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Effect of superadiabatic temperatures in the autoignition of dimethyl ether mixtures

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By numerical methods, it is shown that, under constant pressure and conditions of adiabatic autoignition of rich dimethyl ether–air mixtures, superadiabatic temperatures are attained at the expense of kinetic competition of chemical reactions.

The superadiabatic temperature (SAT) commonly implies the phenomenon observed in combustion processes for which in the zone of chemical transformations the temperature is attained, which is superequilibrium for the given system and conditions. This effect is of interest, first, from the viewpoint of the chemical physics of the interaction mechanisms of elementary processes that cause SAT. Usually in combustion processes, this is a competition between the processes of molecular diffusion and thermal diffusivity, selective diffusion of fuel and oxidant, heat transfer in two-phase systems, *etc.*[1] Second, the effect is interesting from the viewpoint of its applications.

The SAT effect is observed in the flames of rich hydrocarbon mixtures.[2,3] Rozlovskii[3] paid attention to the formation of superequilibrium water concentrations and drew a conclusion on the SAT origin determined by molecular hydrogen diffusion from the high-temperature to the low-temperature zone. It was then demonstrated that H atom rather than molecular hydrogen can play a significant role in the formation of SAT.[4,5] Therefore, the question arises of the feasible appearance of SAT in the absence of diffusion and temperature gradients upon, *e.g.*, autoignition.

In this work, numerical methods were used to study the adiabatic autoignition of rich dimethyl ether–air mixtures at constant pressure. Dimethyl ether (DME) was chosen as a fuel because the flame of rich DME–air mixtures exhibits a considerable superadiabatic temperature effect.[6] The studies were performed by numerical methods using programs[7,8] and a kinetic scheme.[9] We used a 30% DME–air mixture ($\varphi = 6.12$), initial temperature $T_0 = 600$ K, and pressure $P = 0.1$ MPa. Concentrations are given in either volume percents or molar fractions. The concentration of 30% DME corresponds to the mixtures being beyond the flammability limits (26.7%), *i.e.*, within the area of cold flames.[10]

Figure 1 plots temperature *versus* time for the process of autoignition, which is observed to occur in two stages. At the end of the first stage, the temperature is 840 K. The first maximum in the time dependence of hydroxyl OH is reached in 0.13 s. After a short period of time (~ 0.04 s), the second peak of the reaction is recorded. In this case, OH concentration also exhibits its maximum. At the end of the second stage, the temperature is 1351.8 K and remains highest over the entire process. This temperature exceeds by 362.2 K the equilibrium value. Between the maxima, the hydroxyl concentration tends to zero. The character of hydroxyl peaks indicates that they are caused by chain-thermal explosion. A two-stage character of autoignition is observed at initial temperatures varying from 520 to 900 K. In this temperature range, the first stage stops almost at a constant temperature of 840 K. The time interval

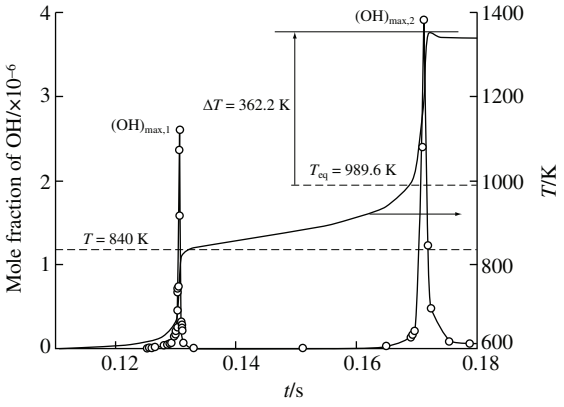

Figure 1 The time dependence of OH concentration and temperature upon adiabatic autoignition of a 30% DME–air mixture. $T_0 = 600$ K, $P_0 = \text{const} = 0.1$ MPa.

between OH maxima is almost independent of initial temperature and amounts to 0.04 s. At higher initial temperatures, the first stage degenerates.

Figure 2 shows the temperature dependence of H_2O, H_2, CO and CO_2 concentrations, normalized to equilibrium values (in molar fractions), during autoignition. Of interest are some peculiarities of concentration dynamics. First, there is a fast increase in water concentrations (direction represented by an arrow) that reach anomalously high values. The equilibrium value of H_2O is reached already at $T = 710$ K. At $T_{eq} = 989.6$ K, the water concentration is three times as high as the equilibrium

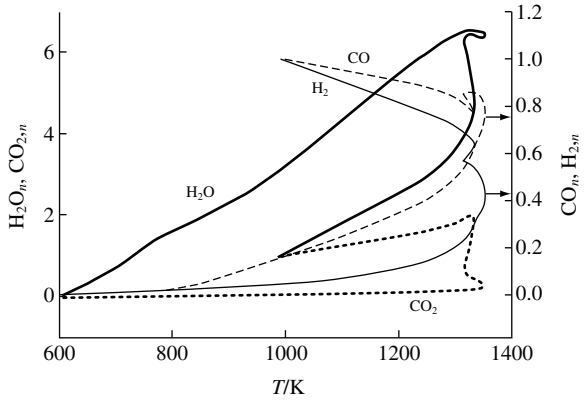

Figure 2 The temperature dependence of H_2O, H_2, CO and CO_2 concentrations normalized to equilibrium values during autoignition. The 30% DME–air mixture. $T_0 = 600$ K, $P_0 = \text{const} = 0.1$ MPa.

