updates

WILEY

# ARTICLE

# Direct measurements of C<sub>3</sub>F<sub>7</sub>I dissociation rate constants using a shock tube ARAS technique

Nikita Bystrov<sup>1,2</sup> | Alexander Emelianov<sup>1</sup> | Alexander Eremin<sup>1</sup>  $\bigcirc$  | Boris Loukhovitski<sup>3</sup> |

Alexander Sharipov<sup>3</sup> | Pavel Yatsenko<sup>1,2</sup>

<sup>1</sup>Joint Institute for High Temperatures of the Russian Academy of Sciences, Moscow, Russia

<sup>2</sup>Bauman Moscow State Technical University, Moscow, Russia

<sup>3</sup>Central Institute of Aviation Motors, Moscow, Russia

#### Correspondence

Alexander Eremin, Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg. 2, Moscow 125412, Russia. Email: eremin@ihed.ras.ru

**Funding information** 

Russian Science Foundation, Grant/Award Number: 14-19-00025P

# Abstract

This work presents the first direct experimental study on the thermal unimolecular decomposition of n-C<sub>3</sub>F<sub>7</sub>I. Experiments were performed behind incident and reflected shock waves using the atomic resonance absorption spectroscopy (ARAS) technique on a resonant line of atomic iodine at 183.04 nm. The reaction  $C_3F_7I + Ar \rightarrow C_3F_7 + I + Ar$  (1) was studied at specific temperature (800–1200 K) and pressure (0.6-8.3 bar) ranges. Under experimental conditions, the obtained values of the rate constant at temperatures below 950 K are close to the high-pressure limit; however, considering theoretical calculations, the influence of pressure on the rate constant at elevated temperatures remains noticeable. The resulting value of the experimental rate constant of reaction 1 is presented in the following Arrhenius form:

$$k_{1st}(\pm 30\%) = 1.05 \times 10^{14} \exp(-200.4 \text{ kJ} \cdot \text{mol}^{-1}/RT) (\text{s}^{-1})$$

Experimental data were found to correlate with the results of the Rice-Ramsperger-Kassel-Marcus -master equation analysis based on quantum-chemical calculations. The following low- and high-pressure limiting rate coefficients were obtained over the temperature range T = 300-3000 K:

$$k_0 \left( n - C_3 F_7 I + Ar \right) = 8.849 \times 10^{19} T^{-1.444} \exp\left(-11,454.4/T\right) (\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}) \text{ and}$$
  
 $k_\infty \left( n - C_3 F_7 I \right) = 9.676 \times 10^{16} T^{-0.378} \exp\left(-26,956.8/T\right) (\text{s}^{-1})$ 

with the center broadening factor  $F_c = 0.119$ .

#### **KEYWORDS**

atomic resonance absorption spectroscopy, chemical kinetics, density functional theory, dissociation rate constant, perfluoropropyl iodide, Rice-Ramsperger-Kassel-Marcus/master equation, shock tube

# **1 | INTRODUCTION**

This work is a continuation of a number of works<sup>1-4</sup> on the study of the kinetics of dissociation of various halocarbons using the precision method of atomic or molecular resonance absorption spectrometry. Scientific interest in these substances is high due to the broad range of their technical and industrial applications. In particular, different freons are used for effective fire protection.<sup>5,6</sup> Note that according to the Montreal Convention, the use of ozone-depleting compounds, in particular, the most effective bromine-containing freons, such as 13B1 (CF<sub>3</sub>Br), 114B2 (C<sub>2</sub>F<sub>4</sub>Br<sub>2</sub>), and 12B1 (CF<sub>2</sub>ClBr), nowadays is forbidden. Therefore, the search for the new chemically active additives to combustible mixtures, well-inhibiting ignition, and detonation processes in different hydrocarbon-air mixtures,<sup>6,7</sup> is very topical. Iodine-containing halogenated hydrocarbons (e.g.,  $CF_3I$ ,  $C_2F_5I$ ,  $C_3F_7I$ ), because of their complete ozone-friendly and perfectly suitable physical properties in spite of their high cost, can be a prospective substitute for brominated-containing freons. Therefore, the perfluoropropyl iodide  $n-C_3F_7I$  was chosen for a detailed study of its kinetic properties.

To the best our knowledge, there are no works in which the unimolecular decomposition rate constant of  $C_3F_7I$  has been directly determined. There are only three works<sup>8–10</sup> that investigate the dissociation kinetics of n- $C_3F_7I$  or *i*- $C_3F_7I$ . All previous studies were carried out using an isothermal pyrolysis method. The temperature range investigated by Dobychin et al.<sup>9</sup> was 380–480 K, and in other works<sup>8,10</sup> it was 560–700 K. The pressure was 0.59 bar in two studies,<sup>8,10</sup> and it was varied from 0.04 to 0.4 bar in another study.<sup>9</sup> All authors also indicated that the high-pressure limit for rate constants was experimentally reached. According to these data, the primary decomposition proceeds through the reaction

$$C_3F_7I + (M) \rightarrow C_3F_7 + I + (M)$$
 (1)

because the C–I bond is by far the weakest bond in the molecule. However, the method applied in works<sup>8–10</sup> does not directly measure the reaction rate constant (1). The observation was carried out for molecular I<sub>2</sub>, which was formed in various secondary reactions at large initial concentrations of  $C_3F_7I$  (from 3%  $C_3F_7I$  in Ar to no diluted  $C_3F_7I$ ). In this case, the correct consideration of all reactions is quite difficult and could lead to inaccuracies.

It is also worth noting that the deficit of experimental kinetic data on the alkyl iodides dissociation is characteristic of the whole range of homologues of  $C_nF_{2n+1}I$ , except for the simplest trifluorodiodomethane.

