Measurements of the oxygen dissociation rate constant with verification of modern models of hydrocarbon combustion

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The dissociation rate of molecular oxygen (O_2) is one of the most important kinetic parameters in the study of combustion and high-temperature air flows. It was shown that in modern models of hydrocarbon combustion there is still no consensus on the value of the rate of dissociation of molecular oxygen. It was also shown that the accuracy of knowing the rate of this reaction requires special attention, as one of the components of the "core" of any comprehensive combustion models. Therefore, to resolve existing contradictions, new, more accurate measurements of the dissociation rate of molecular oxygen at temperatures close to conventional combustion were carried out. The presented rate constant of the O_2 dissociation reaction with a very low uncertainty will undoubtedly contribute to the development of more reliable modern combustion models.

The data available in the literature on measurements of the rate coefficient of molecular oxygen dissociation were considered and structured. Modern models of hydrocarbons combustion were analyzed considering values of the O_2 dissociation rate constant. Precision measurements of the rate of O_2 dissociation behind shock waves at temperatures of 2500–5000 ± 50 K and pressures of 1.2–2.5 bar were carried out using atomic resonance absorption spectrometry on O atom (O-ARAS). The ARAS measurements of the absolute concentration of oxygen atoms were calibrated in the conditions of complete dissociation of N_2O and O_2, considering the temperature splitting of the calibration curves. Using kinetic modeling, a detailed analysis of experimental uncertainties was carried out with an assessment of the influence of impurities of various origin at the dissociation of O_2. An updated expression for the rate constant of the reaction $O_2 + Ar = 2O + Ar$ was obtained in the form k_{diss} (±15%) = $1.30 \cdot 10^{14} \cdot exp(-108.95\ [kcal/mol]\ /\ RT)$ cm^3 mol^{-1} s^{-1}. A significant influence of the O_2 dissociation rate constant on the predictive ability of modern models of hydrocarbons (on the example of biofuels) combustion at high temperatures was shown. Recommendations were formulated on the use of the corresponding oxygen dissociation rate constant in the development and/or refinement of combustion kinetic models.

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