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Numerical characteristics of the low-temperature oxidation of dimethyl ether with air

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In the oxidation of dimethyl ether at the first stage of autoignition at low temperatures, the branching process involves not only hydroxyl radicals but also H atoms.

The autoignition of dimethyl ether (DME) mixtures at low initial temperatures occurs in two stages.[1,2] The first low-temperature stage is accompanied by a temperature rise followed by the attainment of a constant value. The second stage completes the oxidation process. A numerical simulation showed the presence of two peaks in the time profile of hydroxyl.[3] The first stage of ignition of DME mixtures is accompanied by the branching of an active center (OH).[1] At initial temperatures below 850 K and an initial pressure of 1 MPa, the process includes branching reactions. The branching index is determined based on the following low-temperature oxidation reactions involving radical OH:[1]

$$Me_2O + \mathbf{OH} \leftrightarrow MeOCH_2 + H_2O \quad (1)$$

$$MeOCH_2 \rightarrow HCHO + Me \quad (2)$$

$$MeOCH_2 + O_2 \leftrightarrow MeOCH_2O_2 \quad (3)$$

$$MeOCH_2O_2 \leftrightarrow CH_2OCH_2O_2H \quad (4)$$

$$CH_2OCH_2O_2H \rightarrow 2HCHO + \mathbf{OH} \quad (5)$$

$$CH_2OCH_2O_2H + O_2 \leftrightarrow O_2CH_2OCH_2O_2H \quad (6)$$

$$O_2CH_2OCH_2O_2H \rightarrow HO_2CH_2OCHO + OH \quad (7)$$

$$HO_2CH_2OCHO \rightarrow HCHO + HOCO + \mathbf{OH} \quad (8)$$

Note that this reaction scheme does not consider the hydrogen atom as an active center. The branching index for hydroxyl is[1]

$$\alpha = \{k_3[O_2]/(k_3[O_2] + k_2)\}\{(2k_6[O_2] + k_5)/(k_6[O_2] + k_5)\},$$

where k_i are the constants of the corresponding reactions. The index α characterizes the number of OH species resulting from reactions (5) and (6) in terms of one reacting species $CH_2OCH_2O_2H$ with a correction for the probability of reaction (3). Reactions (2) and (5) are competing decomposition steps that lower the OH reproduction rate at higher temperatures; hence, they are responsible for the negative temperature coefficient.[1] Using the kinetic scheme of dimethyl ether oxidation,[4] Yamada *et al.*[1] obtained the temperature dependence of α at T_0 = 600 K, an initial pressure of 1 MPa, and a DME equivalence ratio of 0.29. At the very beginning of the process, α = 2. According to the published scheme,[1] this implies that, at the beginning of the process, two hydroxyls are formed instead of the hydroxyl lost by reaction (1), and α is greater than unity at 600–850 K. The first stage should be completed at 850 K. Note that, according to these concepts, the branching index decreases during the process.

The aim of this study was to test by numerical methods whether the concepts[1,2] of the branched chain oxidation of DME in the first stage at low temperatures are consistent with the kinetic scheme[4] for DME.

Numerical simulations make it possible to determine the branching factor φ for hydroxyl and the most active intermediate species. For this, one needs to numerically obtain the function $d[OH]/dt = A + \varphi[OH]$. The autoignition of the mixtures of DME and air at a constant volume was simulated according to a kinetic scheme.[4] Calculations[5,6] were performed under the following initial conditions: T_0 = 500–1200 K, p_0 = 0.1–1.0 MPa, and V = const. The simulation was carried out for mixtures containing 3–30 vol% DME and air.

We first determined the branching index for the mixtures of 30% DME and air according to ref.1. Figure 1 shows the branching index at T_0 = 600 K, P_0 = 0.1 MPa and V = const. It is evident that α is greater than unity at temperatures below 750 K. In this plot, points are shown for $[O_2]$ = const and for the case of varying oxygen concentration during the process. Figure 1 also shows a curve of α for an initial pressure of 1 MPa. Increasing the initial pressure leads to an increase in temperature with a branching index of unity. Since Yamada *et al.*[1] determined α for lean mixtures, it can be concluded that the temperature for α = 1 is almost independent of the DME concentration in the mixture with air. Figure 2 gives the temperature dependence of α for 30 and 5% concentrations of DME. The temperature for α = 1 is almost independent of the concentration of DME. The branching index was determined with and without accounting for reverse reactions (3) and (6). Accounting for the reverse reactions does not affect the temperature dependence of α. Thus, the results of the numerical simulation show that the index α depends significantly on the initial pressure and does not depend on the DME

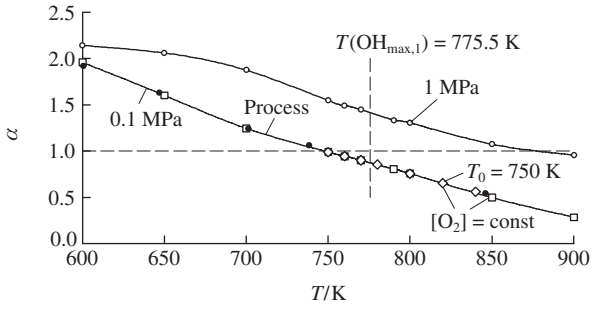

Figure 1 Branching index α *vs.* initial or current temperature for the autoignition of mixtures containing 30% DME and air: (•) during the process, (□) *vs.* initial temperature, (◇) *vs.* current temperature at T_0 = 750 K. The vertical dotted line indicates the temperature at which the first peak of OH concentration is reached at T_0 = 600 K.