The CF<sub>3</sub>I molecule has been studied quite well by various methods in a wide temperature range (from 400 to 3000 K) at fairly low pressures (from 0.04 to 11 bar). After the publication of the first work of Modica and Sillers,<sup>11</sup> a series of studies<sup>12–14</sup> by stationary pyrolysis in the low-temperature region followed. The first direct measurements of the dissociation of CF<sub>3</sub>I by detecting the CF<sub>3</sub> radical were carried out by Saito et al.<sup>15</sup> at a wavelength of  $290 \pm 1.5$  nm. Brouwer and Troe<sup>16</sup> and Zaslonko et al.<sup>17</sup> determined the primary dissociation rate constant of trifluorodiodomethane directly by the change in the concentration of CF<sub>3</sub>I itself in the range of 230-350 and 316 nm, respectively. Kumaran et al.<sup>18</sup> studied a mixture of CF<sub>3</sub>I with Kr and used the atomic resonance absorption spectroscopy (ARAS) method to observe atomic iodine in the spectral range of 165-185 nm. The high-temperature region was experimentally studied in the work of Kiefer and Sathyanarayana<sup>19</sup> using the schlieren method. A theoretical calculation of the CF<sub>3</sub>I dissociation rate constant by the Rice-Ramsperger-Kassel-Marcus theory (RRKM) was also carried out in this work under the corresponding experimental conditions. In our recent work,<sup>1</sup> direct ARAS measurements of the dissociation rate constant of this molecule on the resonance line of atomic iodine at 183.04 nm were carried out. This paper<sup>1</sup> contains a detailed analysis of all previously published data and summarizes the results obtained.

The kinetics of  $C_2F_5I$  dissociation<sup>9,20,21</sup> was studied by the same groups of coauthors as the  $C_3F_7I^{8-10}$  molecule. To determine the rate constant, Zaslonko et al.<sup>21</sup> detected the iodine molecule in a wide spectral range of 500–800 nm behind shock waves at a temperature of 600–1400 K. Dobychin et al.<sup>9</sup> and Skorobogatov et al.<sup>20</sup> used the stationary pyrolysis method; therefore, their kinetic data are only available in the low-temperature regions (380–480 and 610–790 K, respectively).

In addition, the same papers present the dissociation rate constants at low temperatures for such molecules as  $C_4F_9I^{9,20}$  and  $C_6F_{13}I^{10}$ 

Data on other fluoroalkyl iodides could not be found in the existing literature. Therefore, in the future, the study of the kinetic properties of larger iodine-containing halogenated hydrocarbons should be continued. The specific goal of the present study was to obtain the direct kinetic data on reaction (1) at high temperatures (T > 800 K) and at a wide range of pressures using the highly sensitive ARAS technique and to compare these data with the results of the RRKM-based master equation (RRKM/ME) analysis.

# 2 | EXPERIMENTAL INSTALLATION

All experiments were carried out in a high-vacuum kinetic shock tube with an internal diameter of 108 mm and made of stainless steel. The driven and driver sections of the shock tube were 6 and 2 m long, respectively. The high sensitivity of the ARAS measurements requires high purity of substances. Therefore, the driven section was pumped out successively by scroll oil-free and turbo-molecular pumps up to a pressure of  $4 \times 10^{-7}$  mbar. The leakage did not exceed  $10^{-6}$  mbar min<sup>-1</sup>. Only pure gas components were used at the composition of the gas mixtures studied: Ar (Linde Gas Rus): 99.9999%, CF<sub>3</sub>I: 99%, and *n*-C<sub>3</sub>F<sub>7</sub>I: 96% (both P&M Invest). The *i*-C<sub>3</sub>F<sub>7</sub>I isomer is the main impurity to n-C<sub>3</sub>F<sub>7</sub>I. All other impurities are less than 1%. No further purification was carried out. The experimental setup is described in more detail elsewhere.1 Iodine atom concentration-time profiles were measured in the vacuum ultraviolet (VUV) range of the spectrum at a wavelength 183.04 nm, which corresponds to the transition I  $({}^{4}P_{5/2} - {}^{2}P_{3/2})$ .<sup>22</sup> As a source of resonance radiation of iodine atoms, a microwave discharge lamp with the flow of 0.4% CF<sub>3</sub>I in He at 6 mbar of pressure and excited by a 60-W microwave discharge was used. The radiation from the microwave discharge lamp was recorded using an Acton



**FIGURE 1** Calibration curve showing the dependence of absorption on  $\lambda = 183.04$  nm on the concentration of iodine atoms. Square: experimental data, line: modified Lambert–Beer equation

VM-502 vacuum monochromator and a PMT-181 (*MELF*) detector.

# **3 | CALIBRATION MEASUREMENTS**

To determine the absolute dependence of concentration of atomic iodine on its absorption, a series of calibration experiments were performed in our previous work.<sup>1</sup> Calibration measurements were carried out in mixtures with varying initial concentrations of CF<sub>3</sub>I in 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 temperatures, the iodine atom is known to be in a free state as a result of the complete dissociation of the CF<sub>3</sub>I molecule.<sup>1</sup> The spectral resolution of the monochromator was 0.4 nm and was determined by the presence of nearby lines of a given atom or bands of the CF<sub>3</sub> and CF<sub>2</sub> radicals. Within the VUV lamp, self-absorption at the resonance frequency occurs causing a self-reversal of the emission profile. Moreover, the emission line can be broader then the absorption line of the detected I atoms. Therefore, the Lambert-Beer law is not directly

$$A = 1 - \exp\left[-\left(\sigma l[\mathbf{I}]^n\right)\right] \tag{2}$$

where A is the measured absorption, l is the optical length in cm, [I] is the iodine atoms concentration in cm<sup>-3</sup>, and  $\sigma$ and n are the fitting parameters providing the best correlation of expression (2) with the measurements. The best agreement with the experimental data is observed for  $\sigma = 8.64 \times 10^{-12}$  cm<sup>1.25</sup> and n = 0.75.

