics of the oxidation of rich methane—oxygen mixtures at high pressures there exist data showing a very distinct S-shaped dependence of oxygen conversion in flow reactors on temperature.[8,9] In some experiments the transition from practically negligible to almost complete conversion took place in a very narrow temperature interval — 20—30 °C. Such a sharp transition, difficult to explain in the framework of the usual temperature dependence of chemical reactions, receives from our point of view a natural explanation on the basis of the concept of the critical dependence of the process of methane oxidation at high pressures on its parameters (p, T).[10]

Taking into account the principal importance of these issues for the understanding of the mechanism of methane oxidation at high pressures, the new experimental data concerning the dependence of oxygen conversion in a flow reactor on its concentration and temperature are presented in this study. Their theoretical interpretation on the basis of kinetic simulation of the process is given.

Experimental

Experiments were performed in a heated flow stainless steal reactor with an internal diameter of 10 mm and a length of the operating section of 100 mm (Fig. 1). A quartz liner (*5*) with an internal diameter of 7 mm was inserted in the operating section (*B*). Preliminarily heated separate flows of methane and oxygen were cofed into a narrow annular slit in section *A*, which was also located in a heated part of the reactor. In this slit the final heating and mixing of the reagents took place for a time that did not exceed 10 % of the residence time of the gases in the reactor. The range of operating pressures was up to 15 atm, and that of temperatures — up to 600 °C. The average residence time of the gas flow in the operating section of the reactor in this experimental run was 10—15 s. The output gases were quickly cooled to ~150 °C in an annular slit in section *C* by means of an opposing flow of cool air and then entered either a gas chromatograph with 5A molecular sieves and Porapack Q columns or the optical cavity of an IR FT spectrometer. Gases of "chemically pure" grade from cylinders were used in these experiments.

Results and Discussion

Figure 2 (curves *1—3*) demonstrates that increase in the oxygen concentration leads to increase in the tem-

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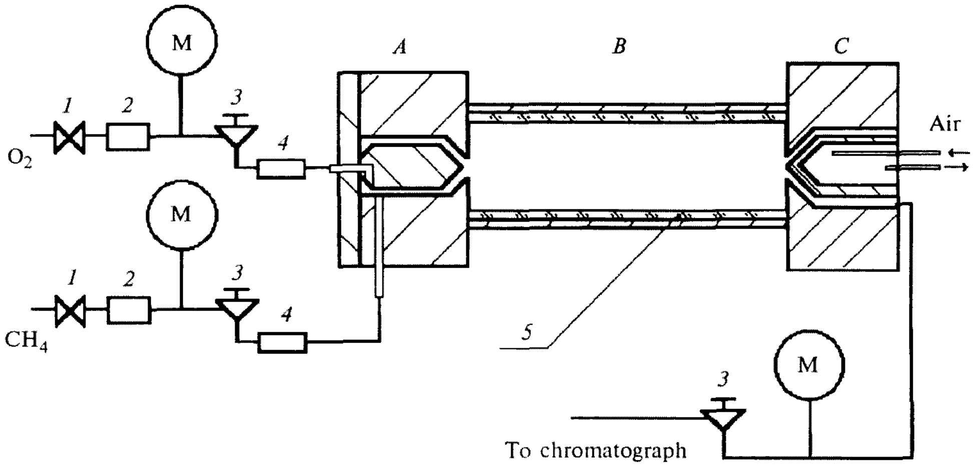

Fig. 1. Schematic presentation of the experimental setup: *A*, section of heating and mixing of reagents; *B*, operating section; *C*, section of cooling of reagents; M, manometer; *1* and *3*, locking and control valves; *2*, flow governor; *4*, check valves; *5*, quartz liner.

perature at which a high conversion of oxygen is attained, that is, to retardation of the process. As in the Refs. 8 and 9, in which experimental conditions are the most similar to this work and the results of which are also shown in Fig. 2 (curves *4*—*6*), the temperature interval between scarcely noticeable conversion and complete conversion is extremely small and does not exceed 50 °C. Unfortunately, it is difficult to obtain the concentration of oxygen for these particular curves from the presented data.[8] It is only possible to conclude that it falls in the interval between 2.5 and 4.9 %. It is also necessary to take into account that the higher temperatures for curves *5* and *6* (see Fig. 2) are due to the lower pressures in these experiments.

