Monomolecular decomposition of C$_3$F$_7$I and CF$_3$I:
Theory meets experiment

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Abstract. For the first time, the rate constant of the thermal monomolecular decomposition of n-C$_3$F$_7$I in Ar was measured directly using the technique of atomic resonance absorption spectroscopy on a resonant line of iodine atom. Experiments were conducted behind the incident and reflected shock waves in a broad range of thermodynamic parameters ($T = 800–1200$ K and $P = 0.6–8.3$ bar). Experimental data were found to conform reasonably to the results of the Rice–Ramsperger–Kassel–Marcus theory master equation modeling based on the results of quantum chemical calculations. The obtained low- and high-pressure limiting rate constants for n-C$_3$F$_7$I and CF$_3$I dissociation in Ar were reported. Third body efficiencies for Kr were also evaluated.

1. Introduction

This work is virtually a continuation of the series [1–3] devoted to the investigation of dissociation kinetics of various halocarbons by using the precision methods of atomic or molecular resonance absorption spectrometry (ARAS or MRAS). Fundamental interest in these substances is invoked by the broad range of their technological applications, specifically, for fire protection [4,5]. Note that according to the Montreal Convention, the ozone-depleting compounds, in particular, the most effective bromine-containing freons, such as 13B1 (CF$_3$Br), 114B2 (C$_2$F$_4$Br$_2$), and 12B1 (CF$_3$CBr), today are forbidden in practice. Hence, the search for the new reactive additives to combustible compositions, well-suppressing chain processes, and, consequently, ignition and detonation in different hydrocarbon–air mixtures, is of vital importance [5,6]. Iodine-containing halogenated hydrocarbons (such as CF$_3$I, C$_2$F$_5$I, and C$_3$F$_7$I), thanks to their absolute ozone-friendliness and perfect service properties, despite their high cost, can be a prospective substitute for bromine-containing freons. Thus, the perfluoropropyl iodide n-C$_3$F$_7$I was chosen for the present kinetics study.

As far as we know, there are no published works devoted to direct measurements of the rate constant of monomolecular decomposition of C$_3$F$_7$I. Although there are a number of works [7–9] that investigate the dissociation kinetics of n-C$_3$F$_7$I or i-C$_3$F$_7$I in a narrow temperature and pressure ranges employing an isothermal pyrolysis method, the techniques applied there did not...
provide the direct measurement of the primary decomposition process. In compliance with these data, the primary decomposition proceeds via the reaction

\[ \text{C}_3\text{F}_7\text{I} + (\text{M}) \rightarrow \text{C}_3\text{F}_7 + \text{I} + (\text{M}), \tag{1} \]

because the C–I bond is definitely the weakest bond in the molecule. We also note that the lack of experimental kinetic data on the dissociation of allyliodides is inherent in the entire spectrum of homologues \( \text{C}_n\text{F}_{2n+1}\text{I} \), perhaps, except for the simplest trifluorodiiodomethane [1]. Accordingly, the further study of the reaction kinetics of larger iodine-containing halogenated hydrocarbons is highly desirable. The specific goal of the present study was to treat reaction (1) using the Rice–Ramsperger–Kassel–Marcus theory master equation (RRKM ME) analysis and to compare these findings with the direct kinetic data measured at high-temperatures and at a broad range of pressures applying the highly sensitive ARAS technique.

2. Experiment
All experiments were conducted in a high-vacuum kinetic shock tube. Details of the experimental setup as well as the features of the preparation of working gas mixtures are described in detail in [1]. Temporal profiles of iodine atom concentration were measured in the visible-uv range of the spectrum at a wavelength 183.04 nm, which corresponds to the transition \( \text{I}(^{4}P_{5/2} - ^{2}P_{3/2}) \). As a source of resonance radiation of iodine atoms, a microwave discharge lamp was used.

To determine the dependence of the absolute concentration of atomic iodine on its absorption, a series of calibration measurements was performed, as in [1]. Trial measurements were carried out in mixtures with initial mole fractions of \( \text{CF}_3\text{I} \) in \( \text{Ar} \) from 1 to 4 ppm, temperatures above 1300 K and pressures behind the incident and reflected shock waves from 0.27 to 2.7 bar. At such conditions, the iodine atom is supposed to be in a free state [1]. The spectral resolution of a monochromator (0.4 nm) was restricted by the presence of nearby atomic lines or bands of the \( \text{CF}_3 \) and \( \text{CF}_2 \) radicals. The lowest detected number density of the iodine atoms at a given arrangement of ARAS measurements was about \( 10^{12} \) cm\(^{-3} \). The lower and the upper (about \( 10^{14} \) cm\(^{-3} \)) detection limits were specified by the noise of the detection system and by saturation of the optical transition, respectively.