The lowest detected concentration of the iodine atoms at a given arrangement of ARAS measurements was about  $10^{12}$  cm<sup>-3</sup> (Figure 1). The lower and the upper (about  $10^{14}$  cm<sup>-3</sup>) detection limits are due to noise of the detection system and to saturation of the optical transition, respectively.

# **4 | RESULTS AND DISCUSSION**

The basic experiments measuring the time profiles of the iodine concentrations during the dissociation of  $C_3F_7I$  were carried out in mixtures of 0.13–10 ppm  $C_3F_7I$  in Ar at temperatures of 800–1200 K and pressures of 0.6–8.3 bar. The absorption was registered both behind the incident and behind the reflected shock wave.

Typical absorption profiles at different pressures and similar temperatures are shown in Figure 2. Figure 2 shows an increase in the resonant absorption of atomic iodine followed by relatively steady values. It is noteworthy that the rate of the absorption growth is approximately the same at different pressures. Using a calibration curve given in Figure 1, the atomic iodine concentration profiles were obtained for all experiments (see example in Figure 3). Taking into account the extremely low concentration of  $C_3F_7I$ , secondary reactions could be ignored, and a steady level of iodine concentration at late reaction times indicates the complete decomposition of  $C_3F_7I$ .



**FIGURE 2** Typical examples of an absorption profile at wavelength 183.04 nm. Experimental conditions: (a) 2.5 ppm  $C_3F_7I$  in Ar,  $T_5 = 972$  K,  $P_5 = 2.53$  bar. b) 1 ppm  $C_3F_7I$  in Ar,  $T_5 = 976$  K,  $P_5 = 7.85$  bar

WILEY



**FIGURE 3** Iodine atom concentration–time profile:  $T_5 = 1092$  K,  $P_5 = 2.70$  bar at 4 ppm C<sub>3</sub>F<sub>7</sub>I in Ar. Solid red line: approximation of concentration profile by Equation 4 using the best  $k_{1st}$ value. Upper and lower dash-dotted lines:  $1.3 \times k_{1st}$  and  $0.7 \times k_{1st}$ respectively. Dashed line: initial slope [Color figure can be viewed at wileyonlinelibrary.com]

As mentioned above, under conditions of such a strong dilution, the only significant channel of the formation of iodine at a characteristic observation time is the reaction of  $C_3F_7I$  dissociation (1). In these conditions, the time profile of the iodine concentration can be described by a differential equation:

$$d\left[\mathrm{I}\right]/dt = k_{2\mathrm{nd}} \left[\mathrm{C}_{3}\mathrm{F}_{7}\mathrm{I}\right] \left[\mathrm{Ar}\right]$$
(3)

or under the assumption of a first-order reaction:

$$d\left[\mathrm{I}\right]/dt = k_{1\mathrm{st}}\left[\mathrm{C}_{3}\mathrm{F}_{7}\mathrm{I}\right].$$
(4)

Table 1 provides a list of the experimental conditions as well as the values of the experimental rate constants obtained from approximation of experimental iodine atom concentration profiles by Equations (3) and (4). For all experiments, the determination of the derivative  $d[\Pi]/dt$  in Equations 3 and 4 was carried out using an initial slope method, where the angle between the concentration profile and the *t*-axis at the initial time is used (see the dashed line in Figure 3). The concentration  $[C_3F_7I]$  at an initial time is practically equal to the known initial concentration  $[C_3F_7I]_0$ ; therefore, in expressions (3) and (4), the concentration  $[C_3F_7I]$  is approximately equal to  $[C_3F_7I]_0$ . In addition to estimating the possible inaccuracy of this method, in some experiments the first-order rate constant  $k_{1st}$  was directly derived from  $\ln[\ln(I_t/I_{\infty})/\ln(I_0/I_{\infty})] = -k_{1st} t$ , where  $I_0$ ,  $I_t$ ,  $I_\infty$  are intensities at time t = 0, t, and  $\infty$ , respectively. Alternative analysis was only used for those experiments where the absorption value did not exceed 50%, since the present equation assumes following the Lambert-Beer law. Despite the fact that we used the modified Lambert-Beer law to describe the whole range of experimental points, this condition is well satisfied for low absorption values.<sup>1</sup> It is notable that both methods resulted in practically the same values of the rate constants. The upper temperatures of reliable measurements were about 1200 K since at temperatures above 1200 K the dissociation time of C<sub>3</sub>F<sub>7</sub>I is too fast. At such reaction rates, the limited time resolution of the experimental setup (about 12  $\mu$ s) did not allow us to accurately measure the derivative d[I]/dt and, correspondingly, the rate constant. The inaccuracy of the experimentally obtained values of the rate constant did not exceed 30%. The majority of the error was due to the uncertainty of the calibration curve and by the approximation of the absorption profile (up to 15%and 8%, respectively). Figure 3 shows the calculation of the atomic iodine concentration profile using the experimentally obtained rate constant in the same conditions. Figure 3 also shows the concentration profiles, corresponding to the difference of  $k_{1st}$  by  $\pm 30\%$  from the best value at the experimental rate constant. As can be seen, these calculations lie within the estimated error of the dissociation rate constant. The difference between the steady-state level of the experimental and the simulated concentration profile (up to 20%) in later times could be regarded solely to the error of the calibration curve.

