THERMODYNAMIC PROPERTIES OF n-C_3F_7I AND ITS MONOMOLECULAR DISSOCIATION UNDER SHOCK-TUBE HEATING

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Abstract: The time-resolved absorption profiles of atomic iodine during dissociation of 0.13–10 ppm n-C_3F_7I in Ar were measured by atomic resonance absorption spectroscopy at a wavelength of 183.04 nm. The studies were carried out on a kinetic shock tube behind incident and reflected shock waves at a temperature of 800–1200 K and a pressure of 0.6–8.3 bar. Based on the experimental data obtained, the rate constant of monomolecular dissociation of 1-perfluoropropyl iodide $C_3F_7I + (M) \rightarrow C_3F_7 + I + (M)$ was calculated. The following value of the rate constant in the form of Arrhenius dependence was obtained: $k_{1st}(\pm 30\%) = 1.05 \cdot 10^{14} \exp(-200.4\ [\text{kJ/mol}]/(RT))\ [\text{s}^{-1}]$. Along with the experiments, quantum-chemical calculations of the potential energy surfaces of the n-C_3F_7I molecule and its primary dissociation products were performed using the density functional theory. On the basis of calculations, such thermodynamic characteristics of n-C_3F_7I as the standard enthalpy of formation, entropy, and heat capacity, and also the standard enthalpy of reaction were determined. For these data, temperature dependences were obtained which were approximated in the form of a standard seven-parameter NASA polynomial.

Keywords: 1-perfluoropropyl iodide; enthalpy; entropy; heat capacity; monomolecular dissociation rate constant; shock tube; atomic resonance absorption spectroscopy; quantum chemical calculations

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Figure Caption

Figure 1 An example of the absorption profile at the wavelength of 183.04 nm. Mixture — 2.5 ppm C_3F_7I in Ar, $T_5 = 972$ K, and $p_5 = 2.53$ bar

Figure 2 Iodine atom concentration-time profile in the mixture of 4 ppm C_3F_7I in Ar: $T_5 = 1092$ K and $p_5 = 2.70$ bar. Black curve — experimental concentration profile; solid gray line — approximation of the concentration profile by Eq. (3) using the best value of k_{1st}; and upper and lower dash-dot lines — $1.3k_{1st}$ and $0.7k_{1st}$, respectively. Dotted line — initial slope

Figure 3 Temperature dependence of the first-order rate constant of monomolecular dissociation for the reaction $C_3F_7I + (M) \rightarrow C_3F_7 + I + (M)$ and data from previous works [3–5]: *1* — 0,6 bar; *2* — 2,5; *3* — 8,0 bar; *4* — n-C_3F_7I [3]; *5* — i-C_3F_7I [3]; *6* — n-C_3F_7I [4]; *7* — n-C_3F_7I [5]; and *8* — i-C_3F_7I [5]

Table Captions

Table 1 The values of the standard enthalpy of formation ΔH_f^0 as well as the heat capacities at constant pressure $C_p(T)$ and entropy $S(T)$ for n-C_3F_7I depending on temperature

Table 2 The NASA 7-coefficients polynomials for n-C_3F_7I for low and high temperature range

References

1. Hastie, J. W. 1973. Molecular basis of flame inhibition. *J. Res. Nat. Bur. Stand.* 77A:733–754.
2. Shebeko, Yu. N., V. V. Azatyan, I. A. Bolodian, *et al.* 2000. The influence of fluorinated hydrocarbons on the combustion of gaseous mixtures in a closed vessel. *Combust. Flame* 121:542–547.