3. Results and discussion
The basic measurements of the temporal profiles of iodine atom concentration in the course of the \( \text{C}_3\text{F}_7\text{I} \) dissociation were carried out in mixtures of 0.13–10 ppm \( \text{C}_3\text{F}_7\text{I} \) in \( \text{Ar} \) at temperatures of 800–1200 K and pressures of 0.6–8.5 bar. The absorption was registered behind both the incident and the reflected shock waves. As stated above, under conditions of such a strong dilution of the substance under study, the only important source of atomic iodine at the time of observation is the reaction of \( \text{C}_3\text{F}_7\text{I} \) dissociation (1). In this case, the evolution of iodine concentration is governed by a single differential equation

\[ \frac{d[I]}{dt} = k_{2\text{nd}}[\text{C}_3\text{F}_7\text{I}][\text{Ar}]. \tag{2} \]

The derivative \( d[I]/dt \) in equation (2) was determined by initial slope method.

The upper temperature limit of reliable measurements was about 1200 K since at higher temperatures the dissociation time of \( \text{C}_3\text{F}_7\text{I} \) is too small. At such reaction rates, the limited time resolution of the experimental setup (about 20 \( \mu \)s) did not allow us to measure the derivative \( d[I]/dt \) and, correspondingly, the sought-for rate constant accurately. The inaccuracy in the experimentally obtained values of the rate constant did not exceed 30%. The main error in the measured rate constant was due to the uncertainty of the calibration curve and by the approximation of the absorption profile (up to 15% and 8%, respectively).

Figure 1 displays the obtained experimental data on the rate constants of reaction (1) in the second-order dimension \( k_{2\text{nd}} \) at different pressures. Here one can observe a generally typical
dependence of the bimolecular decomposition rate constant on pressure: a higher pressure corresponds approximately to a proportionally smaller constant $k_{2nd}$.

Next, we compare the obtained ARAS measurements with the theoretical estimates of RRKM. Thereby, first of all, the activation energy of the process (1) must be definitely determined. Since the activation energy for this dissociation reaction is supposed to be equal to its enthalpy, special attention should be paid to the accurate as possible determination of its dissociation energy $D$.

In the present study, density functional theory (DFT) calculations were done to explore the potential energy surface (PES) relevant to n-C$_3$F$_7$I dissociation. Following Fortin et al [10], the geometries of stationary points on the PES were optimized with the B3LYP DFT functional [11] in the correlation consistent polarized triple zeta basis set cc-pVTZ-PP of Peterson et al with the pseudopotential for the core electrons of iodine atom [12, 13]. When applying gradient optimization of the structure, the DFT electronic energies were augmented with an empirical dispersion correction [14] that can be vitally important to reach the so-called chemical accuracy ($\approx 1$ kcal mol$^{-1}$) for relatively large molecular systems [15, 16].

Routine harmonic frequency analysis was performed at the same level of theory for the PES minima in order to provide the vibrational frequencies required for RRKM ME modeling and to evaluate the zero-point energy of the molecules under consideration. The heights of torsion barriers necessary for RRKM calculations were assessed using the relaxed PES scan technique using the B3LYP/cc-pVTZ-PP level of consideration. All DFT calculations were conducted by using Firefly QC program package [17], which is partially based on the GAMESS (US) source code [18].

The obtained values of dissociation energy of the singlet n-C$_3$F$_7$I molecule into doublet C$_3$F$_7$ and I($^2P$) are listed in table 1. In order to ensure that the sufficient accuracy for $D|_{0K}$ and $D|_{298K}$ values is attained in this case, the respective values for the CF$_3$I molecule are also given here. Notice that the obtained $D|_{298K}$ magnitude for CF$_3$I coincides well with the available thermochemical values (225.6 kJ mol$^{-1}$ [19] and 228.6 kJ mol$^{-1}$ [20]) that support the reasonability of the usage of the current computational scheme. Note also that the only
available in literature theoretical study of the dissociation energy in the C₃F₇I molecule [21] gives a slightly lower value D (from 201 to 213 kJ mol⁻¹, depending on the level of treatment) than was obtained at the B3LYP/cc-pVTZ-PP level of treatment in the present study, however the data [21] are relevant to another (i-C₃F₇I) isomeric form of iodoperfluoropropane.

