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Rate Constant of the Recombination of $CF_3^{\bullet}$ Radicals in a Gas (He, Ar, N_2, or CF_3I)

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Abstract—From recent rate constant data for the recombination reaction $2CF_3^{\bullet} \rightarrow C_2F_6$ ($k^{M}_{(CF_3)_2}$) in the high-pressure limit and from experimental data obtained at intermediate pressures of buffer gases M (M = He, Ar, N_2, CF_3I), analytical expressions for $k^{M}_{(CF_3)_2}$ (in Lindemann's formulation) are derived for the temperature range of 300–1300 K and intermediate pressures of the buffer gases.

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The gas-phase recombination reaction

$$2CF_3^{\bullet} + M \xrightarrow{k^{M}_{(CF_3)2}} C_2F_6 + M \qquad (I)$$

is among the best understood reactions of the type $2R^{\bullet} + (M) \rightarrow R_2 + (M)$ ($k_{rec} = -1/2(d[R]/dt)[R]^{-2}$) (II) [1–17]. Here, M is any third particle: M = R_2, $R^{\bullet}$, or a molecule of an inert diluent (Ar, He, etc.).

Note that the recombination of two identical radicals via reaction (II) can be characterized either by the "small" rate constant $k_{R_2} = k_{rec}$ (see reaction (II)) or by the "large" rate constant

$$d[R]/dt = -k^{*}_{R_2}[R]^2, \qquad (1)$$

as was done in an earlier work [16]. Obviously, $k^{*}_{R_2} = 2k_{R_2}$. This should be kept in mind because the authors of the NIST database [18] do not distinguish these constants. In each particular case, one should see the original publication. For example, according to our earlier study [16], the rate constant of the recombination reaction (II) is 2.55×10^{-11} cm^3/(molecule s) at 300 K. We used [16] the "large" rate constant (1) in that study, so we will use $k^{\infty}_{(CF_3)_2}(300\ K) = \frac{1}{2}k^{*}_{R_2} = 1.27 \times 10^{-11}$ cm^3/(molecule s) here.

Reaction (II) for multiatomic molecules takes place via the ET mechanism [19]:

$$2R \underset{k_{-a}}{\overset{k_a}{\rightleftarrows}} R_2^{\neq}, \quad R_2^{\neq} + M_i \xrightarrow{k_i^{*}} R_2 + M_i, \qquad (III)$$

Accordingly, the apparent second-order recombination rate constant (k_{rec}) depends both on temperature (T) and on the total pressure of the reaction mixture (P):

$$k_{rec}(T, P) = k_{R_2} = \frac{k_a}{1 + \left(k_{-a} \Big/ \sum_i k_i^{*}[M_i] \right)}. \qquad (2)$$

Following Kondrat'ev and Nikitin [19], we assume that k_a and k^{*} in Eq. (2) depend on temperature in the same way as the number of gas kinetic collisions and that k_{-a} obeys the Arrhenius law:

$$k_a = k_{R_2}(300\ K)\sqrt{T/300\ K};$$
$$k_i^{*} = k_i^{*}(300\ K)\sqrt{T/300\ K}; \quad k_{-a} = a\exp\left(-\frac{b}{T}\right). \qquad (3)$$

RECOMBINATION OF $CF_3^{\bullet}$ RADICALS IN CF_3I AS THE BUFFER GAS

The source of $CF_3^{\bullet}$ radicals in our work [17] was the iodide CF_3I = RI, which also served as the buffer gas. Substitution of Eq. (3) into Eq. (2) gives

$$k_{R_2} = \frac{k_a}{1 + \left(k_{-a} \Big/ \sum_i k_i^{*}[M]_i \right)} = \frac{\sqrt{T/300\ K}\, k_{R_2}(300\ K)}{1 + \left(\dfrac{a}{[RI]_0\sqrt{T/300\ K}\sum \mu_i k_i^{*}(300\ K)} \right) e^{-\frac{b}{T}}}, \qquad (4)$$

where $\mu_i = [M_i]/[RI]_0$ is the mole fraction of the ith component relative to the initial halide RI. Isochoric isothermal pyrolysis experiments [17] are conducted so that the extent of decomposition of the halide RX does not exceed a few hundredths of the initial amount

of the halide. In this case, all μ_i terms but $\mu_{RX} \approx 1$ under the summation sign in Eq. (4) can be neglected:

$$k_{R_2} = \frac{\sqrt{T/300\,\mathrm{K}}k_{R_2}(300\,\mathrm{K})}{1+\left(\frac{a}{[RI]_0\sqrt{T/300\,\mathrm{K}}k^*_{RI}(300\,\mathrm{K})}\right)e^{-\frac{b}{T}}}. \quad (5)$$

