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Distribution of O atoms from CH_2O molecules in the combustion products of formaldehyde

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The distribution of O atoms from formaldehyde molecules in the combustion products of CH_2O/air flames was estimated using the method of labeled atoms in a numerical modeling.

Formaldehyde is the most reactive organic compound, which is used as an important reagent in chemical industry. In the production of formalin, reagents and reaction products such as methanol, formaldehyde and hydrogen in mixtures with air or oxygen are explosive. Therefore, a study of formaldehyde combustion is an important problem.

According to Walker,[1] lean and rich concentration flammability limits for CH_2O/air mixtures are 7 and 72%, respectively. Previuosly, the following concentration flammability limits at 383 K and 0.1 MPa were reported:[2] 6.5 and ~75 vol% (method of far extrapolation of linear dependence of a rich limit on nitrogen additives). These data demonstrate that concentration flammability limits for CH_2O/air mixtures are wide and comparable with those for H_2/air mixtures. Considering that a stoichiometric CH_2O/air mixture contains 17.36% formaldehyde, one can foresee the occurrence of rich flames with a low speed in a wide range of equivalence ratios.

The aim of this work was to numerically characterize formaldehyde transformation in flames with various equivalence ratios.

The speed and structure of freely-propagating planar CH_2O/air flames was simulated using CHEMKIN II[3,4] and a detailed kinetic mechanism[5] including 93 elementary reactions involving 21 species. The computation domain was 38 cm.

In a rich formaldehyde/air flame, the released heat is limited by available molecular oxygen in a combustible mixture. Presumably, formation in the flame CO with oxygen atoms from formaldehyde molecules does not result in heat release. Therefore, understanding the combustion mechanism of CH_2O under lean, stoichiometric and rich conditions is of importance. In particular it is important to reveal the pathways of O transfer from CH_2O molecules to the combustion products. The method of labeled atoms in a numerical modeling[6,7] is effective for solving such a problem. It is enough to label O atoms in formaldehyde molecules to discover in which products and in what amounts it will be found.

The speed and structure were computed for $CH_2O^*/O_2/N_2$ mixtures. Therefore, the reaction scheme[5] was modified. The mechanism was updated with new flame species which appeared as the result of the introduction of labeled O atoms in CH_2O molecules. The modification of the mechanism led to a significant increase in the number of reactions up to 333 involving 36 species instead of 89 steps involving 19 components (reactions involving argon and helium as the third bodies were not considered). Let us take chain-branching reaction as an example

$$H + O_2 = O + OH. \quad (1)$$

The presence of labeled O* atoms in formaldehyde results in the following steps:

$$H + OO^* = O^* + OH, \quad (2)$$

$$H + OO^* = O + O^*H, \quad (3)$$

$$H + O_2^* = O^* + O^*H. \quad (4)$$

The rate constants of steps (1) and (4) are the same because the molecules O_2 and O_2^* are symmetrical. The rate constants of steps (2) and (3) should be halved as these reactions have the same reactants but different products formed with equal probabilities. A decrease in the rate constants of steps (2) and (3) is explained by a reduction of the symmetry of OO* molecules in comparison with OO and O*O*.

In the software package,[3,4] the rate constants of reverse reactions are calculated from the equilibrium constants of the reactions

$$K_{pi} = \exp\left(\frac{\Delta S_i}{R} - \frac{\Delta H_i}{RT}\right).$$

Here, ΔS_i and ΔH_i are the entropy and enthalpy changes in the ith reaction, respectively. The entropy and enthalpy of the component k are calculated by the formulas

$$\frac{S_k}{R} = a_{1k}\lg T + a_{2k}T + a_{3k}\frac{T^2}{2} + a_{4k}\frac{T^3}{3} + a_{5k}\frac{T^4}{4} + a_{7k}.$$

$$\frac{H_k}{RT} = a_{1k} + a_{2k}\frac{T}{2} + a_{3k}\frac{T^2}{3} + a_{4k}\frac{T^3}{4} + a_{5k}\frac{T^4}{5} + \frac{a_{6k}}{T}.$$

Coefficients a_{jk} for two temperature ranges are given in the thermochemical database of the used mechanism (totally, 14 values for each species). Note that a change in the symmetry values of molecules containing the labeled atom results in a change in rotational statistic sum and, therefore, in the molecule entropy. As the rotational statistic sum is inversely proportional to the symmetry value of a molecule,[8] for calculation value S_k/R of a labeled molecule, coefficient a_{7k} should be increased for the value of $\ln(\sigma/\sigma^*)$, where σ and σ^* are the symmetry values of unlabelled and labeled molecules, respectively.

