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Numerical study of the distribution of oxygen atoms in the combustion products of CO/H_2/air flames

Valery A. Bunev,* Vladimir M. Shvartsberg and Vyacheslav S. Babkin

V. V. Voevodsky Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: + 7 338 330 7350; e-mail: bunev@kinetics.nsc.ru

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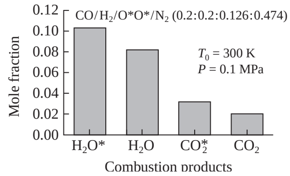
The distribution of air oxygen in the oxidation products of H_2 and CO in syngas flames has been studied by numerical simulation using the tracer method. The reaction pathways and the role of the oxygen atom of the CO molecule in heat release in these flames have been proposed.



The combustion of mixtures containing carbon monoxide and hydrogen is of considerable current interest. These mixed fuels are produced by the gasification of coal and biomass as a clean alternative to hydrocarbon fuels in energy production.[1]

Although the combustion of syngas has been thoroughly studied, the role of the oxygen atom of a carbon monoxide molecule in the combustion and heat release processes remains unclear. In addition, the problem of the selective oxidation of hydrogen in a syngas flame with a deficiency of oxygen has not been solved.

The aim of this work was to study the chemical conversion of atmospheric oxygen in CO/H_2/air (syngas) flames by a numerical simulation using a tracer method. In the fuel-rich mixtures of carbon monoxide and hydrogen, hydrogen can undergo selective oxidation when the amount of oxygen is insufficient for the complete oxidation of multicomponent fuel.

The tracer method[2] is an effective experimental technique for studying multistep chemical reaction mechanisms of combustion. The method of labelled atoms is rarely used in the numerical modeling of combustion, although its potential can hardly be overestimated.[3–5]

The burning velocity and flame structures were calculated using the CHEMKIN II software[6,7] for $CO/H_2/N_2/O^*O^*$ mixtures, where O* is a labeled oxygen atom.

Based on a modern analysis of the combustion mechanisms of CO + H_2 mixtures,[8] we selected two mechanisms for the combustion modeling.[9,10] A published model[9] adequately predicts the flame speed of syngas of various compositions at atmospheric and elevated pressures. Another model,[10] comprising 1500 steps and describing the combustion of C_1–C_4 hydrocarbons, predicts the flame structure and the flame speed, in particular, for CO + H_2 mixtures, according to Olm *et al*.[8] Our comparison of both mechanisms revealed only minor differences in the predicted concentration profiles of stable and labile species in the $CO/H_2/N_2/O_2$ flame.

In further calculations, we used a published kinetic scheme.[9] The computational domain of the simulation was 38 cm (from –8 to 30 cm). Note that all of the results are valid within the kinetic mechanism used.

The labeling of oxygen atoms in atmospheric oxygen molecules necessitated a modification of this reaction scheme by adding new species resulting from the presence of labeled oxygen atoms and new reactions involving these species. The modification of the kinetic scheme[9] led to a significant increase in the number of reactions to 222 involving 30 species instead of the initial 48 reactions involving 16 species.

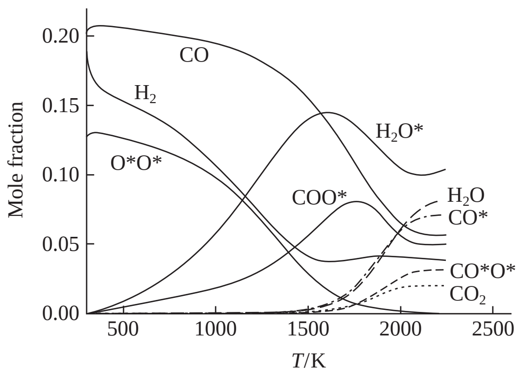


Figure 1 Concentrations of CO, H_2, O*O*, H_2O^*, COO*, CO*, CO*O*, CO_2 and H_2O *versus* temperature in the flame front of $CO/H_2/O^*O^*/N_2$ (0.2/0.2/0.126/0.474) syngas; T_0 = 300 K, P = 0.1 MPa.