In Figures 4 and 5, the obtained experimental data of the rate constants of reaction (1) in Arrhenius coordinates in the second-order and first-order reaction approximations at different pressures are summarized. As one can see from Figure 4, in the second-order reaction approximation (Equation 3), the data at different pressures form three straight lines. In Figure 5, the same data processed under the assumption of a first-order reaction, according to Equation 4, are well approximated by a single relationship described by the equation ( $\pm 30\%$  estimated uncertainty in  $k_{1st}$ ):

$$k_{1\text{st}} = 1.05 \times 10^{14} \exp\left(-200.4 \,\text{kJ} \cdot \text{mol}^{-1}/RT\right).$$
 (5)

Thus, the coincidence of the rate constant values obtained at different pressures in the first-order reaction approximation supposedly indicates that under the investigated conditions, the dissociation of n-C<sub>3</sub>F<sub>7</sub>I proceeds close to the highpressure limit.

Figure 5 also shows the data of previous works<sup>8–10</sup> that were obtained at lower temperatures (below 700 K). The authors carried out studies at various pressures (0.04–0.40 bar), and they claimed that the high-pressure-limit rate constants were reached. It is worth noting that the data in the temperature range 800–1200 K were obtained in the present work for the first time, and extrapolation of the literature data to the high-temperature region indicates a qualitatively good agreement of all the results.

However, it would be interesting to compare the obtained results with the theoretical RRKM estimates and to implement RRKM extrapolation of the rate constant toward a wide range of thermodynamic variables. For this purpose, first of all, the energy barrier of the process (1) must be determined. As far as the activation energy for this dissociation reaction

10

10

0.653

0.667

#### ary of the experimental results TABLE

ADLE I	1 Summary of the experimental results							
$[C_3F_7I]$	$P_2$	$T_2$	<b>P</b> <sub>5</sub>	$T_5$	[Ar]	$[C_3F_7I]$	k <sub>1st</sub>	$k_{2nd} (\times 10^{-19} \text{ cm}^3)$
(ppm)	(bar)	( <b>K</b> )	(bar)	(K)	$(\times 10^{19} \text{ cm}^{-3})$	$(\times 10^{13} \text{ cm}^{-3})$	$(s^{-1})$	$(molecule \cdot s)^{-1})$
4	-	-	2.724	1,183	1.7	6.8	30,441	17,906
4	-	-	2.700	1,092	1.8	7.2	21,402	11,890
4	-	-	2.684	934	2.1	8.4	1,057	503
2	-	-	2.709	1,056	1.9	3.8	13,000	6,842
2	-	-	2.737	1,060	1.9	3.8	23,184	12,202
2	-	-	2.722	923	2.2	4.4	730	332
2	-	-	2.745	879	2.3	4.6	102	44.4
1	-	-	2.684	873	2.3	2.3	102	44.4
10	-	-	2.669	798	2.5	25	4.48	1.79
10	-	-	2.686	838	2.4	24	41.6	17.3
10	-	-	2.662	812	2.4	24	11.3	4.71
10	-	-	2.668	853	2.3	23	59.6	25.9
2.5	-	-	2.668	969	2.0	5.0	1,654	827
2.5	-	-	2.531	972	1.9	4.8	2,273	1,196
2.5	-	-	2.616	972	2.0	5.0	2,100	1,050
2.5	-	-	2.592	875	2.2	5.5	80.7	36.7
2.5	-	-	2.736	1,021	2.0	3.4	9,020	4,510
3	-	-	2.669	910	2.2	6.6	285	130
0.125	-	-	8.516	851	7.3	0.91	164	22.5
0.125	-	-	8.250	948	6.4	0.80	692	108
3	-	-	7.946	846	6.9	21	60.4	8.75
3	-	-	8.233	1,126	5.4	16	13,734	2,543
1	-	-	7.966	1,047	5.6	5.6	7,700	1,375
1	-	-	7.878	880	6.6	6.6	91.3	13.8
1	-	-	7.853	976	5.9	5.9	3114	528
0.2	-	-	8.116	1,087	5.5	1.1	12,727	2,314
0.2	-	_	8.319	1,030	5.9	1.2	7,627	1,293
10	0.666	855	-	-	0.57	5.7	135	237
10	0.692	1012	_	_	0.43	4.3	1,864	4,335
10	0.617	981	-	-	0.46	4.6	2,410	5,239
10	0.642	905	_	_	0.52	5.2	239	460

0.55

0.56

5.5

5.6

is expected to be equal to its enthalpy (or, equivalently, the reverse reaction has no activation barrier), special attention should be paid to the accurate determination of its dissociation energy D.

\_

875

868

In the present work, density functional theory (DFT) calculations were conducted to explore the regions of potential energy surface (PES) relevant to n-C<sub>3</sub>F<sub>7</sub>I dissociation. Following Fortin et al.,<sup>23</sup> the geometries of stationary points on the PES were optimized with the B3LYP DFT functional<sup>24</sup> in conjunction with the correlation consistent polarized triple zeta basis set cc-pVTZ-PP of Peterson et al. with the pseudopotential for the core electrons of heavy atoms.<sup>25,26</sup> When applying gradient optimization of the structure, the DFT energies were augmented with an empirical dispersion correction<sup>27</sup> that can be essential to reach the so-called chemical accuracy for relatively large atomic systems.<sup>28</sup>

301

118

547

211

Conventional harmonic frequency analysis was conducted at the same level of theory for the PES minima to provide the vibrational frequencies required for the subsequent modeling and to assess the zero-point energy contribution to the total energy of the considered species. The heights of torsion barriers required for calculations were also determined using the relaxed PES scan technique at the B3LYP/cc-pVTZ-PP level of treatment. All quantum-chemical calculations were conducted using the Firefly QC program package,<sup>29</sup> which is partially based on the GAMESS (US) source code.<sup>30</sup>

