MECHANISM OF THE COMBUSTION OF METHANE

COMMUNICATION 2. THE "ONE-DIMENSIONAL" ATOMIC FLAME


The elucidation of the mechanism of the high-temperature oxidation of methane is of great theoretical and practical interest. Studies are known [1, 2] in which a mechanism has been proposed for the combustion of methane and kinetic calculations have been compared with the experimental results. On account of the complexity of the mechanism of the combustion of methane and the insufficient study of the rates of individual elementary reactions, it is important that comparisons of this kind for the suggested reaction schemes be performed on the broadest and most varied possible experimental material.

In our work [3]* a mechanism of the combustion of methane with the participation of 17 particles, including 86 elementary reactions, was proposed. It was verified on the basis of a comparison of the calculated ignition lag and those known from the literature according to experiments of shock tubes and in a flow for methane and hydrogen (the mechanism of oxidation of the latter is included as a component in the mechanism of the oxidation of methane). In addition, we compared the calculated kinetic curves of the burnout of methane and the appearance of the reaction product – H₂O, CO, and CO₂ – with the experimental curves, obtained in a shock tube [4]. Unfortunately, there were no other experimental data on high-temperature kinetics at a high degree of conversion at that time. Therefore, subsequently to obtain the necessary information on the mechanism of the combustion of methane, we used the method of atomic flames. As is well known, atomic flames fully correspond to the usual flames (monotypic reaction products, spectral characteristics, etc.), but as a result of the high initial concentration of oxygen atoms, the temperature region with a sufficiently high degree of conversion is lower here and supplements the temperature region of the shock tube.

EXPERIMENTAL METHOD

The apparatus for the production of atomic flames is presented in Fig. 1. In the first experiments we used a scheme of a "coaxial" atomic flame with delivery of methane along the central tube (7 mm diameter) and partially dissociated oxygen along a heated outer tube (22 mm diameter) [5]. In this case, on a large portion of the length of the reactor, the influence of mixing of the central and outer flows was substantial. Later, in the scheme of a "one-dimensional" flame, methane was delivered along a system of 37 quartz capillaries (1 mm diameter), uniformly arranged along the cross-section of the reactor. As a result of such delivery, mixing occupies a small portion of the length of the reactor (only 3-5 mm). The use of section-by-section regulated heating of the reactor permitted maintenance of a practically constant temperature along its entire length. To reduce axial concentration gradients, the rate of flow in the reactor was maintained high (tens of meters per second). A thermocouple combined with a gas collector could be moved along the axis of the reactor. Stable products – CH₄, H₂, CO, and CO₂ – were analyzed chromatographically. The EPR method was used to determine the concentration of oxygen atoms, and the recombination of atoms in the gas collector was taken into consideration: recording was performed at different rates of suctioning of the gas (ν) out into the resonator, and an extrapolation was made to an infinitely high rate (1/ν = 0).

* Communication 1 of this series.
TABLE 1. Experimental and Calculated Composition of Products of the Atomic Flame

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>CH₄, %</th>
<th>C₂H₆, %</th>
<th>T, °C</th>
<th>Contents, %</th>
<th>CH₄, H₂, CO, CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>8,1</td>
<td>735-980</td>
<td>2</td>
<td>0,45, 0,03, 0,28, 0,33</td>
</tr>
<tr>
<td>2</td>
<td>10,4</td>
<td>4,1</td>
<td></td>
<td>765</td>
<td>0,38, 0,16, 0,29, 0,36</td>
</tr>
<tr>
<td>3</td>
<td>10,4</td>
<td>4,1</td>
<td></td>
<td>765</td>
<td>0,38, 0,16, 0,29, 0,36</td>
</tr>
<tr>
<td>4</td>
<td>10,4</td>
<td>4,1</td>
<td></td>
<td>765</td>
<td>0,38, 0,16, 0,29, 0,36</td>
</tr>
<tr>
<td>5</td>
<td>2,5</td>
<td>2,3</td>
<td></td>
<td>765</td>
<td>0,38, 0,16, 0,29, 0,36</td>
</tr>
<tr>
<td>6</td>
<td>2,5</td>
<td>2,3</td>
<td></td>
<td>765</td>
<td>0,38, 0,16, 0,29, 0,36</td>
</tr>
<tr>
<td>7</td>
<td>2,3</td>
<td>3,05</td>
<td>3,5</td>
<td>765</td>
<td>0,38, 0,16, 0,29, 0,36</td>
</tr>
<tr>
<td>8</td>
<td>2,3</td>
<td>2,05</td>
<td>4,3</td>
<td>765</td>
<td>0,38, 0,16, 0,29, 0,36</td>
</tr>
</tbody>
</table>

