

Experimental study and quantum-chemical calculation of C₃H₇I initial dissociation kinetics and its thermodynamic properties in a wide temperature range

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Iodine-containing halocarbons and halohydrocarbons are widely used in various fields of the chemical industry, firefighting, and medicine. At the same time, scientific interest in such substances remains extremely high at the present time. In particular, the C₃H₇I molecule due to presence of the weakest bond of halogen atom with the carbon atom (C-I bond), is the most suitable precursor for the alkyl radical C₃H₇. This substance, as is known, are formed in significant quantities at the combustion and pyrolysis processes of normal alkanes, and without the correct prediction it is impossible to build physically consistent models of real hydrocarbon fuels combustion. That is why this work is aimed at studying the kinetic and thermodynamic C₃H₇I dissociation properties.

The n-C₃H₇I + Ar → n-C₃H₇ + I + Ar reaction at the temperatures 800-1200 K and pressures 3.5±0.5 bar behind reflected shock waves using the atomic resonance absorption spectroscopy (ARAS) technique on a resonant line of atomic iodine at 183.04 nm have been studied. The initial concentration of n-C₃H₇I in Ar was varied from 0.8 to 1.1 ppm.

As a result, the first direct experimental data on the n-C₃H₇I thermal unimolecular decomposition were obtained. Time profiles of iodine atom concentration were used to determine the rate constant temperature dependence and its activation energy. Based on the data, the dissociation rate constant n-C₃H₇I was obtained in the two-parameter Arrhenius form for further using in kinetic databases.

At the same time, using modern methods of quantum chemical calculations at the level of the B3LYP/cc-pVTZ-PP theory, individual characteristics of n-C₃H₇I, i-C₃H₇I molecules, their products, and transition states were calculated. Among them, optimized geometry, harmonic frequencies, rotational constants, total electron energy, zero-point energy, etc were obtained. The data made it possible, in the ideal gas approximation, to determine the standard enthalpy of dissociation and isomerization reactions, as well as all necessary thermodynamic properties, such as enthalpy, entropy, and isobaric heat capacity in the temperature range from 200 to 5000 K.

And finally, based on quantum chemical calculations, the theoretical calculation of the monomolecular n-C₃H₇I dissociation rate constant was performed using the Rice-Ramsperger-Kassel-Marcus (RRKM) model in a wide thermodynamic parameters range (T = 300–3000 K, p = 10⁻⁴–10² bar). For this substance, Arrhenius dependences of the rate constants in the high and low pressure limit are presented, as well as the central broadening factor. Comparison of the theoretical and experimental results with literature data confirmed their reliability. The RRKM calculations has allowed to conclude, under the studied conditions, the n-C₃H₇I dissociation rate constant is close to the high-pressure limit; nevertheless, at elevated temperatures (above 900 K), the effect of pressure still remains significant.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation № 075-15-2020-806.



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