The experiment can alternatively be arranged in such a way that the halide RX is diluted with a large excess of a buffer gas M. In this case, all μ_i terms but $\mu_M = [M]/[RI]_0$ under the summation sign in Eq. (4) can be neglected at any extent of decomposition:

$$k_{R_2} = \frac{\sqrt{T/300\,\mathrm{K}}k_{R_2}(300\,\mathrm{K})}{1+\left(\frac{a}{[M]\sqrt{T/300\,\mathrm{K}}k^*_{M}(300\,\mathrm{K})}\right)e^{-\frac{b}{T}}}. \quad (6)$$

Kinetic experiments should allow the following three unknowns to be determined: $k_{R_2}(300\,\mathrm{K})$, $\left(a/k^*_M(300\,\mathrm{K})\right)$, and b.

In an earlier work [17], based on kinetic measurements for isochoric isothermal CF_3I pyrolysis, we recommended the following expression for calculating the rate constant:

$$k^{CF_3I}_{(CF_3)_2} = \frac{(1.10-1.27)\times10^{-11}(T/300\,\mathrm{K})^{0.25-0.50}}{1+\frac{10^{9.4\pm0.3}\exp(-(2000\pm500\,\mathrm{K})/T)}{4\times10^{-11}\sqrt{T/300\,\mathrm{K}}[CF_3I]}}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}. \quad (7)$$

Here, based on the same experimental data, we suggest the following refined expression:

$$k^{CF_3I}_{(CF_3)_2} = \frac{10^{-10.9\pm0.1}\sqrt{T/300\,\mathrm{K}}}{1+\frac{10^{9.6\pm0.2}\exp(-(2800\pm500\,\mathrm{K})/T)}{4\times10^{-11}\sqrt{T/300\,\mathrm{K}}[CF_3I]}}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}, \quad (7^*)$$

which coincides with (7) in the 300–800 K range within the experimental error.

In the low-concentration limit, the third-order rate constant is obtained from formula (7*):

$$k^{CF_3I}_{(CF_3)_2} = \frac{k_a k^*}{k_{-a}} = 10^{-30.9\pm0.3}\left(\frac{T}{300\,\mathrm{K}}\right)e^{\frac{(2800\pm500)K}{T}}\,\mathrm{cm^6\,molecule^{-2}\,s^{-1}}, \quad (8)$$

which is identical to the rate constant recommended in [17] within the experimental error.

RECOMBINATION OF $CF_3^{\bullet}$ RADICALS IN THE HIGH-CONCENTRATION LIMIT

All of the rate constant data available on the $CF_3^{\bullet}$ recombination reaction (II) at various temperatures and buffer gas (M ≡ Ar) pressures are presented graphically in Fig. 1. Our earlier data for M ≡ CF_3I [17] are also plotted in Fig. 1. This plot makes a sad impression because the scatter of data reported by different authors is as great as three orders of magnitude and is always one order of magnitude greater than the errors specified by the authors. We will single out reliable data that can be used with confidence.

The data presented in Fig. 1 demonstrate that the formerly very popular value of $k^{\infty}_{(CF_3)_2} = 3.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [1], which appears in many handbooks (see, e.g., [20]), is 3 times larger than the more realistic value. Conversely, the more recent values of $k^{\infty}_{(CF_3)_2}(300\,\mathrm{K}) = (5 \pm 1) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [5–8] are underestimated by a factor of over 2. It would be appropriate to refine the reference data [20] for those (quite numerous) rate constants which were calculated using old $k^{\infty}_{(CF_3)_2}$ values [1] as the reference.