3. Tedeev, R. S., B. P. Dymov, and G. A. Skorobogatov. 1989. Izmerenie konstanty ravnovesiya $RI = R + I$ dlya $R = n$-C_3F_7, i-C_3F_7 i konstanta skorosti dissotsiatsii $RI = R + I$ [Measurement of the equilibrium constant $RI = R + I$ for $R = n$-C_3F_7, i-C_3F_7 and the dissociation rate constant $RI = R + +I$]. *Vestnik of Leningrad University. Ser. 4* 1:37–42.
4. Dobychin, S. L., V. I. Mashendzhinov, V. I. Mishin, V. N. Semenov, and V. S. Shpak. 1990. Kinetika termicheskogo razlozheniya perftoralkiliodidov i energiya svyazi $D(R–I)$, gde $R = CF_3$, C_2F_5, n-C_3F_7, iso-C_3F_7, nC_4F_9, tert-C_4F_9 [Kinetics of thermal decomposition of perfluoroalkyl iodides and $D(R\text{-}I)$ binding energy, $R = CF_3$, C_2F_5, n-C_3F_7, iso-C_3F_7, nC_4F_9, and tert-C_4F_9]. *Dokl Akad. Nauk SSSR* 312:494–496.
5. Skorobogatov, G. A., B. P. Dymov, and R. S. Tedeev. 1991. Izmerenie konstant skorosti i konstant ravnovesiya $RI = R + I$, $I + RI = I_2 + R$ dlya $R = C_3F_7$, iso-C_3F_7, C_6F_{13}, $CF_3OCF_2CF_2$ ili $C_3F_7OCF_2CF_2$ [Measurement of rate constants and equilibrium constants of $RI = R + I$ and $I + RI = I_2 + R$ for $R = C_3F_7$, iso-C_3F_7, C_6F_{13}, $CF_3OCF_2CF_2$, or $C_3F_7OCF_2CF_2$]. *J. Gen. Chem. USSR* 61:158–165.
6. Kramida, A., Y. Ralchenko, J. Reader, and NIST ASD Team. 2014. NIST Atomic Spectra Database (ver. 5.2). Gaithersburg, MD: National Institute of Standards and Technology. Available at: http://physics.nist.gov/asd (accessed August 14, 2020).
7. Bystrov, N. S., A. V. Emelianov, A. V. Eremin, and P. I. Yatsenko. 2018. Direct measurements of rate coefficients for thermal decomposition of CF_3I using shock-tube ARAS technique. *J. Phys. D Appl Phys.* 51:181004.
8. Granovsky, A. A. Firefly V. 8.2.0. Available at: http://classic.chem.msu.su/gran/firefly/index.html (accessed October 2018).
9. Lee, C., W. Yang, and R. G. Parr. 1988. Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* 37:785.
10. Becke, A. D. 1993. Density–functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* 98:5648.
11. Peterson, K., B. Shepler, D. Figgen, and H. Stoll. 2006. On the spectroscopic and thermochemical properties of ClO, BrO, IO, and their anions. *J. Phys. Chem. A* 110:13877–13883.
12. Pritchard, B., D. Altarawy, B. Didier, T. Gibson, and T. Windus. 2019. A new basis set exchange: An open, up-to-date resource for the molecular sciences community. *J. Chem. Inf. Model.* 59(11):4814–4820.
13. Ochterski, J. W. 2009. *Thermochemistry in Gaussian*. Wallingford, CT: Gaussian Inc.
14. Curtiss, L., K. Raghavachari, P. Redfern, and J. A. People. 1997. Assessment of Gaussian-2 and density functional theories for the computation of enthalpies of formation. *J. Chem. Phys.* 106:1063.
15. Chase, M. W., Jr. 1998. NIST-JANAF themochemical tables. Fourth edition. *J. Phys. Chem. Ref. Data*. Monograph 9. 1961 p.
16. Bystrov, N., A. Emelianov, A. Eremin, B. Loukhovitski, A. Sharipov, and P. Yatsenko. 2019. Direct measurements of C_3F_7I dissociation rate constants using a shock tube ARAS technique. *Int. J. Chem. Kinet.* 51(3):206–214.
17. Gilbert, R. G., K. Luther, and J. Troe. 1983. Theory of thermal unimolecular reactions in the fall-off range. II. Weak collision rate constants. *Ber. Bunsen. Phys. Chem.* 87:168.

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