The temperature dependences of oxygen conversion of the type shown in Fig. 2 allow us to obtain a rough estimation of an effective energy of activation of the process (E_{eff}) in this temperature range. Figure 3 shows such estimations that were obtained based on the present study and published data[8,9] for the pressure range from 1 to 50 atm.

At pressures >10 atm this estimation leads to the values $E_{\mathrm{eff}} \approx$ 100—150 kcal mol^{-1}. The unreality of such values is confirmed by comparison with the value

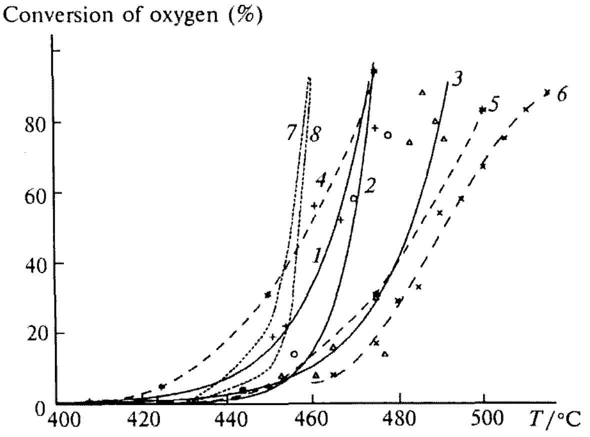

Fig. 2. Oxygen conversion *vs.* temperature with constant residence time in the reactor (τ_r). Curves *1*—*3* correspond to the results of the present study, p = 10 atm, τ_r = 11—15 s, $[O_2]_0$ (%) = 2.7 (*1*), 4.25 (*2*), 5.0 (*3*). Curves *4* and *5* correspond to the results of Ref. 8, $[O_2]_0$ = 2.5—4.9 %, p/atm = 10 (*4*), 5 (*5*). Curve *6* corresponds to the results of the Ref. 9, $[O_2]_0$ = 7 %, p = 1.5 atm. Curves 7 and *8* are calculated temperature dependences of oxygen conversion, p = 10 atm, $\tau_r \approx$ 3 s, $[O_2]_0$ (%) = 3 (*7*), 5 (*8*).

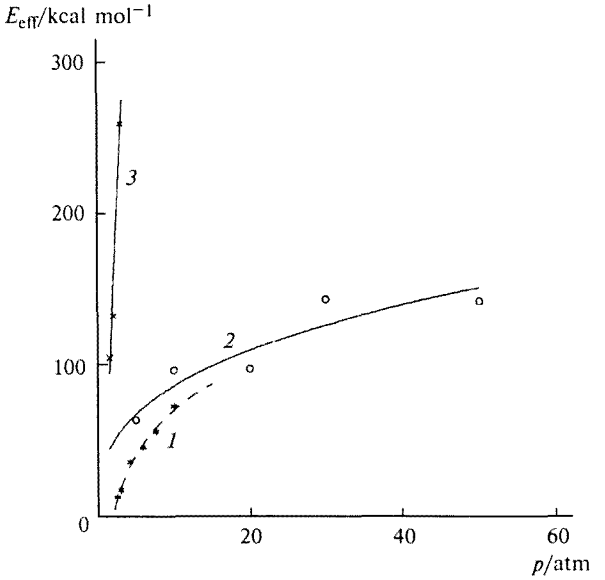

Fig. 3. Estimation of the effective activation energy (E_{eff}) of the process: *1*, results of the present study, $[O_2]_0$ = 3 %; *2*, results of the Ref. 8, $[O_2]_0$ = 2.5—4.9 %; *3*, results of the Ref. 9, $[O_2]_0$ = 7 %.