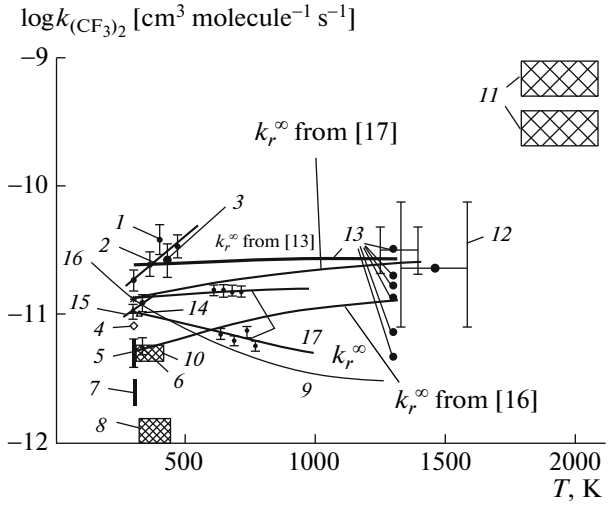

Fig. 1. Rate constant data (k_{rec}) for the recombination of R = $CF_3^{\bullet}$ radicals in a buffer gas M (reaction (II)): (*1–3*): experimental data for M = $(CF_3)_2CO$ [1–3]; (*4–8*) experimental data for M = Ar from [4–8]; (*10–16*) the same from [10–16]; (*17*) M = CF_3I [17]; (*9*) theoretical calculation in the high-pressure limit for the flexible transition complex model [9].

The systematic overestimation of $k^{\infty}_{(CF_3)_2}$ is the studies using hexafluoroacetone as the source of $CF_3^{\bullet}$ free radicals [1–3] is most likely caused by the neglect of the fast reactions of $CF_3^{\bullet}$ with the initial compound:

$$CF_3^{\bullet} + (CF_3)_2CO$$
$$\rightarrow (CF_3)_3CO^{\bullet} \xrightarrow{CF_3^{\bullet}} (CF_3)_3COCF_3.$$

The existence of these reactions was established reliably [21, 22], and they inevitably lead to a higher $CF_3^{\bullet}$ disappearance rate than is implied by the simplified kinetic schemes accepted in [1–3]. Even hexafluoroazomethane, a very popular source of $CF_3^{\bullet}$ free radicals, has the same flaw, for it reacts rapidly with $CF_3^{\bullet}$ free radicals [23]:

$$CF_3^{\bullet} + CF_3{-}N{=}N{-}CF_3$$
$$\rightarrow (CF_3)_2N{-}N^{\bullet}{-}CF_3 \xrightarrow{CF_3^{\bullet}} (CF_3)_2N{-}N(CF_3)_2.$$

It is also possible that the "large" rate constant of reaction (III) was determined in [1–3]; however, the kind of rate constant was not specified in those studies.

In a number of studies [4–11], the large errors and the marked deviation of the mean $k^{\infty}_{(CF_3)_2}$ value from the more realistic value are undoubtedly due to the large number of parallel reactions in the general kinetic network describing the experiment. Furthermore, the rate constants of these parallel reactions are either unknown or known with large uncertainty. For example, the kinetic network accepted in [11] consists of 15 reactions, whose rate constants were obtained by the authors by numerical fitting of rate equations to a single kinetic curve constructed from only five to ten data points. Clearly, this problem cannot have a unique solution. The kinetic network used in [8–10] includes 14 elementary reactions, whose rate constants were obtained by numerical fitting of rate equations to a kinetic curve constructed from six to nine data points. In addition, the experiments reported in [8–10] did not ensure the isothermicity of the process as the kinetic curve was recorded. In another work [6], as many as four rate constants were derived (by numerical fitting) from a single kinetic curve.

The rate constant of the thermal dissociation reaction

$$C_2F_6 \underset{k_{rec}}{\overset{k_{diss}}{\rightleftarrows}} 2CF_3 - 397.32\ \text{kJ/mol} \qquad \text{(IV)}$$

was measured in a shock tube with a fairly high accuracy [12]. The author of that study did not record the transitional curve, but the following first-order rate constant was obtained close to the high-pressure limit:

$$k^{\infty}_{diss} = 4.3\times10^{17}\exp\left(-\frac{47500\pm2000}{T/\text{K}}\right)\text{s}^{-1} \qquad (9)$$
$$\text{for } 1300\text{–}1600\ \text{K}.$$

For 1450 K, the middle of this temperature range, Eq. (9) gives $k^{\infty}_{diss} = 10^{3.4\pm0.6}\ \text{s}^{-1}$.

