ARAS-STUDY OF REACTION OF PROPANOL ISOMERS WITH OXYGEN BEHIND SHOCK WAVES

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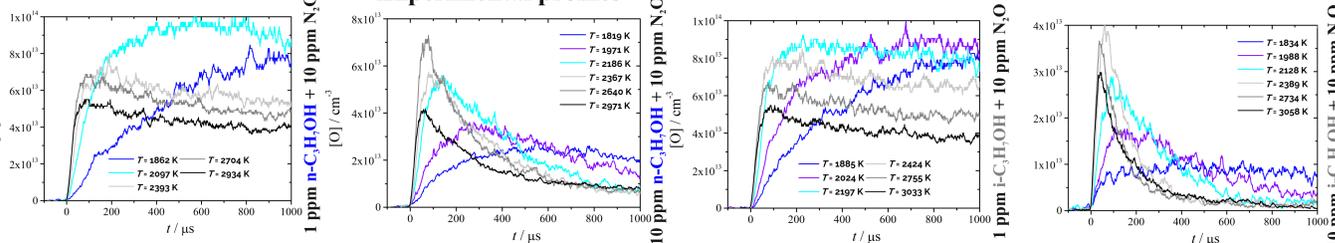**LABORATORY OF NONEQUILIBRIUM PROCESSES**

MOTIVATION

Problem

In recent years, n-propanol and isopropanol, along with many short-chain hydroxylated compounds, have been at the center of growing interest among researchers, since they can reduce emissions of polycyclic aromatic hydrocarbons (PAHs), particulate matter and soot [1-4], carbon oxides and nitrogen, while having a high octane number (118) and low emission potential of NO_x, CO_x, SO_x, etc. In addition to the obvious environmental advantages of alcohols and ethers over traditional hydrocarbon fuels, they can provide a higher thermal efficiency [2-4], while possessing many physicochemical properties compatible with the requirements of modern engines, which makes them attractive as a complete replacement for fossil fuel and as fuel additives.

Goal of this work

In light of the above, the main goal of this study was to provide new experimental information on the interaction of oxygen atoms with propyl alcohols at high temperatures. For this, the formation and consumption of atomic oxygen behind the reflected shock waves were measured using the methods of atomic resonance absorption spectroscopy (ARAS) in mixtures of 1 and 10 ppm n-propanol + 10 ppm N_2O + Ar; 1 and 10 ppm isopropanol + 10 ppm N_2O + Ar in the temperature range 1700-3200 K and pressures 2-3 bar; the adequacy of modern detailed kinetic mechanisms of combustion by Konnov [5] and POLIMI [6-9] was analyzed according to experimental data - the data obtained in comparison with this mechanism were used to study the key reaction mechanisms affecting the dynamics of oxidation of fuel mixtures under the conditions under study. The influence of the isomer structure on the formation and decay of oxygen atoms was analyzed by modeling the [O] profiles at 1819, 2367, and 2971 K.
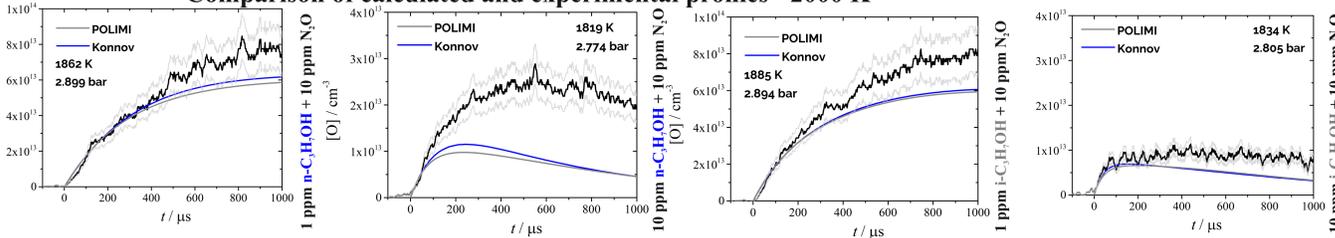
EXPERIMENT

The parameters of the shock tube

vacuum
4E-7 mbar
leakage
8E-7 mbar/min

Experimental conditions

mixture
1/10 ppm n-C_3H_7OH + 10 ppm N_2O in Ar
1/10 ppm i-C_3H_7OH + 10 ppm N_2O in Ar
temperature
1800-3200 K
pressure
2-3 bar
gas mixture in FQT
1% O_2 in He at P = 15 mbar

Experimental installation

Investigation section of shock tube and atomic resonance absorption spectroscopy measurement scheme. Photomultiplier (PMT); flowing quartz tube (FQT).