E_{eff} = 39—45 kcal mol^{-1}, which was obtained experimentally from the temperature dependence of self-ignition delays,[7] as well as with the value $E_{eff} \approx 40$ kcal mol^{-1} that was obtained from kinetic simulation.[5] A natural explanation of such high values of E_{eff} may be given in a framework of the concept of the existence of a critical transition between two stationary regimes of the oxidation with rates that differ by three or four orders of magnitude.[10] This critical transition takes place at either the change in the pressure or in temperature, because the increase in the temperature decreases the pressure of the critical transition.[10]

The decrease in the value of E_{eff} with pressure decrease is, probably, caused by the significant increase in the role of heterogeneous processes at $p < 10$ atm. This suggestion is confirmed by simple estimations of the diffusion rate of intermediate products to the walls of the reactor. Our results are in a good agreement with the data of Ref. 8 that was carried out under very similar conditions and in an overlapping pressure range. Considerable overestimations of E_{eff} that were obtained using the data of other study[9] may be explained by a higher concentration of oxygen (7 %) in these experiments. Under this concentration of oxygen the autoacceleration of the process due to the release of the heat of reaction becomes significant, this leads to a more sharp temperature dependence.

Our experimental data were compared with the results of kinetic simulation of the process.[5] Figure 2 shows experimental temperature dependences of the conversion of oxygen and the corresponding calculated curves, which have practically the same shape. The shorter time of conversion obtained from simulation is likely due to insufficient exactitude in taking into account the heterogeneous processes in the model.[5] These processes play a more important role under the conditions of the present study. But we did not change the parameters of the model to obtain a better fit for the time of the process.

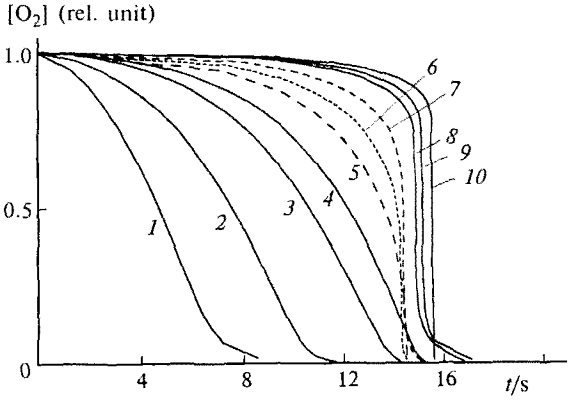

Fig. 4. Calculated kinetics of oxygen conversion (in relative units) with different initial oxygen contents in the mixture: $[O_2]_0$ (%) = 0.5 (*1*), 1 (*2*), 2 (*3*), 3 (*4*), 5 (*5*), 7 (*6*), 10 (*7*), 15 (*8*), 17 (*9*), 20 (*10*); T = 693 K, p = 10 atm.

The calculation of the kinetics of the change of the relative concentration of oxygen (Fig. 4) and the values of the time of conversion obtained on the basis of this calculation (Fig. 5) show that, as in the experiments described above,[7] the induction period of the process which may be defined as the time of conversion of 5 % of the oxygen in the mixture, monotonically increases with increase of the concentration of oxygen (see Fig. 5, curve *1*). The same monotonic dependence is found for the time of conversion of 50 % of the oxygen, although its rise proceeds somewhat slowly, and curve *2* in Fig. 5 gradually converges with curve *1* for the induction period. However, the time of complete conversion (95 % O_2) increases only when the concentration of oxygen increases to 3—4 %. Sufficient spontaneous heating of the mixture at higher oxygen concentrations leads to thermal autoacceleration of the process with increase of the conversion of reagents. Therefore the complete time of the reaction begins to decrease and at $[O_2]_0$ = 10 % practically coincides with the time of 50 % conversion of oxygen. Such extreme dependence of the duration of complete conversion of oxygen on its concentration illustrates well the increase of temperature of complete oxygen conversion experimentally observed by us with increase in its content from 2.7 to 5 % and the decrease of this temperature with change of O_2 concentration from 7 to 20 %, mentioned earlier.[9]