The thermodynamic databank by Gurvich et al. [24] makes it possible to calculate the equilibrium constant $K_c = k_{diss}/k_{rec}$:

$$K_c = 10^{29.184}\left(\frac{T}{300\ \text{K}}\right)^{-0.55}\exp\left(-\frac{47786}{T/\text{K}}\right)\text{molecule/cm}^3 \qquad (10)$$
$$\text{for } 300\text{–}600\ \text{K},$$

$$K_c = 10^{29.184}\left(\frac{T}{300\ \text{K}}\right)^{-1.162}\exp\left(-\frac{47786}{T/\text{K}}\right)\text{molecule/cm}^3 \qquad (10^*)$$
$$\text{for } 300\text{–}1600\ \text{K}.$$

From (10*) and (9), we can derive the recombination rate constant for the temperature range of 1300–1600 K in the high-pressure limit:

$$k^{\infty}_{rec} = 10^{-11.554}\left(\frac{T}{300\ \text{K}}\right)^{1.162} \times\exp\left(\frac{286}{T/\text{K}}\right)\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}. \qquad (11)$$

As a result, it follows from the data presented in [12] that

$$k^{\infty}_{rec}(1450\ \text{K}) = 10^{-10.67\pm0.6}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}. \qquad (11^*)$$

It is clear from Fig. 1 that the rate constant k^{∞}_{diss} from [12] is quite realistic. However, it was obtained not in the high-pressure limit; besides, it is "depreciated" by its large error.

As for the theoretical calculation within the canonical flexible transition state model [9], it does not even lead to the correct topology of the temperature dependence of $k^{\infty}_{(CF_3)_2}$ in the high-pressure limit. Thus, the best model is still the barrierless recombination of two free radicals with the attractive potential $-\text{const}\,r^{-6}$ of the dispersion interaction [25], which leads to the relationship $k^{\infty}_{(CF_3)_2} \approx T^{1/6}$, or the simpler model with the rate constant depending on temperature as $T^{1/2}$ [26], which is characteristic of gas-kinetic collisions of free particles.

Finally, we accept only the measurements reported in [13–17] as reliable data. In those studies, the concentrations of the initial/final components were measured directly and the kinetic network for the process examined consisted of no more than three elementary reactions. However, even the data reported in [13–17] cannot be used without some refinement. For example, Ogawa et al. [15], who used unsurpassed experimental technique, observed a strikingly strong temperature dependence of the rate constant $k^{\infty}_{(CF_3)_2}$ in the high-concentration limit. As compared to the mean of the data presented in [15], the value reported in [14] is smaller and the value reported in [16] is larger. For this

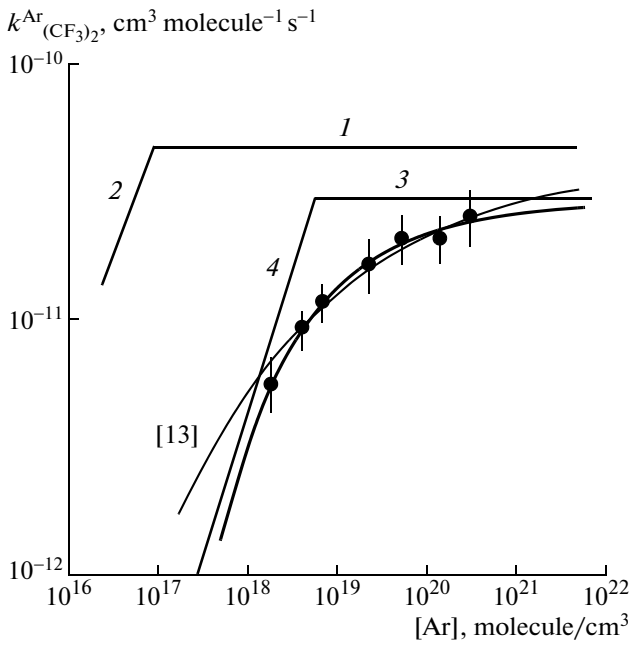

Fig. 2. $k^{Ar}_{(CF_3)_2}$ data measured at $T = 1300$ K as a function of the buffer gas (M = Ar) pressure [13] (points). (*1*, *2*) Asymptotes in the (*1*) high- and (*2*) low-pressure limits in the interpretation of Glänzer et al. [13]. (*3*, *4*) Asymptotes in the (*3*) high- and (*4*) low-pressure limits in our interpretation.