Figure 1 shows the calculated speed of CH_2O/air flames *vs.* formaldehyde concentration in the unburnt gases. The maximal flame speed was observed at a CH_2O concentration of 24 vol%, while the stoichiometry corresponds to 17.36 vol%; *i.e.*, a maximal speed was reached under sufficiently rich conditions. Considering the rich concentration flammability limit of a CH_2O/air mixture (75 vol% CH_2O), we can propose that there is a wide range of rich conditions where a low flame speed is observed. It is reasonable to suggest that, in this range, the flames propagate due to superadiabatic flame temperatures. This phenomenon is observed in the rich flames of methane, propane, ethanol and dimethyl ether with oxygen and air. Nevertheless, the results of modeling and

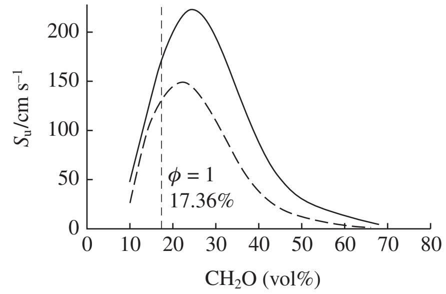

Figure 1 Speed of CH_2O/air flames *versus* formaldehyde concentration in the unburnt gases; dashed line, $T_0 = 373$ K, $P = 0.1$ MPa; solid line, $T_0 = 503$ K, $P = 0.15$ MPa.

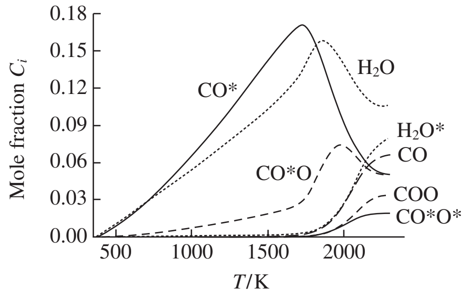

Figure 4 Concentration of main combustion products in the CH_2O*/air (0.24 : 0.76) flame *versus* flame temperature.

thermodynamic calculations demonstrate the temperature in a rich CH_2O/air flame to be lower than the equilibrium one. Thus, superadiabatic temperatures in CH_2O/air flames are not observed.

Analysis of the modeling results revealed that, in the rich CH_2O*/air flames, the labeled O* atoms mainly pass into CO* and in small numbers into CO*O throughout the flame zone (Figure 2). In the rich flames, the following transformations occur: CH_2O* → HCO* → CO*. Free oxygen in the combustible mixture is mainly consumed for H_2O formation. Concentration of CO is four orders of magnitude less than that of CO*. Therefore, heat mainly releases in reactions of H_2O formation and in small numbers in those of CO*O formation. Formation of CO* conversely proceeds with energy consumption as CO* was shown to be formed mainly in reaction of HCO destruction HCO* + M → CO* + H + M. Molecules CO* are produced, thus, as a result of a separation of two atoms of hydrogen from a formaldehyde molecule with energy expense.

In the lean flame (10 vol% of CH_2O*, Figure 3) the situation is quite different. The atom O* passes into CO* and CO*O and their concentration constantly grows up to the flame temperature of 1400 K. At a higher flame temperature, CO* concentration decreases to zero while the CO*O concentration grows. In the same temperature range, the concentrations of CO_2 and H_2O* increase. The labeled oxygen atom is mainly concentrated in CO*O molecules. The formation of CO*O occurs as the result of the following transformations: CH_2O* → HCO* → CO* → CO*O. Molecular oxygen at the flame temperature of 1500 K is consumed for the formation of water and CO*O. Consequently, in this temperature range, the heat releases in the reactions of the formation of H_2O and carbon dioxide CO*O from CO*. At the flame temperature above 1500 K, the reactions of COO formation largely contribute to the heat release. Carbon monoxide is produced in insignificant amounts, and its contribution to total heat release can be neglected.

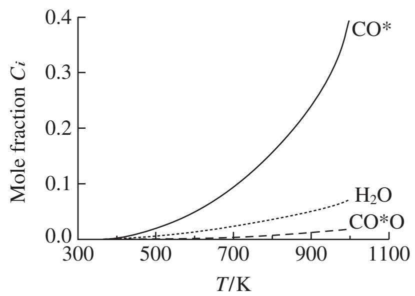

Figure 2 Concentration of main combustion products in the rich CH_2O*/air (0.66 : 0.34) flame *versus* flame temperature.

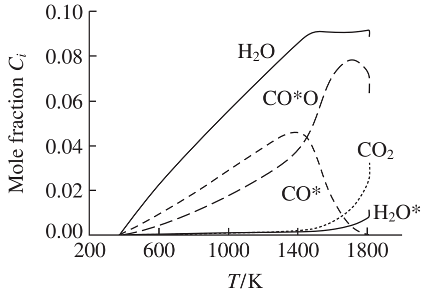

Figure 3 Concentration of main combustion products in the lean CH_2O*/air (0.1 : 0.9) flame *versus* flame temperature.

In the flame containing 24 vol% CH_2O*, in the flame temperature range 373–1700 K the labeled oxygen basically passes into CO* and CO*O (Figure 4) due to the following transformations: CH_2O* → HCO* → CO* → CO*O. At the equilibrium state, 54% of the labeled oxygen remains with carbon atoms (modeling predicts 63% at the very end of computational domain). At the flame temperature above 1800 K, the labelled oxygen atom is observed in the molecules of H_2O* and CO*O. According to Figure 4, the heat release is basically determined by the formation of H_2O, H_2O*, CO, COO, CO*O and CO*O*.

Thus, the results obtained, fair within the used kinetic mechanism, allow one to understand the distribution of the O atoms from formaldehyde molecules in the combustion products. The high value of rich concentration flammability limit is not explained by phenomenon of superadiabatic temperature but may be connected with an alternative combustion chemistry of formaldehyde, which is realized under rich conditions at relatively low temperatures.

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