

DETERMINATION OF THE RATE OF THERMAL DISSOCIATION OF *n*-PROPANOL BEHIND REFLECTED SHOCK WAVES

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Abstract: For the first time, an experimental and computational study of the thermal decomposition of *n*-propanol at temperatures typical for combustion and ignition of alcohols was carried out. The experiments were performed behind reflected shock waves in temperature and pressure ranges of 1120–1550 K and ~1.0–1.5 atm, respectively. Information about the decomposition process was obtained by recording the light absorption of the products — propylene ($\lambda = 197 \pm 1.0$ nm) and methyl radicals ($\lambda = 216.6 \pm 0.2$ nm). The interpretation of the experimental data was carried out within the framework of the model proposed by A. A. Konnov and modified in the present work taking into account the new data. As a result of modeling and its comparison with experimental data, the Arrhenius equation for the rate constant of elimination of a water molecule from *n*-propanol molecule was obtained: $k_1(T) = (8.3 \pm 2.6) \cdot 10^{13} \exp(-64000/(RT)) \text{ s}^{-1}$. Estimation of the maximum limit of the energy for the abstraction of the methyl group from the alcohol molecule is estimated to be 82.9 kcal/mol. The results obtained were compared with the available literature data.

Keywords: decomposition of *n*-propanol; reactions of elimination and cleavage of C–C bonds; formation of propylene and methyl radicals; shock waves; spectrophotometry; kinetic simulation

DOI: 10.30826/CE24170102

EDN: AZGIJC

Figure Captions

Figure 1 Structure of the *n*-propanol molecule and dissociation energies of its bonds (kcal/mol): $D_{01} = 102.0$ (101.1); $D_{02} = 91.0$ (88.7); $D_{03} = 86.2$ (87); $D_{04} = 100.3$ (99.9); $D_{05} = 95.5$ (95.1); $D_{06} = 95.8$ (93.9); and $D_{07} = 105.2$ (105.2). Data from [18] and [17] (in parentheses)

Figure 2 Time profiles of pressure and optical density of the working mixture at wavelengths corresponding to the absorption of methyl radicals ($\lambda = 216.6$ nm) and propylene ($\lambda = 197$ nm) at initial temperatures $T_{50} = 1390$ (a) and 1187 K (b) and pressures $P_{50} = 1.07$ (a) and 0.96 atm (b). For better perception, the CH_3 time profile is shifted up 0.2 units

Figure 3 Decimal absorption coefficient of propylene (1) and *n*-propanol (2) at a wavelength of $\lambda = 197$ nm

Figure 4 Comparison of the experimental time profile of the optical density of the heated working mixture (curve with noise) with its simulation (black curves) within the framework of the chosen reaction scheme for various values of the preexponential factor in the Arrhenius equation for the rate constant of reaction (R1): 1 — $A_1 = 4 \cdot 10^{13} \text{ s}^{-1}$; 2 — $7 \cdot 10^{13}$; and 3 — $A_1 = 10 \cdot 10^{13} \text{ s}^{-1}$. A mixture of 0.15% *n*-C₃H₇OH in argon; $T_{50} = 1187$ K; and $P_{50} = 0.96$ atm

Figure 5 Illustration of the procedure for determining the value of A_1 that provides the minimum square deviation of the calculated profile from the experimental one and estimating the corresponding uncertainty in this value: 1 — values of σ_D calculated for 10 values of A_1 ; 2 — deviation approximation; 3 — uncertainty interval; and 4 — position of the minimum

Figure 6 Temperature dependence of the rate constant for the reaction of elimination of H₂O from *n*-C₃H₇OH (R1) obtained in this work: 1 — experiment; and 2 — Eq. (5)

Figure 7 Comparison of the rate constant for the elimination of H₂O from *n*-C₃H₇OH (reaction (R1)) obtained in this work with literature data: 1 — present work, experiment; 2 — [15], calculation; 3 — [13], experiment; 4 — extrapolation of 3; and 5 — [20], *i*-propanol, experiment

Figure 8 Temperature dependence of the lower estimate of the reaction (R2) rate constant for the abstraction of a methyl radical from an *n*-propanol molecule (signs). The line corresponds to the minimum possible values of the reaction rate constant (R2) in the high-pressure limit

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Received December 19, 2023

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