reason, we will take the mean of all data reported in [14–16] to be the most likely (and reliable) value of $k^{\infty}_{(CF_3)_2}$ (300 K):

$$k^{\infty}_{(CF_3)_2}(300\,\mathrm{K}) = (1.2 \pm 0.1) \times 10^{-11}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1} = 10^{-10.9\pm0.1}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1}. \quad (12)$$

The results reported in [13] were obtained in a shock tube by directly measuring the time evolution of the $[CF_3]$ concentration. However, even these reliable data will be subjected to refinement. Figure 2 reproduces Fig. 4 from [13], displaying the $k^{Ar}_{(CF_3)_2}$ data measured in the transitional region. It is demonstrated here that smooth extrapolation of the same experimental data [13] leads to significantly different asymptotic values of the second-order rate constant in the high-concentration limit,

$$k^{\infty}_{(CF_3)_2}(1300\,\mathrm{K}) = 10^{-10.6\pm0.1}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1} \quad (12^*)$$

and of the third-order rate constant in the low-concentration limit,

$$k^{Ar}_{(CF_3)_2}(1300\,\mathrm{K}) = 10^{-29.5\pm0.2}\,\mathrm{cm}^6\,\mathrm{molecule}^{-2}\,\mathrm{s}^{-1}. \quad (13)$$

It follows from (12) and (12*) for the entire temperature range of 300–1300 K that

$$k^{\infty}_{(CF_3)_2}(T) = 10^{-10.9\pm0.1}\sqrt{\frac{T}{300\,\mathrm{K}}}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1} \quad (14)$$
$$(300\ \mathrm{K} \le T \le 1300\ \mathrm{K}),$$

and this expression was used in formula (7*).

RECOMBINATION OF $CF_3^{\cdot}$ RADICALS IN THE LOW-CONCENTRATION LIMIT

There have been no systematic measurements of the rate constant $k^{Ar}_{(CF_3)_2}$ in wide temperature and pressure ranges, so we will use the scarce data that we were able to mine from the literature (table). Our estimates (a) and (c) (see notes to the table) are based on published experimental data. Along with the interpolated value (b), they provide realistic $k^{Ar}_{(CF_3)_2}$ data since all of them fall between $k^{N_2}_{(CF_3)_2}$ and $k^{CF_3I}_{(CF_3)_2}$. (This is consistent with the ET mechanism of recombination (III) because the rate constant k_i^* increases monotonically in the order $N_2 \to Ar \to CF_3I$.) Using Lindemann's theory, we derive the following analytical expression from the $k^{Ar}_{(CF_3)_2}$ data listed in the table:

$$k^{Ar}_{(CF_3)_2} = \frac{10^{-10.9\pm0.1}\sqrt{T/300\,\mathrm{K}}}{1 + \dfrac{10^{9.6\pm0.2}\exp(-(2800\pm500\,\mathrm{K})/T)}{2.2\times10^{-11}\sqrt{T/300\,\mathrm{K}}\,[\mathrm{Ar}]}}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1}. \quad (15)$$

In the low-concentration limit, Eq. (15) leads to the following expression for the third-order rate constant:

$$k^{Ar}_{(CF_3)_2} = \frac{k_a k^*}{k_{-a}} = 10^{-31.2\pm0.3}\left(\frac{T}{300\,\mathrm{K}}\right)e^{\frac{(2800\pm500)\,\mathrm{K}}{T}}\,\mathrm{cm}^6\,\mathrm{molecule}^{-2}\,\mathrm{s}^{-1}. \quad (16)$$

It is natural that the values of the third-order rate constant $k^{Ar}_{(CF_3)_2}$ calculated via formula (16) are equal to those appearing in row 3 of the table because it is from the data presented in this table that formula (15) was derived. The predicted values based on data from [13] (table, row 7) exceed our data by 2 and 4 orders of magnitude in the 700–1300 and 300–500 K ranges, respectively. Therefore, they are inconsistent with the totality of published experimental rate constant data.