1% O_2 in He at P=14 mbar

CALIBRATION PROCEDURE

All the experimental points of the absorption $A = (I_0 - I)/I_0$, where I_0 and I are the initial and transmitted signals from the lamp, and dependent on the concentration of atomic oxygen [O], are well described by the modifier Bouguer-Lambert-Beer Law.

The parameter $\sigma(T) = \sigma_b(1 + \alpha[(T_b - T_e)/T_b]$ where T_b - the base calibration temperature from [Bystrov et al. Phys. Chem. Kinet. Gas Dynamic 20(1) 2019) 1-15] in K, T_e - the temperature in each experiment in K, α - the empirical parameter. The best fit was reached at the parameters n, α and σ_b, determined by the least squares method n (O) = 0.7 ± 0.04, α (O) = 0.75 ± 0.15 and σ_b(O) = 1.8E(-11±0.4) cm1.1.

$A = 1 - \exp[-(\sigma(T)L[O]^n)]$

exp. ser. 1 (T = 1800 K)
exp. ser. 2 (T = 2300 K)
exp. ser. 3 (T = 3100 K)
calibration curve 1
calibration curve 2
calibration curve 3

A – the measured absorption
L – the absorption path length
[O] – the concentration of the oxygen atom
$\sigma(T)$ – cross section is a function of temp.
n – the empirical parameter

Calibration curves 1, 2 and 3 of the absolute concentration of oxygen atoms: [O] = [A] at different temperatures.

## KINETIC MODELING AND RESULTS

Experimental profiles

An increase in the absorption signal behind the RSW front is clearly seen, caused by the rapid dissociation of N_2O into N_2 and O and a decrease in absorption, reflecting the consumption of O by the secondary kinetics. The time profiles of the appearance and consumption of O isomers are similar to each other with the corresponding parameters. In mixtures with 10 ppm alcohol, the O yield is noticeably lower, which is associated with fast, increasing with T, secondary reactions, after the first 50 μs, of O atoms with the decay products of n-/isopropanol.

### Comparison of calculated and experimental profiles <2000 K

Modeling gives an adequate idea of the experimental tendency of the [O] profiles upon decomposition of N_2O and mixtures of 1 ppm n- and isopropanol + 10 ppm N_2O. At T <2000 K, the strongest discrepancies between the models and experiment are observed. The predictive efficiency of the models decreases with an increase in the fuel concentration in the initial mixture at T <2000 K, which leads only to qualitative agreement in the simulation of experimental data.

