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Abstract

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ON THE MECHANISM OF HIGH-TEMPERATURE OXIDATION OF METHANE IN SHOCK WAVES

Earlier (^{1}) we considered the scheme of self-ignition of a hydrogen-oxygen mixture in shock waves and showed that, from experimental data on the dependence of ignition delays on temperature, one can reveal certain characteristic features of the mechanism of the process—the existence of a "leading" reaction in the high-temperature region and the appearance, upon transition to a lower temperature, of a limit associated with the termination of branched chains in the volume. The ignition scheme of a methane-oxygen mixture is more complex and has been studied in detail only at temperatures below 800° K, where, as is known (^{2,3}), the reaction has the character of so-called degenerate branching (through formaldehyde). The experimental data now available on ignition delays in the temperature range from 800 to 2800° K are rather contradictory. Thus, according to (^{4}), in methane-air mixtures there is a break in the experimental curve in coordinates $\lg\tau - 1/T$ at $T \sim 1600°$ K, corresponding to a transition from an activation energy $\varepsilon \sim 26$ kcal/mole at higher temperatures to $\varepsilon \sim 85$ kcal/mole in the low-temperature region. In work (^{5}), on the contrary, a transition was observed from $\varepsilon \sim 53$ kcal/mole to $\varepsilon \sim 20$ kcal/mole, respectively, in approximately the same temperature region. In experiments (^{6}) for $T = 1800$-$2500°$ K the activation energy is estimated at about 33 kcal/mole. Finally, in a recent work (^{7}) it was also found that $\varepsilon = 33.8$ kcal/mole at $T = 1050$-$2100°$ K for the induction period of the reaction as a whole, and $\varepsilon' = 21.5$ kcal/mole for the delay in the appearance of hydroxyl. Analysis of the data obtained is usually limited to comparison with the low-temperature mechanism. Only in (^{6}) was an attempt made to introduce branching through $\mathrm{H} + \mathrm{O}_2 \rightarrow \mathrm{OH} + \mathrm{O}$ ($\varepsilon = 16 \div 18$ kcal/mole), which does not correspond to the activation energy of the process found there.

Considering Schlieren photographs of the self-ignition process of methane-oxygen mixtures (see Figs. 1, 2), it is not difficult to notice an analogy with the ignition of hydrogen-oxygen mixtures (^{1}). Here too the explosive character of the development of the reaction in the high-temperature region is clearly ex-

Fig. 3

Figure 1: Fig. 3

pressed (Fig. 1), as is the "soft" process (of the "laminar" flame type) upon transition to temperatures below 1100-1200° K (Fig. 2). The region of transition from one regime to the other in a stoichiometric mixture depends very little on the nature of the diluent. Figure 3 shows data on ignition delays behind the reflected wave for the pure mixture and for mixtures diluted with argon and helium (all data are reduced to the pressure of the pure mixture $p = 2 \pm 0.4$ atm). Part of the experiments was carried out in a bypass tube "cutting out" the central part of the flow, by cross section, behind the incident wave–in order to exclude interaction of the reflected shock wave with the boundary layer. As is seen from Fig. 3, the results of these experiments practically coincide with the results obtained by the method of the usual shock tube.

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Fig. 1. *a* –sweep and oscillogram of the pressure and gas luminosity ($\lambda = 3064$ Å, $\Delta\lambda = 25$ Å) upon ignition of a mixture
$0.8\,\mathrm{Ar} + 0.2\,(\mathrm{CH_2} + 2\mathrm{O_2})$.
b –sweep of the process in the mixture
$0.8\,\mathrm{He} + 0.2\,(\mathrm{CH_4} + 2\mathrm{O_2})$

Fig. 2. Sweep of the process in the mixture $0.7\,\mathrm{He} + 0.2\,(\mathrm{CH_4} + 2\mathrm{O_2})$ with a large delay

For comparison with the data of work (7), a series of experiments was carried out in which, simultaneously with streak photography and recording of the pressure of the process, photometry was performed of the intrinsic emission of the compressed mixture in the hydroxyl emission region ($\lambda = 3064$ Å). In these experiments, the gas layers near the end wall were focused onto the entrance slit of a quartz monochromator, i.e., precisely the region where ignition kernels originate. The oscillogram of the emission is shown in Fig. 1a. The onset of ignition was identified with the first appearance of the recorded luminous flux, and not with the emission maximum. The data on measurements of ignition delays by this method are also given in Fig. 3. Within the scatter of the experiments they practically do not differ from the measurements from streak photographs, i.e., the change in effective activation energy observed in (7) was not found in our experiments.

