XXXIV International Conference: Interaction of Intense Energy Fluxes with Matter

Elbrus, Russia
March 1-6, 2021

Experimental study of kinetics of C_3H_7I dissociation behind shock waves

Bystrov N S[1,2], Emelianov A V[1], Eremin A V[1], Yatsenko P I[1,2,@]
[1]JIHT RAS, Moscow, Russia
[2]BMSTU, Moscow, Russia
@pavelyatcenko@yandex.ru

Motivation

Problem

Iodine-containing halocarbons and halohydrocarbons are widely used in various branches of the chemical industry, firefighting, and medicine. Therefore, scientific interest in such substances remains extremely high at the present time. In particular, the C_3H_7I molecule, due to the presence of the weakest bond between halogen and carbon atom (C-I bond), is the most suitable precursor for the alkyl radical C_3H_7. These radicals, as it is known, are formed in significant quantities at the combustion and pyrolysis processes of normal alkanes, and without their correct prediction it is impossible to build physically based models of combustion of real hydrocarbon fuels.

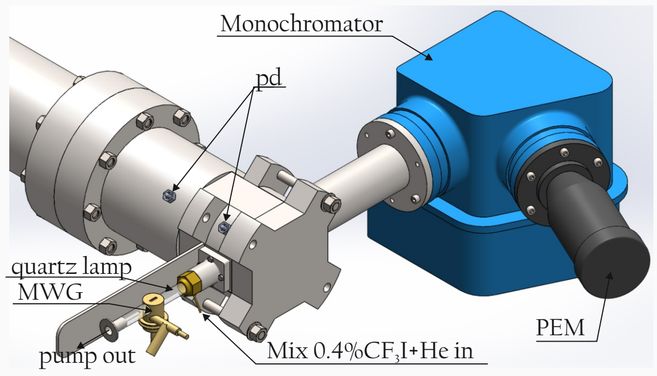
Goal of this work

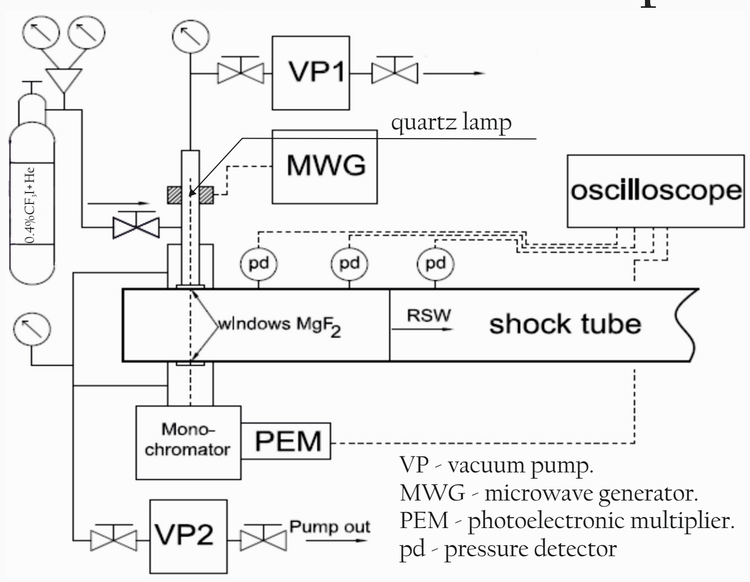
To study the kinetics of C_3H_7I dissociation and to obtain new experimental data about the it's dissociation rate constant over a wide temperature and pressure range.