Figure 1 shows the concentration profiles of the reactants CO, H_2 and O*O* and the reaction products H_2O^*, COO*, CO*, CO*O* and H_2O in a fuel-rich flame of $CO/H_2/O^*O^*/N_2$ (0.2/0.2/0.126/0.474) syngas at an initial temperature of 300 K and a pressure of 0.1 MPa. For this mixture, the numerical value of the normal burning velocity is in good agreement with the experimental data[11] (165 and 168 cm s^{-1}, respectively). The presence of labeled oxygen atoms (O*O*) solves the problem of how the labeled oxygen atom appears in the reaction products. It is evident that, in this rich flame (φ = 1.58) in a temperature range of 1600–1800 K, the O* atoms appear only in the molecules of water H_2O^* and carbon dioxide COO*. Thus, the concentration of initial O*O * molecules at 1600 K is close to zero. A further increase in the flame temperature results in a redistribution of the labeled atoms from water H_2O^* and carbon dioxide COO* to CO*O* and CO* molecules. The appearance of a labeled O* atom in a CO* molecule indicates that O atoms in CO molecules are replaced by labeled air oxygen atoms O*, which ultimately leads to the formation of water, H_2O. The fact that the initial air

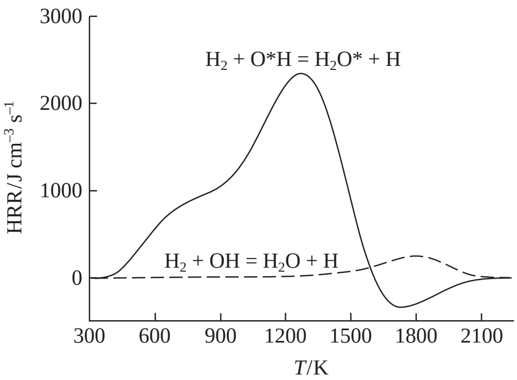


Figure 2 Heat release rate (HRR) in the reaction $H_2 + OH = H_2O + H$ *versus* temperature in the flame front in the $CO/H_2/O^*O^*/N_2$ (0.2/0.2/0.126/0.474) syngas; T_0 = 300 K, P = 0.1 MPa.

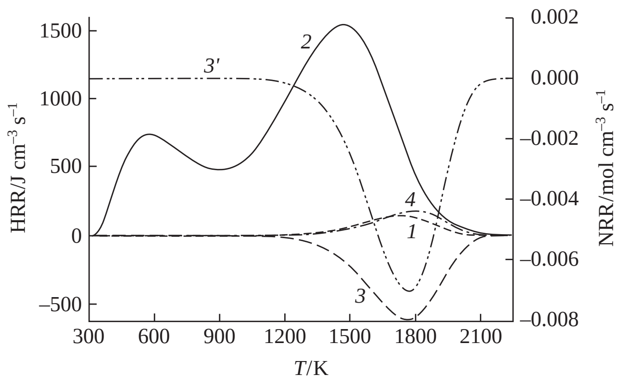


Figure 3 Heat release rate (HRR) in the reactions (*1*) $CO + OH = CO_2 + H$, (*2*) $CO + O^*H = H_2O^* + H$, (*3*) $CO^* + OH = COO^* + H$, (*4*) $CO^* + O^*H = CO^*O^* + H$, net reaction rate (NRR) of $CO^* + OH = COO^* + H$ (*3′*) *versus* temperature in the flame front of the $CO/H_2/O^*O^*/N_2$ (0.2/0.2/0.126/0.474); T_0 = 300 K, P = 0.1 MPa.

oxygen has been completely converted to the products, water (H_2O^*) and carbon dioxide (COO*), suggests that a further rise in temperature is associated only with a redistribution of unlabeled oxygen from CO to other products (CO_2, H_2O) with additional heat release.

Using the tracer method, we can determine difference between the rates of heat release in reactions involving labeled and unlabeled O atoms. For example, consider the reactions

$$H_2 + OH = H_2O + H, \tag{1}$$

$$H_2 + O^*H = H_2O^* + H. \tag{2}$$

Figure 2 depicts the profiles of heat release rates in reactions (1) and (2). Thus, the rate of heat release in reaction (2) is positive only at temperatures below 1600 K. This corresponds to the flame region in which the H_2O^* concentration increases and reaches a maximum. After the maximum, the H_2O^* concentration decreases (Figure 1) and the heat release rate becomes negative, indicating a negative rate of reaction (2) in this flame zone (Figure 2).

The heat release rate in reaction (1) is very low and different from zero in a temperature range of 1500–2100 K. Consequently, the reaction involving O*H makes a major contribution to the heat release.