Comparison of calculated and experimental profiles ~2400 K
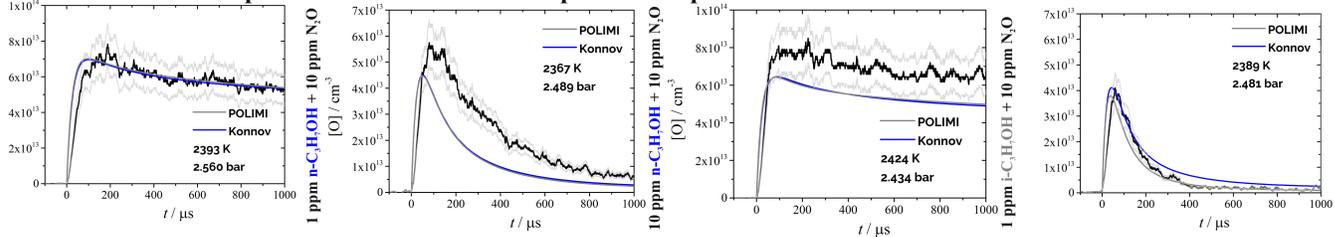
The best agreement between experiment and kinetic modeling was achieved at a temperature of ≈ 2400 K for both mixtures. However, for both models, an overestimation of the consumption of atomic oxygen is observed: in the case of mixtures with 1 ppm isopropanol and in the case of 10 ppm n-propanol for the first 50 ms of decomposition of alcohols and nitrous oxide.
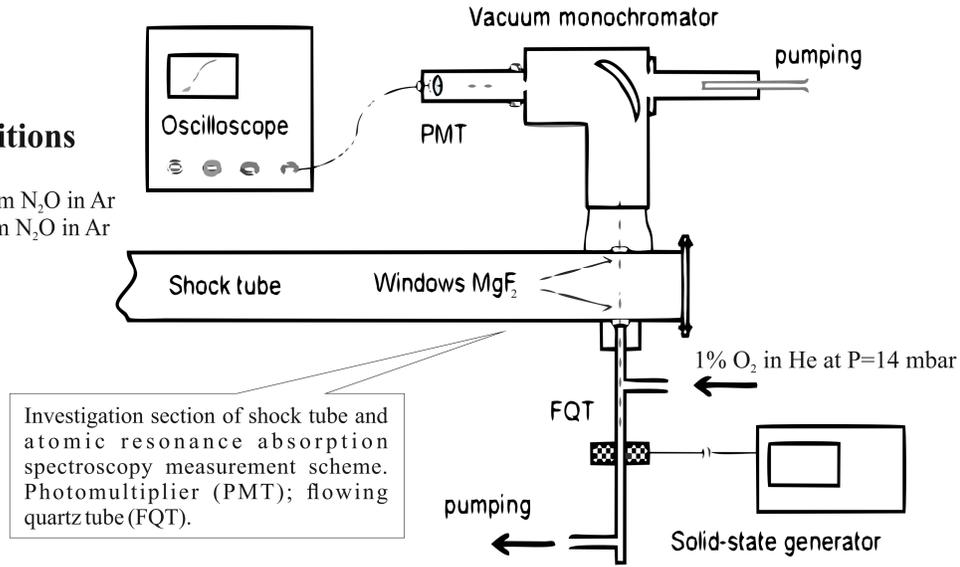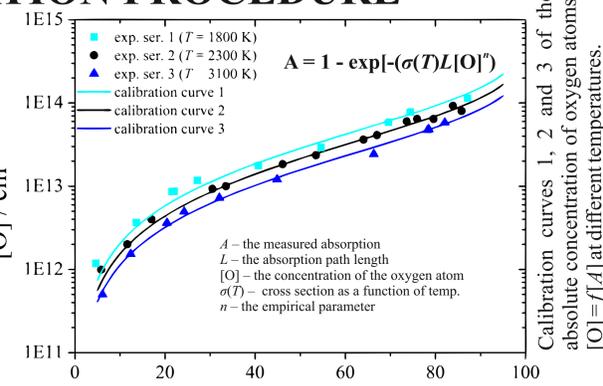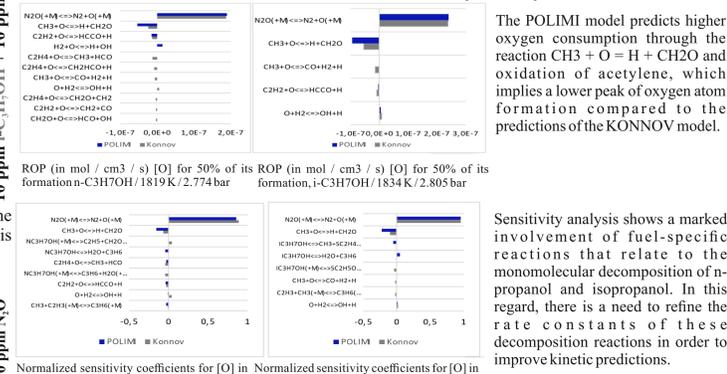
~3000 K
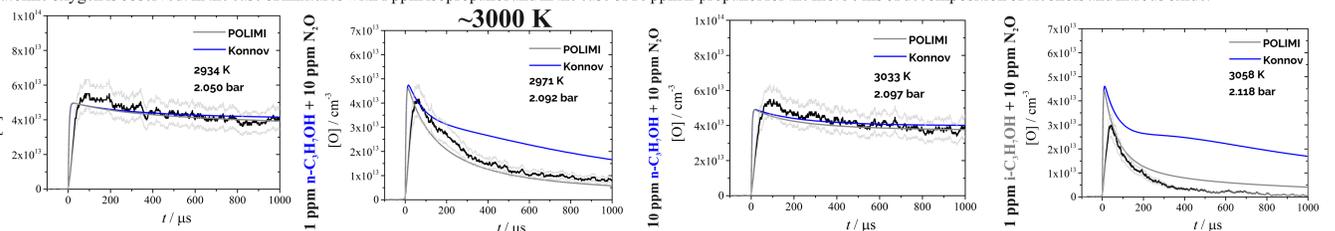
Excellent agreement with both models for mixtures with 1 ppm n-/iso-propanol in the initial mixtures at high temperatures. For mixtures with 10 ppm, differences in kinetic models in determining the main reaction pathways of oxygen consumption are clearly manifested. The POLIMI mechanism is more accurate in predicting the consumption of oxygen atoms at high temperatures, with both models overestimating its consumption in the first 50 μs.