WILEY  $\perp$ 



**FIGURE 4** Arrhenius plot of the measured second-order rate constant for  $C_3F_7I(+M) = C_3F_7 + I(+M)$  [Color figure can be viewed at wileyonlinelibrary.com]



**FIGURE 5** Arrhenius plot of the measured first-order rate constant for  $C_3F_7I(+M) = C_3F_7 + I(+M)$  and data of previous works.<sup>8–10</sup> The solid dark line is a linear least-squares fit of the present data [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Parameters used for RRKM/ME modeling

Molecule	D(0 K) (kJ/mol)	D(298 K) (kJ/mol)	$\sigma$ (Å)	<i>ε</i> (К)
CF <sub>3</sub> I	224.6	227.3	5.07	125
$n-C_3F_7I$	212.5	214.8	6.03	130
Ar	-	-	3.33	135

The obtained values of dissociation energy of the singlet n-C<sub>3</sub>F<sub>7</sub>I molecule into doublet C<sub>3</sub>F<sub>7</sub> and I(<sup>2</sup>*P*) are presented in Table 2. To ensure that the reliable values of D(0 K) and D(298 K) are achieved in this case, the respective values for the CF<sub>3</sub>I molecule are also given here. One may observe that the obtained D(298 K) magnitude for CF<sub>3</sub>I coincides well with the available thermochemical values (225.6<sup>31</sup> kJ mol<sup>-1</sup> and 228.6<sup>32</sup> kJ mol<sup>-1</sup>) that support the reasonability of applying the current computational scheme.

Note that the average value of C–I dissociation energy in different molecules of homologues  $C_nF_{2n+1}I$  is about  $D = 210 \text{ kJ mol}^{-1}$ , and it decreases as follows:  $CF_3I$ ,<sup>20</sup>  $C_2F_5I$ ,<sup>20</sup>  $C_3F_7I$ ,<sup>8</sup>  $C_4F_9I$ ,<sup>20</sup> and  $C_6F_{13}I^{10}$  (228, 219, 212, 206, and 201 kJ mol<sup>-1</sup>, respectively). An analogous regularity is presented by Skorobogatov et al.,<sup>10</sup> indicating a decrease in the activation energy with an increase in molecular weight, not only for iodine compounds but also for fluorine, chlorine, and bromine compounds.

Note also that the only available theoretical study of the dissociation energy in the  $C_3F_7I$  molecule<sup>33</sup> gives a slightly lower value *D* (from 201 to 213 kJ mol<sup>-1</sup>, depending on the calculation method) than was obtained at the B3LYP/cc-pVTZ-PP level of theory in the present work; however, these results are relevant to another (*i*-C<sub>3</sub>F<sub>7</sub>I) isomeric form of iodoperfluoropropane.

To estimate the appropriate pressure-dependent rate constants, RRKM/ME analysis was performed with the use of the ChemRate program package.<sup>34,35</sup> Energy-dependent rate constants for the C–I bond fission were obtained using the procedure for loose transition state dating back to Benson's restricted rotor concept<sup>34</sup> and implemented in Chemrate program.<sup>35</sup> In doing so, the exponential-down model of collisional energy transfer was applied, and the parameter  $\alpha$ , which governs the magnitude of average energy transferred during collisional deactivation, was specified in a temperaturedependent form  $\alpha(T) = \alpha_0 + \alpha_1 T$  (cm<sup>-1</sup>).

The collisional diameter  $\sigma$  and the well depth of the Lennard–Jones potential  $\varepsilon$  for CF<sub>3</sub>I and C<sub>3</sub>F<sub>7</sub>I species required for RRKM/ME analysis were estimated using the methodology<sup>36</sup> on the basis of computed spatial structures and electric properties (dipole moment and polarizability). The same quantities for Ar were adopted from the work of Cambi et al.<sup>37</sup> These values are also summarized in Table 2.

To treat the pressure-dependent dissociation of n-C<sub>3</sub>F<sub>7</sub>I in Ar, the following parameters of the simple exponentialdown model for collisional energy transfer were applied:  $\alpha_0 = 50 \text{ cm}^{-1}$ ,  $\alpha_1 = 0.2 \text{ cm}^{-1} \text{ K}^{-1}$ . Just such  $\alpha(T)$  dependence governing the collisional deactivation of vibrationally excited n-C<sub>3</sub>F<sub>7</sub>I\* complex in Ar ensures (together with the collision parameters given in Table 2) the most accurate RRKM/ME description of the CF<sub>3</sub>I decay in the same bath gas registered by Bystrov et al.<sup>1</sup>

In the course of RRKM/ME analysis, the mole fraction of n-C<sub>3</sub>F<sub>7</sub>I in a bath gas was specified to be ~10<sup>-4</sup>. The calculations of the effective dissociation rate constant and the subsequent fitting to the Troe form<sup>38,39</sup> were carried out in the following range of thermodynamic parameters: T = 300-3000 K,  $P = 10^{-4}-10^2$  bar. As a result, the limiting low- and high-pressure rate coefficients were obtained:

$$k_0 (n-C_3F_7I + Ar) = 8.849 \times 10^{19}T^{-1.444}$$
  
exp (-11, 454.4/T) (cm<sup>3</sup>mol<sup>-1</sup>s<sup>-1</sup>) and



**FIGURE 6** Measured and calculated rate constant for  $C_3F_7I$  (+M) =  $C_3F_7 + I$  (+M) and its dependence on the total concentration. Numbers 1, 2, 3, and 4 are RRKM/ME-based approximations at the temperatures of T = 1050, 970, 850, and 720 K, respectively. Dotted lines are low- and high-pressure limiting rate constants for the same temperatures. Symbols represent experimental data: the triangle,  $T = 1050 \pm 20$  K; the square,  $T = 970 \pm 10$  K; the circle,  $T = 850 \pm 25$  K; the rhombus, data from Tedeev et al.<sup>8</sup> at T = 720 K [Color figure can be viewed at wileyonlinelibrary.com]

$$k_{\infty} \left( n - C_3 F_7 I \right) = 9.676 \times 10^{16} T^{-0.378}$$
  
exp (-26, 956.8/T) (s<sup>-1</sup>)

with the center broadening factor  $F_c = 0.119$ .