The results of experiments on the composition of the products at the end of the reactor are cited in Table 1. Here also are cited the experimental conditions and the reaction time τ. All the experiments were conducted at a pressure of 7.5 mm. In experiment 1, the scheme of a "coaxial" flame was used, and in the remaining experiments the scheme of a "one-dimensional" flame. As an example, in the case of experiment 8, Fig. 2 indicates the data on the length of the reactor by points.

In the course of the experiment it was discovered that CO₂ may appear in appreciable amounts under conditions when there is practically no consumption of artificially introduced additions of CO to the methane (as well as propane, propylene). Consequently, there is a pathway of appearance of CO₂, bypassing the step of formation of CO, which was also noted earlier by other authors under different conditions [6, 7].

DISCUSSION OF RESULTS

Method of Calculation. For the calculation we used a somewhat modified standard program [8], permitting integration of a system of kinetic differential equations of the type

\[
\frac{dx_i}{dt} = \sum_{l, j, s} k_{ljs} x_l x_j x_s - \sum_{l, j, s} k_{ljs} x_l x_j x_s; \quad x_i(0) = x_{i0},
\]

where \( x \) is the concentration (here \( l = 1, 2, \ldots, 17 \), \( k_{ljs} \geq 0 \) represents the kinetic constants of the reaction rates. In this work the system of equations is solved according to an implicit scheme of the type

\[
x^{i+1} = x^i + \frac{h}{i, j, s} k_{ljs} x^i x^{j+1} x^{s+1} \quad \text{for system (1) scheme (2) takes the form}
\]

\[
\frac{x^{i+1} - x^i}{h} = \sum_{l, j, s} k_{ljs} x^i x^{j+1} x^{s+1} - \sum_{l, j, s} k_{ljs} x^i x^{j+1} x^{s+1}.
\]

The solution of the differential scheme (3) is found with the aid of the iterations

\[
\frac{x^{n+1} - x^n}{h} = \sum_{l, j, s} k_{ljs} x^i x^{j+1} x^{s+1} - \sum_{l, j, s} k_{ljs} x^i x^{j+1} x^{s+1},
\]

where \( x = x(\tau) = [x_1(\tau), x_2(\tau), \ldots, x_n(\tau)] \) is a vector, the components of which \( x_l(\tau) \) are the values of the concentrations at the moment of time \( \tau \) \( x^i \) is the vector of the concentrations at some moment of time \( \tau_0 \); \( x^i \) is the vector of the concentration at the moment of time \( \tau_0 + h \).

For system (1) scheme (4) takes the form

\[
\frac{x^{i+1} - x^i}{h} = \sum_{l, j, s} k_{ljs} x^i x^{j+1} x^{s+1} = \sum_{l, j, s} k_{ljs} x^i x^{j+1} x^{s+1}.
\]

The solution of the differential scheme (3) is found with the aid of the iterations

\[
\frac{x^{n+1} - x^n}{h} = \sum_{l, j, s} k_{ljs} x^i x^{j+1} x^{s+1} = \sum_{l, j, s} k_{ljs} x^i x^{j+1} x^{s+1},
\]