ROP and sensitivity analyzes

The POLIMI model predicts higher oxygen consumption through the reaction CH3 + O = H + CH2O and oxidation of acetylene, which implies a lower peak of oxygen atom formation compared to the predictions of the KONNOV model.

ROP (in mol / cm3 / s) [O] for 50% of its formation n-C3H7OH/1819 K / 2.774 bar

ROP (in mol / cm3 / s) [O] for 50% of its formation, i-C3H7OH/1834 K / 2.805 bar

Sensitivity analysis shows a marked involvement of fuel-specific reactions that relate to the monomolecular decomposition of n-propanol and isopropanol. In this regard, there is a need to refine the rate constants of these decomposition reactions in order to improve kinetic predictions.

Normalized sensitivity coefficients for [O] in mixtures with 10 ppm alcohol at 50% of its formation, n-C3H7OH/1819 K / 2.774 bar

Normalized sensitivity coefficients for [O] in mixtures with 10 ppm alcohol at 50% of its consumption, i-C3H7OH / 3058 K / 2.118 bar

Both models indicate the great importance of reactions related to the chemistry of acetylene. Konnov - O consumption is controlled by the reactions O + C2H = CO + CH and C2H + H2 = C2H2 + H. POLIMI - C2H2 + O = HCCO + H, which determine the beginning. The O consumption stage, followed by the branching H2 + O = H + OH.

Normalized sensitivity coefficients for [O] in mixtures with 10 ppm alcohol at 50% of its consumption, n-C3H7OH / 2971 K / 2.092 bar

Normalized sensitivity coefficients for [O] in mixtures with 10 ppm alcohol at 50% of its consumption, i-C3H7OH / 3058 K / 2.118 bar

Influence of isomer structure

The difference in the position of the hydroxyl group of n- and isopropanol leads to different specific pathways for the decomposition of isomers. Iso-propanol, in contrast to n-propanol, decomposes mainly with the formation of a methyl radical, which actively interacts with an oxygen atom, forming a hydrogen atom and formaldehyde. Therefore, in the studied temperature range, isopropanol is characterized by a lower level of oxygen formation, which can be observed in all graphs.

CONCLUSIONS

New kinetic data for the oxidation of propanol isomers are provided. Mixtures with a concentration of 1 ppm alcohol are satisfactorily described by the Konnov and POLIMI models over the entire investigated range of temperatures and pressures. The predictive power of the models at 10 ppm alcohol and T <2000 K is noticeably weaker, but good enough at T ≥ 2500 K. At T ≈ 3000 K: POLIMI - good; Konnov - satisfactory. Sensitivity analysis showed that for both models, oxygen decomposition is largely controlled by small C2-C1 particles - the acetylene chemistry needs to be refined. In this regard, this work is a step forward in minimizing the uncertainty of the propanol combustion model, as well as in identifying the key channels for the oxidation of alcohols.

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