Figure 6 shows the theoretically calculated pressure dependence of the  $n-C_3F_7I$  dissociation rate constants at different temperatures. In this figure, the experimental values of the rate constant at the corresponding close temperatures are also given. Despite the fact that, within the experimental error, it was impossible to detect conclusively the experimental dependence of the rate constant on the pressure value, the RRKM/ME results under appropriate conditions still exhibit a noticeable pressure dependence for temperatures above 900-950 K. This fact does not allow us to conclude unequivocally that the high-pressure limit has been reached for the whole range of our experimental conditions. In this case, the fitting of the experimental data by one Arrhenius equation can give a slightly underestimated value of the activation energy in comparison with the value of the dissociation energy at the C-I bond fission, and their values cannot be directly correlated with each other. As shown in Table 2, the theoretical value of the dissociation energy is in good agreement with the available experimental data<sup>8-10</sup> on the activation energy at the high-pressure limit.

A comparison of the absolute values of the experimental and theoretical rate constants of reaction (1) presented in Figure 6 shows a good match. Therefore, the theoretical calculation matches well with the work of Tedeev et al.<sup>8</sup> in the low-temperature region.

Finally, it would be interesting to compare present results with the rate constants of dissociation for similar molecules. One of the most similar molecules in structure and properties with the  $C_3F_7I$  is the molecule  $C_3H_7I$ . Note that the kinetics involving this molecule is noticeably lacking from the literature. Only some data on the rate constant of dissociation have been presented in old works<sup>40,41</sup> for a very narrow temperature range (533-573 and 703-767 K, respectively). Owing to the absence of high-temperature kinetic data, we did not directly compare the present data with the C<sub>3</sub>H<sub>7</sub>I molecule. The results of our work were matched with the data in a similar temperature range of all available homologues of  $C_n H_{2n+1}I$ and some other substances with the C-I bond, including a number of smaller  $C_n F_{2n+1}$  I molecules. The results comparison are shown in Figure 7. Larger molecules such as C<sub>4</sub>F<sub>9</sub>I and  $C_6F_{13}I$  are also not included in Figure 7, because like  $C_3H_7I$ , they have only been studied in a narrow range of low temperatures.

As can be seen from the plot, the rate constants of the primary dissociation for all the presented molecules of the  $C_nH_{2n+1}I$  and  $C_nF_{2n+1}I$  series are located in a close range of values. The results of Kumaran et al.,42 with the activation energy of the  $C_2H_5I$  molecule 132.2 kJ mol<sup>-1</sup>, differ significantly from the general values, that can be explained by the deviation of the rate constant from the high-pressure limit in the high-temperature region. The new data obtained in our work fall well within the general range of literature values. Although at thermal decomposition of the  $C_n H_{2n+1}I$ molecules, the parallel reaction  $C_n H_{2n+1} I \rightarrow C_n H_{2n-1} + HI$ plays an important role, it is clear that this process does not significantly affect the rate of the C-I bond fission in comparison with the  $C_n F_{2n+1}I$  series. Therefore, in future investigations, comparing the kinetic properties of C<sub>3</sub>H<sub>7</sub>I with the C<sub>3</sub>F<sub>7</sub>I molecules, we can expect that the values of their rate constants will also be similar. The only thing that should be noted is that the density of energy states in the homologous series  $C_n H_{2n+1}I$  is lower than in the  $C_n F_{2n+1}I$ series. Thus, the falloff curve is shifted to a region of lower pressures in case of  $C_n H_{2n+1}I$ . Accordingly, to approach the limiting rate constant of high pressure, it will be necessary to perform experiments at pressures higher than for  $C_3F_7I$ .

As for the iodobenzene molecules, the value of the dissociation rate constant of this cyclic substance noticeably differs from the constants of the above-mentioned molecules with a linear structure. Despite the fact that during dissociation in the same way as in the molecules  $C_nH_{2n+1}I$  and  $C_nF_{2n+1}I$ , the primary formation of the iodine atom occurs, the mechanism of this process seems to be different. Therefore, it is incorrect to make comparisons with other cyclic molecules and assume similar kinetic properties.



# **5 | CONCLUSION**

Using the precise ARAS technique on the atomic iodine line at 183.04 nm, the rate constant of dissociation of  $C_3F_7I$ at different temperatures (800-1200 K) and pressures (0.6-8.3 bar) was experimentally measured. Compared with previous studies, the ranges of pressures and temperatures were significantly expanded. Theoretical RRKM/ME calculations in a wide range of thermodynamic parameters were carried out, and values of the limiting low- and high-pressure rate coefficients were obtained. Comparison of the performed RRKM/ME calculations with the present experimental data and data of previous works confirmed the plausibility of the obtained values. By analyzing all available results on the rate constant of reaction  $C_3F_7I$  (+M) =  $C_3F_7$  + I (+M), it was concluded that the process of initial dissociation of perfluoropropyl iodide under our experimental pressure range at elevated temperatures still does not reach the high-pressure limit.