Simulation shows that at higher oxygen concentrations (15—17 %) after the consumption of 90 % O_2, which is accompanied by heating of the mixture to 700—900 °C, a sharp decrease of the rate of its consumption takes place (see Fig. 4). The second maximum on the curve of the dependence of the time of 95 % O_2 consumption corresponds to this phenomena (see Fig. 5). It is a well-known phenomenon of the

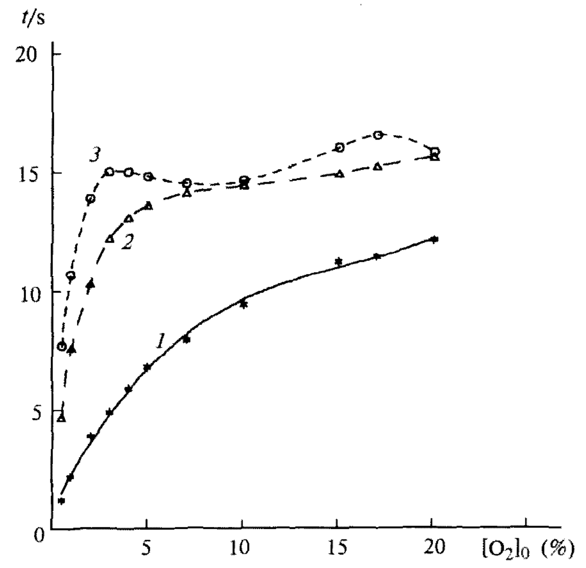

Fig. 5. Calculated time of 5 % (*1*), 50 % (*2*), and 95 % (*3*) conversion of oxygen in the mixture; T = 693 K, p = 10 atm.

negative temperature coefficient of the reaction rate (NTC) of the oxidation of hydrocarbons[11] including methane.[12] In our calculations the NTC region was obtained at higher temperatures, and it has a more extended temperature interval than the NTC region that was revealed experimentally for methane[12] in the region of ~600 °C. Apparently, this discrepancy is due to shortcomings of the model used to describe this phenomenon. Thus, the second maximum in the dependence of the time of 95 % O_2 consumption on its concentration caused by NTC actually should appear at lower oxygen concentrations. It cannot be excluded that it merges with the first maximum.

The known facts of permanent registration of the residual oxygen concentration (at a level of 5 % $[O_2]_0$) in the products of the reaction even if the residence time in the reactor is much higher then the characteristic time of the process[13] can be regarded as an additional argument in support of the real influence of the calculated effect of the retardation of the rate of the running process on the kinetics of oxidation of rich methane—oxygen mixtures at high pressures. The effect of the retardation of the process before the completion of the reaction obtained from simulations disappears at $[O_2]_0 \geq 20$ %.

The monotonic increase of the induction period (time of conversion of 5 % O_2) was observed at the simulation of the reaction in the whole range of pressures from 1 to 100 atm. Despite the fact that at high pressures (10—100 atm) and at $[O_2]_0 \leq 3$ % the time of complete conversion (95 % O_2) increases, this time, on the contrary, decreases with the increase of oxygen concentration at atmospheric pressure.

One more peculiarity of gas phase oxidation of rich methane—oxygen mixtures that was noted on the basis of the results of kinetic simulation[3,4] and was recently confirmed experimentally[9] should be noteworthy. Methanol and formaldehyde are formed in this process by different pathways, with the rate of formaldehyde formation being even somewhat higher than that of methanol. It leads to the fact that at the initial stage of the process (conversion of CH_4 <1 %) the selectivity of formaldehyde formation (54 %) exceeds the selectivity of methanol formation (46 %) (see Ref. 9 and Fig. 2 in this work). Due to a higher chemical stability of methanol in subsequent oxidation processes it appears as a predominant product of the reaction at higher conversion of the reagents.

Comparison of the experimental data and the results of simulation of the process of homogeneous oxidation of rich methane—oxygen mixtures at high pressures performed in this study confirmed the fruitfulness of kinetic simulation for analysis and complete interpretation of the experimental results and for understanding the peculiarities of the mechanism of this process.

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