Experiment

Scheme of ARAS measurements on «NEFRIT» set-up

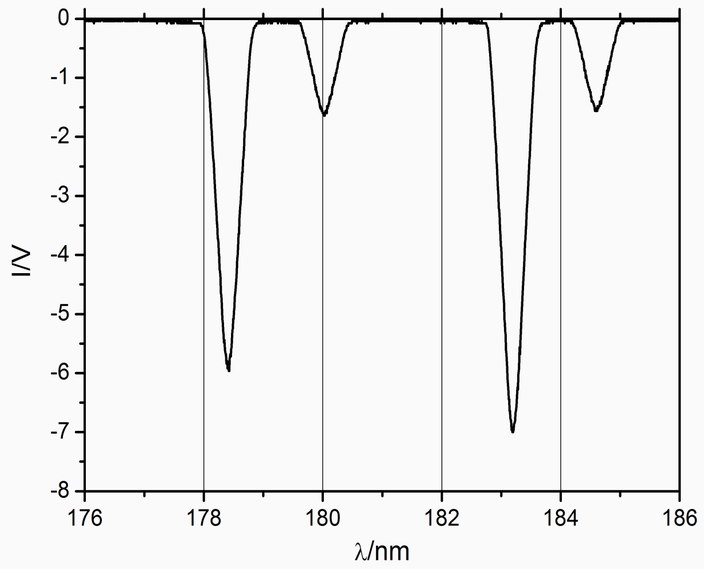
The parameters of the shock tube
Vacuum level: $4{\cdot}10^{-7}$ mbar leakage: $5{\cdot}10^{-6}$ mbar/min
Experimental conditions
Mixture: 0.8-1.1ppmC_3H_7I+Ar T=800 - 1200 K p=3.5±0.5 bar
Gas mixture in the quartz lamp:
0.4%CF_3I+He for the iodine atom ARAS at 183.0 nm





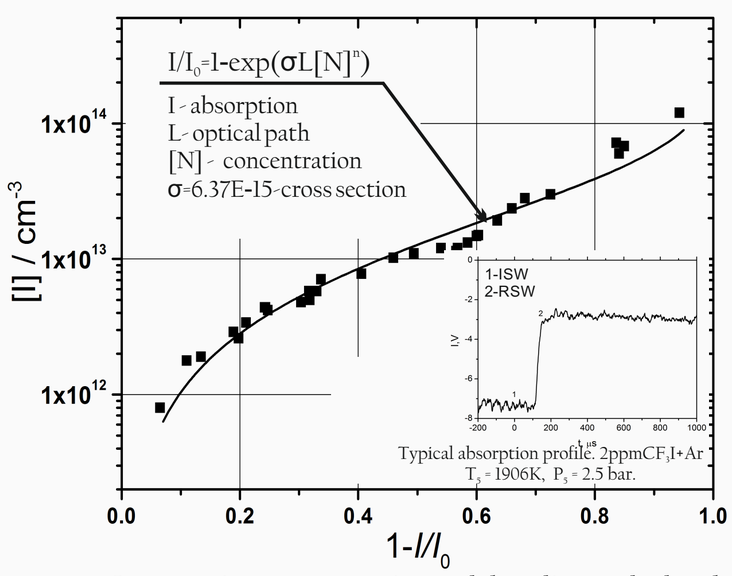
Calibration

Spectra of emission of resonance lines in the QL. Mixture of 0.4%CF_3I+He.



