

OVERALL REACTION MECHANISM  
OF TWO-STAGE *n*-BUTANE OXIDATION

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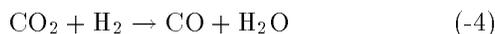
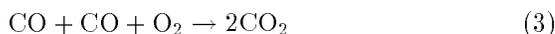
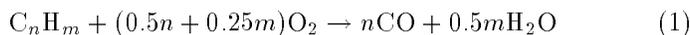
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## Introduction

The objective of the work described in this paper is the development of a short reaction mechanism of *n*-butane oxidation, which is feasible for multidimensional simulation of low-temperature autoignition, forced ignition, and flame propagation in *n*-butane–oxygen mixtures.

It is well known that the kinetic description of hydrocarbon oxidation chemistry requires consideration of several thousands elementary reactions involving hundreds species. It is hardly possible to reduce such detailed reaction mechanisms to very compact reaction schemes without applying some far reaching approximations and overall reactions. The short schemes thus obtained, regardless of the way they were deduced, are by all means not universal and should be treated as empirical or semiempirical. The lack of universality is the main drawback of such schemes. They can be applied only within the parametric domains (in terms of temperature, pressure, and mixture composition) where they were validated against available measurements or computational data based on reliable detailed reaction mechanisms. Any extrapolation of such schemes should be firmly substantiated.

One of the approaches to develop a short reaction mechanism has been suggested by the authors in [1, 2]. The mechanism of [1, 2] is presented below:



This mechanism has been successfully applied for modeling laminar and turbulent flames as well as liquid drop combustion. For modeling high-temperature autoignition of hydrocarbons, this mechanism was modified in [3, 4]: the rate constant of the limiting reaction (1) was properly decreased to take into account the intrinsic feature of the autoignition process that is the lack of external delivery of heat and active centers to the reactive mixture. For high-temperature autoignition (at temperatures exceeding 1000 K), this modification is relatively easy to introduce by properly decreasing the preexponential factor in the reaction constant of reaction (1). For taking into account thermal decomposition of reaction products at high temperatures, the reaction mechanism (1)–(4) should be supplemented by an additional overall reaction similar to water molecule dissociation reaction [2]. For low-temperature oxidation (at temperatures below 1000 K), this mechanism has not been applied so far.

## Approach

To model two-stage oxidation of *n*-butane, the following approach was used. The Arrhenius parameters of reaction (1) in the low-temperature region (at temperature  $T^* = 950\text{--}1000$  K) were obtained by fitting the predicted and measured data without regard for high-temperature behavior of the ignition delay. The resulting kinetic parameters for reaction (1) are:

$$k_1 = 3.127 \cdot 10^{11} p^{0.794} \text{ l}/(\text{mol} \cdot \text{s}), \quad E_1 = 27 \text{ kcal/mol} \quad \text{at } T \leq T^*$$

$$k_1 = 1.55 \cdot 10^{12} p^{-0.145} \text{ l}/(\text{mol} \cdot \text{s}), \quad E_1 = 45 \text{ kcal/mol} \quad \text{at } T > T^*$$

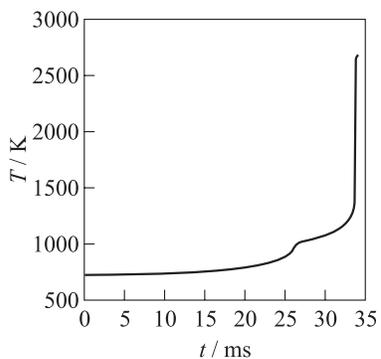
where  $k_1$  and  $E_1$  are the preexponential factor and activation energy of reaction (1) treated as a bimolecular reaction, and  $p$  is pressure in atm. The kinetic parameters for reactions (2) to (-4) are the same as in [1–4]. This approach appeared to be fruitful and easily implemented.

## Mechanism Validation

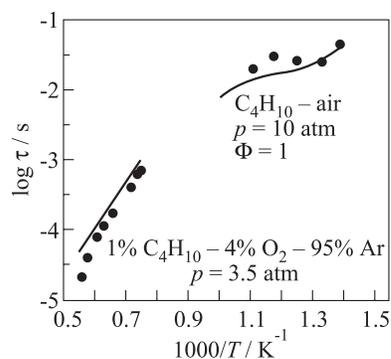
The mechanism with modified reaction rate constants has been validated against the measured ignition delays of *n*-butane.

Figure 1 shows the example of temperature history in the parametric domain relevant to multistage autoignition. One can clearly identify a two-stage temperature rise typical of the cool flame followed by a hot explosion. Figure 2 compares predicted (curves) and measured (points) ignition delays of *n*-butane within a wide range of initial temperature. Low-temperature experimental points [5] correspond to the stoichiometric *n*-butane-air mixture at  $p_0 = 10$  atm. High-temperature experimental points [6] correspond to the 1%  $C_4H_{10}$ -4%  $O_2$ -95% Ar mixture at  $p_0 = 3.5$  atm. In the transition temperature interval (between 700 and 1000 K), the calculated curve exhibits the so-called Negative (or Zero) Temperature Coefficient (NTC) of the reaction rate, which is typical for multistage oxidation of hydrocarbons.

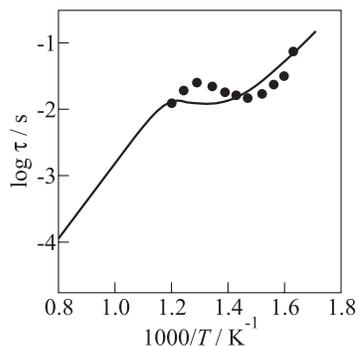
Note that the mechanism (1)-(4) was validated against the same measured data which were used for obtaining the Arrhenius parameters of the rate limiting reaction (1). Despite the available experimental data



**Figure 1** Predicted temperature history at low-temperature autoignition of the stoichiometric *n*-butane-air mixture at initial temperature of 720 K and pressure of 10 atm



**Figure 2** Comparison between predicted (curves) and measured (points [5, 6]) ignition delays for two *n*-butane mixtures



**Figure 3** Comparison between predicted (curve) and measured (points) ignition delays for the stoichiometric *n*-butane–air mixture (ON  $\approx$  90) at initial pressure of 15 atm. Experimental points are obtained for the sample 90% *iso*-octane–10% *n*-heptane mixture with ON = 90 [1]

are very limited, there is a possibility of further mechanism validation based on some indirect data. *n*-Butane is known to have the Octane Number (ON) of about 90. The sample mixture of 90% *iso*-octane and 10% *n*-heptane has the same ON. Therefore, it could be anticipated that ignition delays of *n*-butane–air mixtures are somewhat similar to those observed for the sample mixture containing 90% *iso*-octane and 10% *n*-heptane. Figure 3 shows such a comparison of calculations (curve) for the stoichiometric *n*-butane–air mixture at  $p_0 = 15$  atm with the measurements (points [1]) for the sample mixture at similar conditions. Taking into account inevitable experimental uncertainties, the agreement of the results can be treated as satisfactory. In Fig. 3, the calculations also reveal the NTC behavior typical for multistage oxidation.

## Concluding Remarks

A compact overall mechanism of low- and high-temperature *n*-butane oxidation is suggested and validated against available experimental data for autoignition delay at the initial pressure of 3.5 and 10 bar and the initial temperature from 710 to 2000 K. With proper values of the reaction constants for the rate limiting reaction step, the mechanism

can be applied to model both autoignition and combustion of *n*-butane–oxygen and *n*-butane–air mixtures.

## Acknowledgments

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