# ACKNOWLEDGEMENTS

The support of this study by the Russian Science Foundation grant no. 14-19-00025P is gratefully acknowledged.

# ORCID

Alexander Eremin 🝺 https://orcid.org/0000-0002-6835-7933

### REFERENCES

- Bystrov NS, Emelianov AV, Eremin AV, Yatsenko PI. Direct measurements of rate coefficients for thermal decomposition of CF<sub>3</sub>I using shock – tube ARAS technique. *J Phys D: Appl Phys.* 2018;51:181004.
- Drakon AV, Emelianov AV, Eremin AV, Yatsenko PI. Study of trifluoromethane within wide pressure and temperature range by molecular resonance absorption. *High Temp.* 2017;55:239–245.



- Bystrov NS, Emelianov AV, Eremin AV, Yatsenko PI. ARAS monitoring of various halogen atoms formation in pyrolysis reactions behind shock waves. *IOP Conf Ser: J Phys: Conf Ser.* 2018;946:012069.
- Emelianov AV, Eremin AV, Yatsenko PI. The study of C<sub>2</sub>F<sub>4</sub>Br<sub>2</sub> dissociation kinetics using methods of atomic and molecular resonance absorption spectroscopy behind shock waves. *IOP Conf Ser: J Phys: Conf Ser.* 2018;946:012070.
- Hastie JW. Molecular basis of flame inhibition. J Res Nat Bur Stand. 1973;77A:733–754.
- Shebeko YuN, Azatyan VV, Bolodian IA, et al. The influence of fluorinated hydrocarbons on the combustion of gaseous mixtures in a closed vessel. *Combust Flame*. 2000;121:542–547.
- Drakon AV, Eremin AV, Matveeva NA, Mikheyeva EY. The opposite influences of flame suppressants on the ignition of combustible mixtures behind shock waves. *Combust Flame*. 2017;176:592–598.
- 8. Tedeev RS, Dymov BP, Skorobogatov GA. Measurement of the equilibrium constant for reactions RI = R+I. *Vestn Leningr Univ, Ser 4: Fiz, Khim.* 1989;1:37–42 (in Russian).
- 9. Dobychin SL, Mashendzhinov VI, Mishin VI, Semenov VN, Shpak VS. Kinetics of thermal decomposition of perfluoroalkyl iodides and D(R-I) binding energy,  $R = CF_3$ ,  $C_2F_5$ , n- $C_3F_7$ , iso- $C_3F_7$ , n- $C_4F_9$ , tert- $C_4F_9$ . *Dokl Phys Chem (Engl Transl)*. 1990;312:494–496.
- Skorobogatov GA, Dymov BP, Tedeev RS. Measurement of rate constants and equilibrium constants of RI = R + I and I + RI = I<sub>2</sub> + R for R = C<sub>3</sub>F<sub>7</sub>, iso-C<sub>3</sub>F<sub>7</sub>, C<sub>6</sub>F<sub>13</sub>, CF<sub>3</sub>OCF<sub>2</sub>CF<sub>2</sub> or C<sub>3</sub>F<sub>7</sub>OCF<sub>2</sub>CF<sub>2</sub>. *J Gen Chem USSR*. 1991;61:158–165.
- Modica AP, Sillers SJ. Experimental and theoretical kinetics of high-temperature fluorocarbon chemistry. *J Chem Phys.* 1968;48:3283–3289.
- Danilov OB, Elagin VV, Zalesskii VY, Yachnev IL. Thermal dissociation of trifluoroiodomethane. *Kinet Catal*. 1975;16:257–260.
- Zalesskii VY, Kokushkin AM. About pyrolysis, thermodynamic equilibrium and erroneous conclusions. *Kinet Catal*. 1980;21:553– 556.

- 15. Saito K, Yoneda Y, Tahara H, Kidoguchi S, Murakami I. The thermal decomposition of  $CF_3I$  in Ar. Bull Chem Soc Jpn. 1984;57:2661–2224.
- Brouwer L, Troe J. Shock wave study of the UV spectrum of CF<sub>3</sub>I. *Chem Phys Lett.* 1981;82:1–4.
- Zaslonko IS, Mukoseev YuK, Skorobogatov GA, Khripun VK. Measurement of the rate constant for the thermal dissociation of gaseous CF<sub>3</sub>I in a shock tube. *Kinet Catal*. 1990;31:912–918.
- Kumaran SS, Su MC, Lim KP, Michael JV. Thermal decomposition of CF<sub>3</sub>I using I-atom absorption. *Chem Phys Lett.* 1995;243: 59–63.
- Kiefer JH, Sathyanarayana R. Vibrational relaxation and dissociation in the perfluoromethyl, halides CF<sub>3</sub>Cl, CF<sub>3</sub>Br and CF<sub>3</sub>I. *Int J Chem Kinet*. 1997;29:705–716.
- 20. Skorobogatov GA, Dymov BP, Khripun VK. Determination of rate constants and equilibrium constants of RI = R + I and I + RI = I<sub>2</sub> + R for R = CF<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>, or C<sub>4</sub>F<sub>9</sub>. *Kinet Catal.* 1991;32:220–227.
- Zaslonko IS, Mukoseev YuK, Skorobogatov GA, Smirnov VN, Khripun VK. Rate constant of thermal dissociation of gaseous C<sub>2</sub>F<sub>5</sub>I. *Kinet Catal.* 1991;32:468–473.
- Kramida A, Ralchenko Y, Reader J, and NIST ASD Team (2014). NIST Atomic Spectra Database (ver. 5.2). http://physics.nist.gov/asd. National Institute of Standards and Technology, Gaithersburg, MD. Published October 7, 2015.
- Fortin C, Khanniche S, Khiri D, et al. Reactivity of hydrogen peroxide with Br and I atoms. *J Phys Chem A*. 2018;122:1053–1063.
- Becke AD. Density-functional thermochemistry. III. The role of exact exchange. J Chem Phys. 1993;98:5648–5653.
- Peterson KA, Shepler BC, Figgen D, Stoll H. On the spectroscopic and thermochemical properties of ClO, BrO, IO, and their anions. *J Phys Chem A*. 2006;110:13877–13883.
- 26. EMSL Basis Set Exchange Library https://bse.pnl.gov/bse/portal. Accessed October 2018.
- Grimme S, Antony J, Ehrlich S, Krieg HA. Consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J Chem Phys.* 2010;132:154104.
- Schwabe T, Grimme S. Double-hybrid density functionals with long-range dispersion corrections: higher accuracy and extended applicability. *Phys Chem Chem Phys.* 2007;9:3397–3406.
- Granovsky AA, Firefly V. 8.2.0 http://classic.chem.msu.su/gran/ firefly/index.html. Accessed October 2018.
- Schmidt MW, Baldridge KK, Boatz JA, et al. General atomic and molecular electronic structure system. *J Comput Chem.* 1993;14:1347–1363.
- Afeefy HY, Liebman JF, Stein SE. In: Linstrom PJ, Mallard WG, eds. *Neutral Thermochemical Data in NIST Chemistry WebBook*, *NIST Standard Reference Database Number 69*. Gaithersburg, MD: National Institute of Standards and Technology; 2018:20899. http://webbook.nist.gov. Accessed October 2018.
- 32. Ruscic B, Bross DH. Active Thermochemical Tables (ATcT) values based on ver. 1.122d of the Thermochemical Network; 2018.