The strongest line corresponded to a wavelength of 180.0 nm

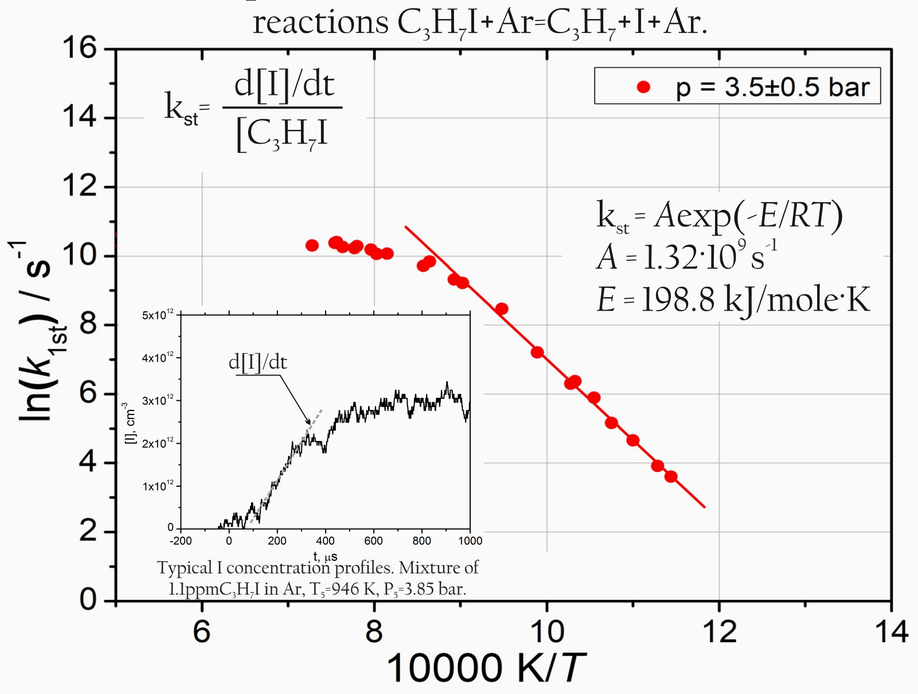
I–atom calibration curves for different mixtures of CF_3I in Ar



Square points - our experimental data; line - calculated the curve of the modified Beer-Lambert law.

Dissociation rate constant of C_3H_7I

Arrhenius dependence of the dissociation rate constant of reactions $C_3H_7I+Ar=C_3H_7+I+Ar$.