To evaluate the corresponding pressure-dependent rate constants, we performed a routine RRKM ME analysis using the ChemRate program package [22, 23]. Energy-dependent rate constants for the C–I bond fission were obtained using the procedure for loose transition state RRKM ME analysis using the ChemRate program package [22, 23]. Energy-dependent rate dependence of corresponding rate constant is given in figure 2.

Figure 1 shows the calculated temperature dependences for the dissociation rate constants of n-C₃F₇I at various pressures. As one can see, quite a good agreement has been reached between theoretical predictions and the kinetic experiment (especially, at lower pressures). Thus, theoretical calculations can be considered reliable and applicable to extrapolation over a wide range of temperatures and pressures.

The calculations of the effective rate constant for the subsequent bivariate fitting were carried out for dissociation of n-C₃F₇I in Ar in the following range of thermodynamic parameters: $T = 300–3000$ K, $P = 10^{-4}–10^{2}$ bar. The obtained temperature and pressure dependences $k_{2nd}$ were elaborated in the well-known Troe form [29]:

$$k_{2nd} = \frac{k_0[M]k_\infty}{k_0[M] + k_\infty} F,$$

where $c = -0.4 - 0.67 \log F_c$, $n = 0.75 - 1.27 \log F_c$, $d = 0.14$; $k_0$ and $k_\infty$ are the limiting low- and high-pressure rate constants; $F_c$ is the broadening factor; $R$ is the universal gas constant; $[M]$
is the molar density. Note that this form of constant approximation [29] given by equations (3) to (4) allows for the fact that at high pressure limit, the effective rate constant in the second order dimension $k_{2nd}$ becomes independent on the molar density $[M]$. The approximation for CF$_3$I dissociation rate constant presented in figure 2 was elaborated analogously. The obtained coefficients for reactions of dissociation of n-C$_3$F$_7$I and CF$_3$I in Ar bath gas are presented in table 2.

However, the fact the experimental studies of the present work and in [1] were carried out in Ar only partially detracts from the significance of the results obtained, since the obtained rate constants cannot be straightforwardly converted for other bath gases. The point is that in other bath gases, vibrational relaxation of excited complexes n-C$_3$F$_7$I$^*$ and CF$_3$I$^*$ can proceed quite differently than in argon. In this regard, it would be desirable to describe, as far as possible, the available experimental data in other gases.

In particular, in [27,28], the decomposition of CF$_3$I was registered in Kr. In order to describe quantitatively these data (see figure 2), the following parameters of the simple exponential-down model for collisional energy transfer (together with the collision parameters given in table 1) were selected: $\alpha_0 = 450$ cm$^{-1}$, $\alpha_1 = 0.2$ (cm K)$^{-1}$. Note that the chosen value of $\alpha(T)$ on Kr, substantially larger than on Ar, is in remarkable agreement with the findings [27,28]. The obtained theoretical decomposition rate constant on Kr can be expressed via the rate constant on

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{The measured [1,27,28] (symbols) and calculated (curves) temperature dependences of the second-order rate constant for process (1) with M = Ar and Kr process for different pressures.}
\end{figure}

\begin{table}[h]
\centering
\caption{Reactions rate constants coefficients.}
\begin{tabular}{ccccccc}
Molecule & $A_0$, cm$^3$(mol s)$^{-1}$ & $n_0$ & $E_{a0}$, K & $A_{\infty}$, s$^{-1}$ & $n_{\infty}$ & $E_{a\infty}$, K & $F_c$ \\
--- & --- & --- & --- & --- & --- & --- & --- \\
n-C$_3$F$_7$I & $8.849 \times 10^{10}$ & -1.444 & 11454.4 & $9.676 \times 10^{16}$ & -0.378 & 26956.8 & 0.119 \\
CF$_3$I & $1.855 \times 10^{30}$ & -3.967 & 26433.8 & $1.581 \times 10^{30}$ & -4.728 & 29814.9 & 1 \\
\end{tabular}
\end{table}
Ar applying the third-body efficiency $E = 3.5$ (relative to Ar). If we assume that the deactivation of n-C$_3$F$_7$I* in Kr is described by the same temperature dependence as the deactivation of CF$_3$I*, the third-body efficiency for reaction (1) in Kr can also be obtained by using RRKM ME analysis ($E = 5.7$).