- Cheng L, Shen Z, Lu J, Gao H, Lu Z. Theoretical study on the dissociation energies, ionization potentials and electron affinities of three perfluoroalkyl iodides. *Chem Phys Lett.* 2005;416:160–164.
- Knyazev VD, Tsang W. Chemically and thermally activated decomposition of secondary butyl radical. J Phys Chem A. 2000;104:10747–10765.
- Mokrushin V, Bedanov V, Tsang W, Zachariah M, Knyazev V, McGivern WS, ChemRate, version 1.5.10; 2011.
- Sharipov AS, Loukhovitski BI, Tsai C-J, Starik AM. Theoretical evaluation of diffusion coefficients of (Al<sub>2</sub>O<sub>3</sub>)<sub>n</sub> clusters in different bath gases. *Eur Phys J D*. 2014;68:99.
- Cambi R, Cappelletti D, Liuti G, Pirani F. Generalized correlations in terms of polarizability for van der Waals interaction potential parameter calculations. *J Chem Phys.* 1991;95:1852–1862.
- Gilbert RG, Luther K, Troe J. Theory of thermal unimolecular reactions in the fall-off range. II. Weak collision rate constants. *Ber Bun*senges Phys Chem. 1983;87:168.
- Kee RJ, Rupley FM, Miller JA, et al. *Chemkin Collection, Release* 3.6. San Diego, CA: Reaction Design, Inc.; 2000.
- Richard A, Ogg J. Kinetics of the thermal reaction of gaseous alkyl iodides with hydrogen iodide. J Am Chem Soc. 1934;56:526–536.
- 41. Butler ET, Polanyi M. Rates of pyrolysis and bond energies of substituted organic iodides (Part I). *Trans Faraday Soc.* 1943;39:19–36.
- Kumaran SS, Su M-C, Lim KP, Michael JV. The thermal decomposition of C<sub>2</sub>H<sub>5</sub>I. Symp Int Combust Proc. 1996;26:605–611.
- Bentz T, Szori M, Viskolcz B, Olzmann M. Pyrolysis of ethyl iodide as hydrogen atom source: kinetics and mechanism in the temperature range 950–1200 K. Z Phys Chem. 2011;225:1117–1128.
- Yang J-H, Conway DC. Pyrolysis of ethyl iodide by the toluenecarrier flow technique. J Chem Phys. 1965;43.
- 45. Yang XL, Tranter RS. High-temperature dissociation of ethyl radicals and ethyl iodide. *Int J Chem Kinet*. 2012;44:433–443.
- Kumaran SS, Su M-C, Lim KP, Michael JV. The thermal decomposition of C<sub>2</sub>H<sub>5</sub>I. Symp Int Combust Proc. 1996;26:605–611.
- Awan IA, Burgess DR, Manion JA. Pressure dependence and branching ratios in the decomposition of 1-pentyl radicals: shock tube experiments and master equation modeling. *J Phys Chem A*. 2012;116:2895–2910.
- Tranter RS, Klippenstein SJ, Harding LB, Giri BR, Yang XL, Kiefer JH. Experimental and theoretical investigation of the self-reaction of phenyl radicals. *J Phys Chem A*. 2010;114:8240–8261.
- Kumaran SS, Su MC, Michael JV. Thermal decomposition of iodobenzene using I-atom absorption. *Chem Phys Lett.* 1997;269:99–106.
- Robaugh D, Tsang W. Thermal decomposition of phenyl iodide and o-iodotoluene. J Phys Chem. 1986;90:5363–5367.

How to cite this article: Bystrov N, Emelianov A, Eremin A, Loukhovitski B, Sharipov A, Yatsenko P. Direct measurements of  $C_3F_7I$  dissociation rate constants using a shock tube ARAS technique. *Int J Chem Kinet*. 2018;1–9. <u>https://doi.org/10.1002/kin.21244</u>