Rate constants of recombination reactions (II) in the low-concentration limit

Reaction	Reference	$k^{M}_{X_2}$, $cm^6\ molecule^{-2}\ s^{-1}$				
		300 K	500 K	700 K	1000 K	1300 K
$2CH_3 + Ar \longrightarrow C_2H_6 + Ar$	[27]	$10^{-26.4}$	$10^{-26.8}$	$10^{-26.9}$	–	–
$2CF_3 + M \longrightarrow C_2F_6 + M$, where $M = (CF_3)_2CO$	[28]	$k^{M}_{(CF_3)_2} = e^{-1080/T} k^{M}_{(CH_3)_2}$		–	–	–
$2CF_3 + Ar \longrightarrow C_2F_6 + Ar$	–	$10^{-27.0 \pm 0.3}$[a]	$10^{-28.2 \pm 0.3}$[a]	$10^{-29.0 \pm 0.3}$[b]	$10^{-29.3 \pm 0.3}$[b]	$10^{-29.5 \pm 0.2}$[c]
$2CF_3 + Ar \longrightarrow C_2F_6 + Ar$	[7, 29]	–	–	–	$10^{-28 \pm 1}$ [7]	$10^{-31.6}$[d]
$2CF_3 + N_2 \longrightarrow C_2F_6 + N_2$	[30]	–	$10^{-28.8}$	–	–	–
$2CF_3 + CF_3I \longrightarrow C_2F_6 + CF_3I$	[17][e]	$10^{-26.8 \pm 0.6}$	$10^{-28.1 \pm 0.4}$	$10^{-28.8 \pm 0.3}$	$10^{-29.1 \pm 0.3}$	$10^{-29.3 \pm 0.4}$
$2CF_3 + Ar \longrightarrow C_2F_6 + Ar$	[f]	10^{-23}	$10^{-24.7}$	$10^{-26.1}$	–	$10^{-27.3}$
$2CF_3 + He \longrightarrow C_2F_6 + He$	[g]	$10^{-30.5 \pm 0.3}$	$10^{-31.0 \pm 0.3}$	$10^{-31.3 \pm 0.3}$	$10^{-31.4 \pm 0.3}$	$10^{-31.5 \pm 0.3}$

[a] Our estimate based on experimental data from [27, 28]. [b] Smooth interpolation in the 500–1300 K range. [c] Our interpretation of experimental data from [13]. [d] Value measured at 1600 K [29]. [e] Calculated via formula (8), derived from experimental data [17].
[f] According to a model derived from experimental data for $T = 1300$ K [13]. [g] Calculated via formula (19), based on experimental data from [31].

The rate constant of the recombination reaction (I) for the buffer gas M = He in the transitional pressure range was measured in [31] (at a single point of $P =$ 600 Torr, however):

$$k^{He}_{(CF_3)_2}(296\ K) = 10^{-11.4 \pm 0.2}\ cm^3\ molecule^{-1}\ s^{-1}. \quad (17)$$

For analytical representation according to Lindemann, it is necessary to know three parameters. We have only two ones, namely, the values given by Eqs. (14) and (17). However, from theoretical considerations, we can set $b = 1400$ K in formula (6) for M = He (two times smaller value than for M =Ar). We will then obtain the following formula from (14) and (17):

$$k^{He}_{(CF_3)_2} = \frac{10^{-10.9 \pm 0.1}\sqrt{T/300\ K}}{1 + \dfrac{10^{9.6 \pm 0.2}\exp(-(1400 \pm 250\ K)/T)}{10^{-12}\sqrt{T/300\ K}\,[He]}}\ cm^3\ molecule^{-1}\ s^{-1}. \quad (18)$$

In the low-concentration limit, Eq. (18) leads to the following expression for the third-order rate constant:

$$k^{He}_{(CF_3)_2} = \frac{k_a k^*}{k_{-a}} = 10^{-32.5 \pm 0.3}\left(\frac{T}{300\ K}\right)e^{\frac{(1400 \pm 250)\ K}{T}}\ cm^6\ molecule^{-2}\ s^{-1}. \quad (19)$$

According to experimental data [30], the efficiency of the buffer gas $M = N_2$ is the same as the efficiency of M = Ar within the measurement error. Therefore, formulas (15) and (16) with Ar replaced with N_2 are applicable to $M = N_2$.