In the temperature range 1250-2500° K there is a linear dependence of $\lg \tau$ on the reciprocal temperature, corresponding to an activation energy of 33 ± 1.7 kcal/mole. It should only be noted that, when the mixture is diluted with 80% helium, the rate constant increases by approximately an order of magnitude in comparison with dilution of the pure mixture with argon. At temperatures below 1200° K, a relatively sharp drop in the reaction rate is observed, down to delays greater than 10^{-3} sec (the limiting observation time in the apparatus).

Fig. 3. Dependence of ignition delays on temperature at reduced pressure $p = 2$ atm.
1 –pure mixture of stoichiometric composition; 2 –mixture $0.8\text{Ar} + 0.2(\text{CH}_4 + 2\text{O}_2)$; 3 –same, in the outlet tube; 4 –mixture $0.9\text{Ar} + 0.1(\text{CH}_4 + 2\text{O}_2)$; 5 –mixture $0.8\text{He} + 0.2(\text{CH}_4 + 2\text{O}_2)$; 6 –mixture $0.8\text{Ar} + 0.2(\text{CH}_4 + \text{CH}_4 + 2\text{O}_2)$, delay determined from emission.

The qualitative analogy noted above with the mixture $\text{H}_2 + \text{O}_2$ and the quantitative results of the experiments on ignition delays make it possible to suggest that in the temperature region 1250–2500° K we have throughout a branched chain with an activation energy of the principal branching process close to 33 kcal/mole. "Competition" with such a process is possible only in the region of lower temperatures, where the reaction mechanism may change and the development of ignition may proceed, for example, along the path of pronounced branching. Let us emphasize once again that the authors of previously published investigations on this question tried to explain the results they obtained precisely from the standpoint of pronounced branching, which caused difficulties in explaining the experimental data (^{5}, ^{7}).

The possibility of the existence of a leading reaction in the form of a fully branched chain for hydrocarbons in the high-temperature region was noted in work (^{8}): $\text{R} + \text{O}_2 \rightarrow \text{RO} + \text{O}$ followed by $\text{O} + \text{RH} \rightarrow \text{R} + \text{OH}$, i.e., the gross reaction according to the scheme

$$\text{R} + \text{O}_2 + \text{RH} \rightarrow \text{RO} + \text{OH} + \text{R},$$

according to which, in addition to reproduction of the initial radical, two new ones are formed.

As applied to methane oxidation, this will mean that in the temperature range of interest to us the branching scheme can be written in the form:

$$(0) \quad \text{CH}_4 + \text{O}_2 \rightarrow \text{CH}_3 + \text{HO}_2 \qquad \text{initiation}$$

$$\left.\begin{array}{ll}(1) & \text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{O} \\ (2) & \text{O} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{OH}\end{array}\right\} \quad \text{branching}$$

$$(3) \quad \text{CH}_3\text{O} + \text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{CH}_3 \qquad \text{etc.}$$

Thus, instead of the branching scheme

$$\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{OH}$$

and

$$CH_2O + O_2 \rightarrow HCO + H_2O \qquad \text{(branching)},$$

which operates at not too high a temperature, we introduce into consideration process (1), which leads to an entirely branched mechanism.

Since the R—O bond is weaker than H—O, the activation energy of process (1) must be higher than 18 kcal/mole—the activation energy of the leading reaction of hydrogen oxidation:

$$H + O_2 \rightarrow OH + O.$$

Knowing the energy of formation of CH_3O (^{3}): $\Delta H = 0.5 \pm 2$ kcal and $\Delta H = -100 \pm 1$ kcal for $CH_3OH \rightarrow CH_3O + H$, we obtain $Q_1 = 27 \pm 3$ kcal. Thus, the expected activation energy of process (1), which may be several kcal/mole greater than Q_1, apparently is in acceptable agreement with the experimental data on ignition delays presented in Fig. 3.

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REFERENCES

1. V. V. Voevodskii, R. I. Soloukhin, DAN, **154**, No. 6, 1425 (1964).
2. N. S. Enikolopyan, VII Symp. Intern. Combustion, London, 1959, p. 157.
3. N. N. Semenov, *On Certain Problems of Chemical Kinetics and Reactivity*, Izd. AN SSSR, 1958, p. 582.
4. A. A. Borisov, S. M. Kogarko, A. V. Lyubimov, DAN, **149**, No. 4, 869 (1963).
5. T. Asaba, K. Yoneda et al., X Symp. Intern. Combustion, N. Y., London, 1963, p. 193.
6. G. B. Kistiakowsky, L. W. Richards, J. Chem. Phys., **36**, 7, 1707 (1962).
7. H. Miyama, T. Takeyama, J. Chem. Phys., **40**, 7, 2049 (1964).
8. V. V. Voevodskii, V. N. Kondrat' ev, Uspekhi khimii, **19**, 6, 680 (1950).

Note: Figure translations are in progress. See original paper for figures.