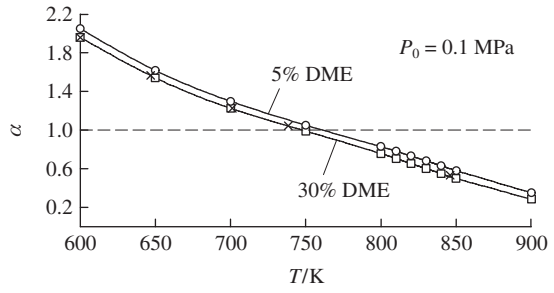

Figure 2 Branching index α *vs.* current temperature for the autoignition of mixtures containing 5 and 30% DME and air: (□) without taking into account reverse reactions, (×) taking into account reverse reactions.

concentration in the mixture with air and the reverse reactions listed above. Note that, in accordance with published data,[1,2] the branching index decreases during oxidation.

According to reported data,[1] at an initial temperature of 750 K, the branching index is always less than unity (Figure 1). This implies that the branching at this temperature follows a different mechanism since the autoignition process at this temperature also proceeds in two stages with two OH peaks (Figure 3). Apparently, the branching index and the above reactions do not adequately reflect the low-temperature stage of the process at different initial temperatures.

As indicated by the vertical dashed line in Figure 1, the first peak of hydroxyl concentration is reached at 775.5 K, which is higher than the temperature at which the branching index is unity (750 K). In other words, the branching process continues at temperatures above 750 K. This implies that the above reactions do not completely reflect the branching process. Numerical simulations showed that the concentration of H atoms is similar to the OH concentration during the whole process up to the first peak of OH. In the initial part of the process, the concentration of H is even several times higher than that of hydroxyl.

Figure 4 shows the dependence of the derivative d[OH]/dt on the OH concentration for the period before the first peak $OH_{max,1}$. There is a range of OH concentrations for which we can write d[OH]/dt = $–7.20\times10^{-8}$ + 1.08×10^{4}[OH]. The branching factor φ is 1.08×10^{4} s^{-1}. The oxidation of DME, naturally, begins at lower values of φ. The group of reactions that determine the initial period of oxidation at the first stage may be different from the set of reactions that provide a branching factor of 1.08×10^{4} s^{-1}. Moreover, what is important, the branching factor increases during

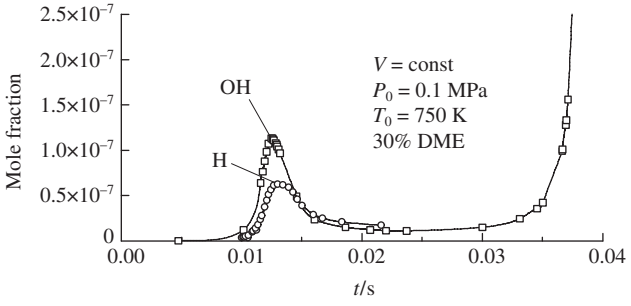

Figure 3 OH and H concentrations *vs.* time.

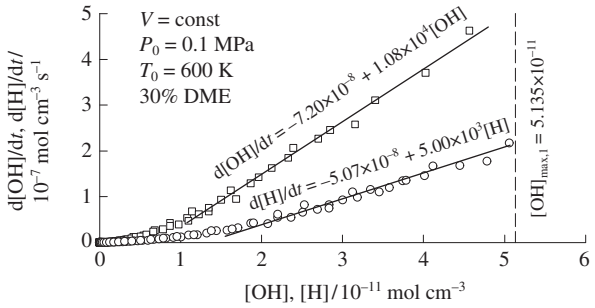

Figure 4 d[OH]/dt and d[H]/dt *vs.* OH and H concentrations, respectively (in the range of concentrations up to $OH_{max,1}$). The symbols are the results of the processing of numerical data.

the first stage of the process, rather than decreases as might be expected in accordance with published data.[1,2]

A reported[1] list of reactions that are thought to determine the branching process in the initial region of DME oxidation does not contain reactions involving hydrogen atoms. However, it is high enough, and the participation of H atoms in the branching process should be taken into account. The numerical simulation reveals that the time profile of the H concentration has two peaks. Figure 3 exhibits only the first peak for H atoms. Accordingly, before the first peak $H_{max,1}$, the derivative d[H]/dt can also be linearly dependent on the concentration of H. Figure 4 shows that, for H atoms in a certain region, we can write d[H]/dt = = $–5.04\times10^{-8}$ + 5.0×10^{3}[H]. The branching factor φ for H atoms in this region before the H concentration peak is 5×10^{3} s^{-1}.

Thus, the numerical simulation demonstrates that the branching for hydroxyl OH at the first stage of low-temperature oxidation of DME is determined not only by the reactions of the $CH_2OCH_2O_2H$ and $O_2CH_2OCH_2O_2H$ radicals; H atoms also participate in the branching process, and the branching factor for both OH and H does not decrease, as might be expected in accordance with published data,[1,2] but increases during the process.

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