RESULTS AND DISCUSSION

In our previous study, we measured $k^{CF_3I}_{(CF_3)_2}$ by the isochoric isothermal pyrolysis (IIP) method, which was used earlier [32, 33] in kinetic studies of thermal gas-phase reactions involving perfluoroalkyl iodides (CF_3I, C_2F_5I, C_3F_7I, etc.) and CF_3Br. The perfluoroalkyl halide RX in the IIP method is decomposed at a fixed temperature under mild conditions, when the overall process is limited to the scheme

$$RX \rightarrow 1/2R_2 + 1/2X_2. \quad (V)$$

The detailed mechanism of the overall reaction (V) is representable as a reaction network involving no radical R$^\cdot$ decomposition or polymerization reactions. This reaction network consists of reaction (II) and the following elementary reactions:

$$RX \leftrightarrow R^\cdot + X^\cdot \quad (K_{C,2} = k_2/k_{-2} = [R]_{eq}[X]_{eq}/[RX]_{eq}), \quad (VI)$$

$$X^\cdot + RX \leftrightarrow R^\cdot + X_2 \quad (K_{C,3} = k_3/k_{-3} = K_{C,2}/K_{C,4}), \quad (VII)$$

$$2X^\cdot + (M) \leftrightarrow X_2 + (M) \quad (K_{C,4} = k_4/k_{-4} = [X]^2_{eq}/[X_2]_{eq}). \quad (VIII)$$

Here, M is any third particle: M = RX, R_2, X_2, R$^\cdot$, X$^\cdot$, or a molecule of an inert diluent (Ar, He, etc.); $[R]_{eq}$, $[X]_{eq}$, and $[RX]_{eq}$ are the equilibrium component con-

centrations; k_i (k_{-i}) is the rate constant of the ith forward (reverse) reaction; and $K_{C,i}$ is the constant of the ith equilibrium.

The overall process rate is determined by the rate of reaction (II) (which is irreversible under the IIP conditions). This makes it possible to derive the rate constant k_{rec} from the buildup rate of the recombination product R_2 or, more conveniently, from the buildup rate of the molecular halogen X_2. In our earlier studies [17, 32, 33], the IIP method proved to be a convenient tool for kinetic measurements in process (V). However, this method is indirect, as distinct from, e.g., pulse methods (pulsed photolysis, pressure jump measurements in a shock tube, etc.). As a consequence, the reliability of the rate constants measured by the IIP method depends crucially on the correctness of the kinetic network accepted for the overall process (V) [19]. In particular, in CF_3I pyrolysis the final product C_2F_6 can accumulate not via the recombination route (II), but via the substitution reaction

$$CF_3^{\bullet} + CF_3I \xrightarrow{k_6} I^{\bullet} + C_2F_6, \qquad \text{(IX)}$$

which is difficult to distinguish kinetically from the sequence of reactions (VI) and (II) or (VII) and (II).

However, *difficult* does not mean *impossible*. Indeed, the rate of the bimolecular reaction (IX) is independent of the pressure of the buffer gas M, while the rate of the recombination reaction (II) depends on the M concentration unless this concentration is so high that the rate constant k_5 is in the high-concentration limit and is independent of [M] (see formula (2)). The kinetic experiments reported in [17] were performed just in the transitional range of CF_3I buffer gas pressures. We observed in these experiments that the rate of the overall process (V) depends on the total pressure. This indicates that recombination (II) is the rate-limiting step of process (V).

This work provides further evidence that it is the rate constant of recombination (II) (reaction (I)) that was measured in [17]. As is clear from the table, the $k^{M}_{(CF_3)_2}$ values reported in [17] for M = CF_3I occupy their logical place among the $k^{M}_{(CF_3)_2}$ values obtained here for M = He, N_2, and Ar. This data array would not be so regular if recombination (I) in [17] were imitated by reaction (IX).

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