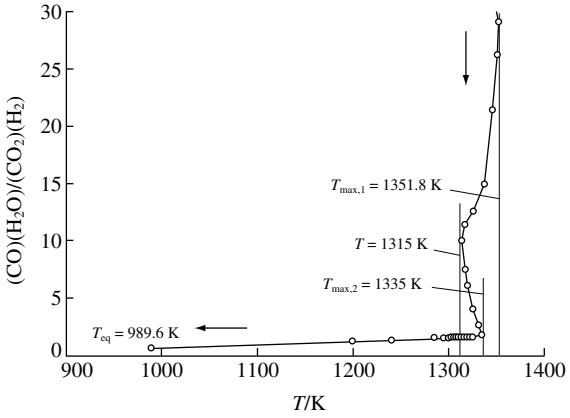

Figure 3 The temperature dependence of $(CO)(H_2O)/(CO_2)(H_2)$ ratio upon system passage from maximum temperature to equilibrium.

value. At a maximal temperature, it exceeds this value by a factor of about 6. On the contrary, the concentration of CO_2 remains almost unchanged (direction represented by an arrow) up to the first temperature peak $T_{max,1} = 1351.8$ K. At this temperature, the CO and CO_2 concentrations fail to reach their equilibrium values: the normalized value of CO concentration is 0.76 and that of CO_2 is 0.25.

Below $T_{max,1}$, a deep drop in water concentration is observed in a narrow temperature range (about 50 K). In this range, the concentration of CO_2 exceeds almost twice the equilibrium values. In addition, within this temperature range, we observed the second maximum $T_{max,2} = 1335$ K. The CO and H_2 concentrations increase continuously up to the point of equilibrium (except for a negligible drop of CO within 1335–1315 K). Note that the maximum $(CO_2)_{max}$ concentration corresponds to the maximum temperature $T_{max,2} = 1335$ K, and the maximum concentrations of $(H_2)_{max}$ and $(CO)_{max}$ correspond to the equilibrium temperature $T = 989.6$ K. In the final stage, at $T < 1335$ K a change in the basic components of products follows the equilibrium reaction of water vapour (Figure 3)

$$CO + H_2O = CO_2 + H_2,$$

which involves the elementary processes

$$CO_2 + H \leftrightarrow CO + OH$$
$$H_2O + H \leftrightarrow H_2 + OH.$$

As mentioned above, the superequilibrum water is formed already at the early stages of the process at low temperatures. It is assumed then that the following reactions can be of importance for water formation:

$$H + O_2 + M \longrightarrow HO_2 + M$$
$$H + HO_2 \longrightarrow 2OH$$
$$OH + MeOMe \longrightarrow H_2O + MeOCH_2$$
$$HO_2 + CO \longrightarrow OH + CO_2.$$

Similarly, it is shown[4] that hydrogen atom diffusion to the low-temperature zone of the propane flame front leads to water formation at low temperatures. In this case, the main reaction of H_2O formation is

$$C_3H_8 + OH \longrightarrow H_2O + C_3H_7.$$

No diffusion processes exist under conditions of adiabatic autoignition. Thus, superadiabatic temperatures can also develop in the absence of diffusion *via* kinetic competition of elementary chemical processes. In our case, this is the competition for lacking oxygen between the fast reactions of H_2O formation and the slow reactions of CO and CO_2 formation. As a result, the high superequilibrium water and low carbon oxides concentrations are observed. Indeed, the thermal effect of two water moles formation, 483.64 kJ, gives more heat than that of one CO_2 mole formation (the thermal effect of one mole formation is 393.51 kJ) and especially, of two CO moles formation (the thermal effect of two moles formation is 220.04 kJ).[11] Note that a practical coincidence of $(OH)_{max,2}$, $(H_2O)_{max}$ and T_{max} in time (Figure 1) indicates that the achievement of the maximum values of temperature and concentrations of water is caused by fast chain-branching reactions in chain-thermal inflammation involving H, OH and O radicals.

Thus, a general reason for SAT is, in our opinion, a kinetic competition of some groups of fast exothermal and slow (not necessarily exothermal) reactions for the lacking main agent, represented, in rich hydrocarbon–air mixtures, by oxygen. The competing reactions, in this case, are the reactions of carbon and hydrogen oxidation. In lean hydrocarbon–air mixtures, the amount of oxygen is sufficed to completely oxidize both carbon and hydrogen. As a result, there is no SAT. The same holds for rich and lean hydrogen–air mixtures. In this case, no competition exists and, consequently, no SAT.

The peculiarity of the SAT phenomenon in hydrocarbon flames lies in the chemical reactions running under concentration and temperature gradient conditions, which makes the interpretation of this phenomenon difficult to perform. However, taking into account the fact that the basic kinetic regularities of autoignition are usually reproduced in the flame of the same mixtures, the SAT is assumed to result mainly from the above competition between fast and slow reactions. The physical processes of heat and mass exchange play an important but minor role.

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