4. Conclusion

Employing the accurate ARAS technique on the iodine atom line at 183.04 nm, the rate constant of thermal decomposition of C$_3$F$_7$I in Ar at a temperature range of 800–1200 K and pressures of 0.6–8.5 bar was measured. Numerical RRKM ME calculations in a wide temperature and pressure ranges were implemented and the values of the limiting low- and high-pressure rate coefficients were derived. The coincidence of obtained RRKM ME results with the obtained experimental data was proven to be reasonable (especially, for low and moderate pressures). The effective rate constants in the Troe form were reported. The third-body efficiency for Kr as a bath gas was also estimated.

References

[1] Bystrov N S, Emelianov A V, Eremin A V and Yatsenko P I 2018 J. Phys. D: Appl. Phys. 51 184004
[2] Bystrov N S, Emelianov A V, Eremin A V and Yatsenko P I 2018 J. Phys.: Conf. Ser. 946 012069
[3] Emelianov A V, Eremin A V and Yatsenko P I 2018 J. Phys.: Conf. Ser. 946 012070
[4] Hastie J W 1973 J. Res. Natl. Bur. Stand. 77A 733–54
[5] Shebeko Y N, Azatyan V V, Bolodian I A, Navzzenya V Y, Kopylov S N, Shebeko D Y and Zaminshevski E D 2000 Combust. Flame 121 542–7
[6] Drakon A V, Eremin A V, Matveeva N A and Mikheyeva E Yu 2017 Combust. Flame 176 592–8
[7] Tedeve R S, Dynov B P and Skorobogatov G A 1989 Vests. Leningr. Univ., Ser. 4: Fiz., Khim. 1 37–42
[8] Dobygin S L, Mashendzhinov V I, Mishin V I, Semenov V N and Shpak V S 1990 Dokl. Phys. Chem. 312 494–6
[9] Skorobogatov G A, Dynov B P and Tedeve R S 1991 Russ. J. Gen. Chem. 61 158–65
[10] Fortin C, Khanniche S, Khiri D, Fevre-Nollet V, Lebegue P, Cousin F, Cermusak I and Louis F 2018 J. Phys. Chem. A 122 1053–63
[11] Becke A D 1993 J. Chem. Phys. 98 5648–53
[12] Peterson K A, Shepler B C, Figgen D and Stoll H 2006 J. Phys. Chem. A 110 13877–83
[13] EMSL Basis Set Exchange Library URL https://bse.pnl.gov/bse/portal
[14] Grimme S, Antony J, Ehrlich S and Krieg H 2010 J. Chem. Phys. 132 154104
[15] Schwabe T and Grimme S 2007 Phys. Chem. Chem. Phys. 9 3397–406
[16] Sharipov A S and Starik A M 2015 J. Phys. Chem. A 119 3897–904
[17] Granovsky A A 2016 Firefly, version 8.2.0 URL http://classic.chem.msu.su/gran/firefly/index.html
[18] Schmidt M W, Baldridge K K, Boatz J A, Elbert S T, Gordon M S, Jensen J H, Koseki S, Matsunaga N, Nguyen K A, Su S, Windus T L, Dupuis M and Montgomery J A 1993 J. Comput. Chem. 14 1347–63
[19] Afeefy H Y, Liebman J F, Stein S E and Burgess Jr D B 2018 NIST Chemistry WebBook, NIST Standard Reference Database Number 69 (Gaithersburg, MD: National Institute of Standards and Technology) chapter Neutral Thermochemical Data
[20] Rusci B and Bross D H 2016 Active Thermochemical Tables (ATcT) values based on version 1.122 of the Thermochemical Network URL https://atct.anl.gov/
[21] Cheng L, Shen Z, Lu J, Gao H and Lu Z 2005 Chem. Phys. Lett. 416 160–4
[22] Knyazev V D and Tsang W 2000 J. Phys. Chem. A 104 10747–65
[23] Mokrushin V, Bedanov V, Tsang W, Zacharias M, Knyazev V and McGivern W S 2011 ChemRate, version 1.5.10 URL http://kinetics.nist.gov/ChemRate
[24] Benson S W 1976 Thermochemical Kinetics (Wiley: New York)
[25] Sharipov A S, Loukhovitski B I, Tsai C J and Starik A M 2014 Eur. Phys. J. D 68 99
[26] Cambi R, Cappelletti D, Liuti G and Pirani F 1991 J. Chem. Phys. 95 1852–62
[27] Kumaras S S, Su M C, Lim K P and Michael J V 1995 Chem. Phys. Lett. 243 59–63
[28] Kiefer J H and Sathyanarayana R 1997 Int. J. Chem. Kinet. 29 705–16
[29] Gilbert R G, Luther K and Troe J 1983 Ber. Bunsenges. Phys. Chem. 87 168