Figure 3 shows the profiles of heat release rates in the reactions

$$CO + OH = CO_2 + H, \tag{3}$$

$$CO + O^*H = COO^* + H, \tag{4}$$

$$CO^* + OH = COO^* + H, \tag{5}$$

$$CO^* + O^*H = CO^*O^* + H, \tag{6}$$

and the net reaction rate (NRR) of $CO^* + OH = COO^* + H$.

In reaction (5), the components react with the absorption of heat. Consequently, the rate of this reaction is negative (graph 3′), *i.e.*, CO* and OH are formed from COO* and H. From the above it is clear how the exchange between labeled O* atoms and O atoms occurs, *i.e.*, how the carbon monoxide CO is converted into CO*. Note that this reaction occurs at temperatures above 1200 K. Then, a part of CO* reacts exothermically with O*H to form CO*O*. Reaction (5) proceeds with heat absorption (Figure 3), *i.e.*, its rate in a range of 1300–2000 K is negative. Consequently, it is in this way that labeled carbon monoxide CO* and unlabeled hydroxyl are formed. Note that heat is released in the reaction of CO and O*H [reaction (4)]. The contribution of steps (5) and (6) to the heat release is negligible. The question inevitably arises as to how the heat release rates in reactions (3)–(6) are related to the heat release rate in the reaction $CO + OH = CO_2 + H$ in the calculation using the mechanism without labeled atoms. We found that the heat release rate in the system without labels is equal to the sum of the heat release rates in steps (3)–(6).

The numerical simulation has shown that the heat release rate in reaction (4) in the initial portion of the front exceeds the heat release rate in reaction (2). In the reactions $H_2 + OH = H_2O + H$, $CO + OH = CO_2 + H$ and $CO^* + OH = COO^* + H$, heat release begins at temperatures above 1200–1500 K. This is because the concentration of the hydroxyl with unlabeled oxygen atom OH begins to increase in this temperature range and reaches a maximum at 2017 K (Figure 4).

The results shown in Figures 1–4 suggest that the oxidation of hydrogen and carbon monoxide in a syngas flame is a stepwise process. Figure 5 exhibits the ratio of the concentrations of

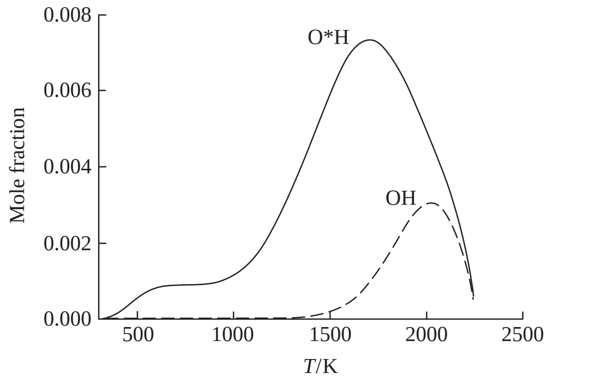


Figure 4 Concentrations of O*H and OH *versus* temperature in the flame front of $CO/H_2/O^*O^*/N_2$ (0.2/0.2/0.126/0.474) syngas; T_0 = 300 K, P = 0.1 MPa.

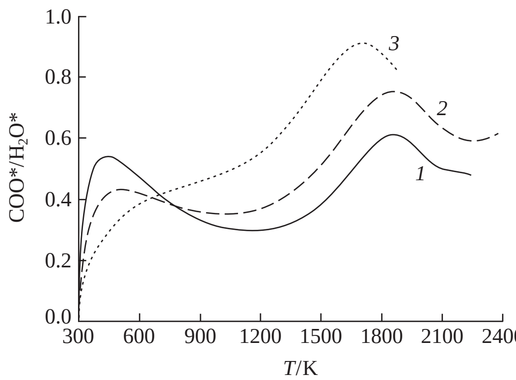


Figure 5 COO^*/H_2O^* ratio *versus* temperature in the flame fronts of (*1*) $CO/H_2/O^*O^*/N_2$ (0.2/0.2/0.126/0.474), (*2*) $H_2/CO/O^*O^*/N_2$ (0.15/0.15/0.147/0.553) and (*3*) $H_2/CO/O^*O^*/N_2$ (0.1/0.1/0.168/0.632); T_0 = 300 K, P = 0.1 MPa.

COO*/H_2O*, the main combustion products containing labeled oxygen atoms. It is evident that, first, this ratio is always lower than unity for an equimolar mixture of hydrogen and carbon monoxide, and, second, this is valid for lean, rich, and stoichiometric equimolar mixtures, in particular, under equilibrium conditions.

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