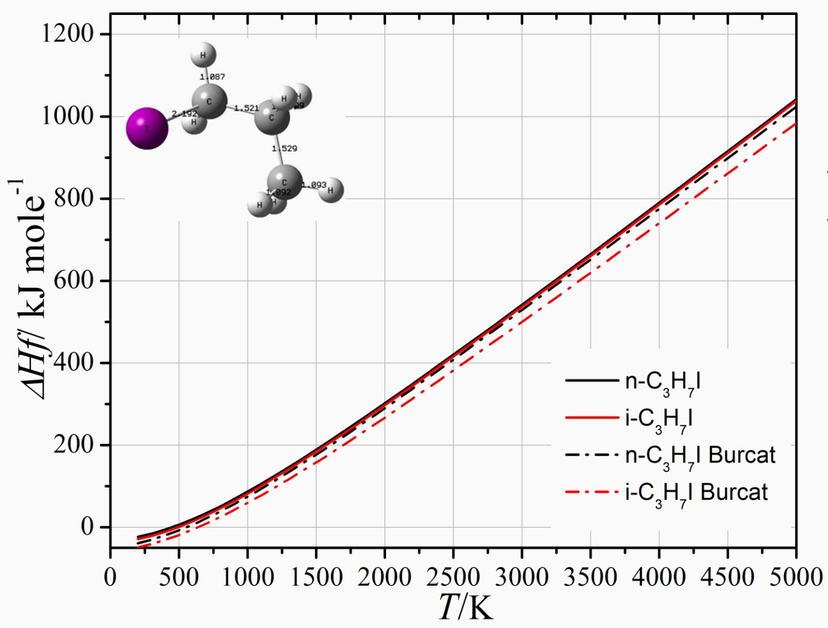


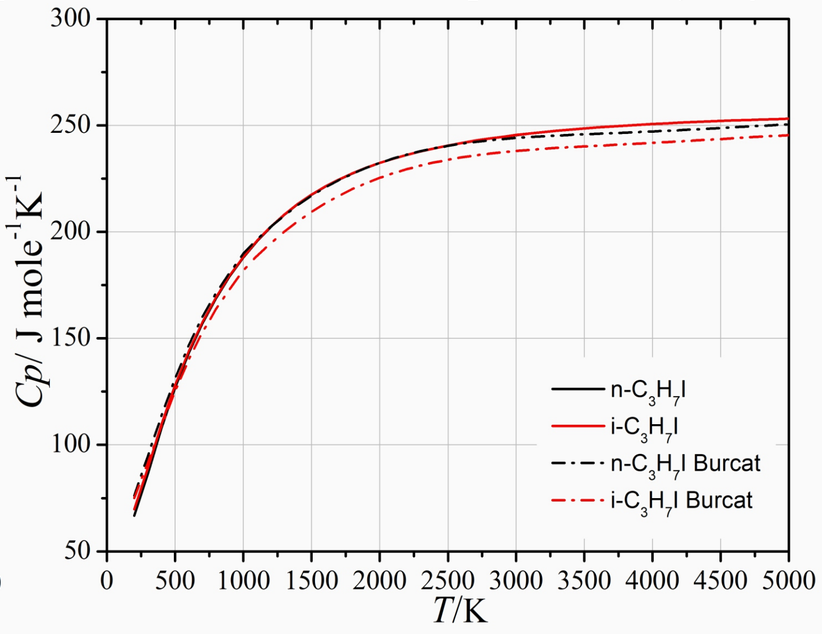
Thermodynamic properties

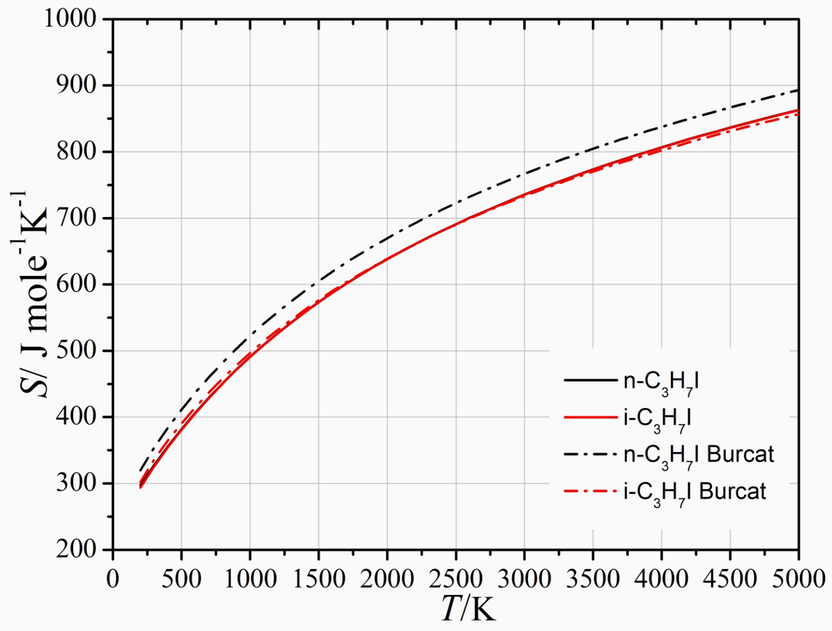
Standard enthalpy of formation ΔH_f^0, heat capacity at constant pressure C_p (T), and entropy S (T) of the n-C_3H_7I molecule depending on temperature

Method: B3LYP DFT Software package: Gaussian09, KiSThelP
Basic set: cc-pVTZ-PP Frequency factor: fvib = 0.970

Calculated bond fission C-I energy D(298 K)=214,8 kJ/mole







Conclusions

- On the basis of direct ARAS measurements, the values of the rate constant of the monomolecular dissociation of n-C_3H_7I were obtained for the first time in a wide temperature range. Its activation energy is determined and an Arrhenius form is obtained.
- It was concluded that the process of initial dissociation of propyl iodide under our experimental pressure range at elevated temperatures still does not reach the high-pressure limit.
- Thermodynamic characteristics such as entropy, heat capacity, and standard entropy of formation were determined for a wide temperature range using the electron density functional theory.

Acknowledgments

This work was supported by the Ministry of Science and Higher Education of the Russian Federation, agreement dated 09.29.2020 No. 075-15-2020-806