Abstract: The thermal dissociation/recombination reactions of the perfluoromethyl halides \( \text{CF}_3 \rightarrow \text{CF}_3 + \text{F} \), \( \text{CF}_3 \text{Cl} \rightarrow \text{CF}_3 + \text{Cl} \), \( \text{CF}_3 \text{Br} \rightarrow \text{CF}_3 + \text{Br} \), and \( \text{CF}_3 \text{I} \rightarrow \text{CF}_3 + \text{I} \) are analyzed with respect to their transition (for increasing pressures) from second-order to first-order dissociation (or from third-order to second-order recombination). The dependence of this transition on the temperature is documented. Practical aspects of the modelling of falloff curves are discussed.

1. Introduction

For over one hundred years,[1] the rate constants of thermal dissociation (and the reverse recombination) reactions have been interpreted as a competition between intermolecular collisional activation (and deactivation) and intramolecular rearrangement processes. The consequence of this competition are pressure- (or bath gas concentration [M]-) dependent rate “constants”, i.e. the falloff curves of the reactions. Information on these curves is of considerable fundamental as well as practical importance. On the one hand, the measured rate constants may provide information on molecular properties of the reacting species. On the other hand, temperature- and pressure-dependences of rate constants are required for a quantitative modelling of numerous phenomena governed by reaction kinetics, such as combustion, atmospheric, or interstellar chemistry.[2–4]

Over the past about 15 years, our group has combined experimental studies of thermal dissociation reactions of fluorocarbons with theoretical treatments based on statistical unimolecular rate theories in combination with quantum-chemical calculations. The results allowed us to represent pressure- and temperature-dependences of rate constants in a compact manner and over wide ranges of conditions. Allowing for an adjustment of few, only incompletely known, molecular parameters at some place of the available experiments, the modelled rate constants then could be extrapolated into ranges which are not easily accessible experimentally. The present article illustrates this for the series of perfluoromethyl halides which so far have been studied only to a limited extent. Reactions of this class of molecules may be of practical importance, e.g., in the search for \( \text{SF}_6 \)-alternative substances, having smaller global warming potential than \( \text{SF}_6 \) and being useful as insulation and arc-suppressing gases in high-pressure electrical switches.[5–7] In addition, such reactions may also be important for the modelling of plasma etching processes, see e.g.[8–9]
Reactions R1–R4 have widely varying reaction enthalpies $\Delta H_0$ and thus should show the influence of this quantity particularly well. The given values of $\Delta H_0$ at 0 K are either from\textsuperscript{[10]} or from the quantum-chemical calculations described below or in the Supporting Information, (SI; the values from the latter are used throughout the present calculations).

As the dissociation rate constants $k_{\text{dis}}$ contain Boltzmann factors $\exp(-\Delta H_0/RT)$, their values may vary over many orders of magnitude. It, therefore, appears plausible to split off the Boltzmann factors and to analyze the remaining part of the rate constants. The analogous is achieved by focusing attention on recombination rate constants $k_{\text{rec}}$. As $k_{\text{dis}}$ and $k_{\text{rec}}$ are related by the equilibrium constant $K_c$ through

$$K_c = k_{\text{dis}}/k_{\text{rec}}, \quad (1)$$

falloff curves of $k_{\text{rec}}$ and of $k_{\text{dis}}$ have the same shape and can be analyzed with respect to the dependence on molecular parameters in a similar manner ($k_{\text{dis}}$ in $s^{-1}$, $k_{\text{rec}}$ in $cm^3/mol/s$).

Falloff curves and, therefore, the kinetic order of the reaction with respect to the bath gas concentration $[M]$, depend on the temperature $T$. This is first illustrated for reaction R1 in Figure 1 with modelled falloff curves for $k_{\text{rec}}$ as a function of $[Ar]$ and $T$. At 300 K and 1 bar of Ar (corresponding to $[Ar] = 4 \times 10^{-5}$ mol cm$^{-3}$), $k_{\text{rec}}$ is predicted to be practically independent of $[Ar]$; i.e., the recombination is close to a second-order process. On the other hand, at 2000 K and 1 bar of Ar ($[Ar] = 0.6 \times 10^{-5}$ mol cm$^{-3}$), $k_{\text{rec}}$ and, hence, also $k_{\text{dis}}$ clearly depend on $[Ar]$, such that the recombination is closer to a third-order process (while the dissociation R1 is closer to a second-order process). Obviously, it is essential to locate the falloff curves of the reaction at the considered conditions of pressure and temperature. Practical aspects of this procedure are the issue of the present article. An analysis of the described kind is often lacking in experimental work. Sometimes, a reaction order is assumed on intuition and the corresponding rate constant is used for arbitrary conditions. As this may introduce considerable errors, it does not appear acceptable. A complete analysis such as described in the following, therefore, has to be made.

2. Calculation of Rate Constants

The dominant quantities characterizing falloff curves like Figure 1 are the limiting high-pressure (subscript $\infty$) and low-pressure (subscript 0) rate constants. The transition between the limiting rate constants is also of importance, but matters less. In the following, we analyze the limiting rate constants first, before intermediate parts of the falloff curves are considered afterwards.

![Figure 1. Falloff curves for the recombination reaction R1, i.e. CF$_3$ + F $\rightarrow$ (Ar), at T = 300, 400, 800, 1000, 2000, and 4000 K (from top to bottom). Modelling results assuming values of $-\langle \Delta E \rangle_{\text{coll}}/\hbar c = 500$ cm$^{-1}$ for collisional energy transfer (for the reason of this choice, see the text and the SI; modelled center broadening factors are $\Gamma_{\text{cen}} = 0.76, 0.57, 0.26, 0.21, 0.12$, and $0.12$ for $T = 300, 400, 800, 1000, 2000, 4000$ K, respectively).](image-url)
2.1 Quantum-Chemical Calculation of Molecular Properties

In this section, we examine relevant properties of the potential energy surfaces (PESs) of reactions R1–R4. All calculations were done at the G4 composite ab initio level of theory using the Gaussian 09 suite of programs[11] with the default integration grid[12] while optimized molecular structures and harmonic vibrational frequencies were derived at the B3LYP/6-311 + G(3df) level of density functional theory.[13]

In all cases, the electronic potential along the C–X-distance \( r \) of the reaction could well be fitted by a Morse potential

\[
V(r) = D_e \left( 1 - \exp \left[ -\beta_e (r - r_e) \right] \right)^2 \tag{2}
\]

(for reaction R1 with the three parameters \( D_e = 587 \text{ kJ mol}^{-1}, \beta_e = 1.66 \text{ Å}^{-1}, \text{ and } r_e = 1.324 \text{ Å}, \) see the SI for the parameters of reactions R2–R4). Besides the electronic potential, also the anisotropy of the PES has to be characterized. This can be done by determining the \( r \)-dependence of the frequencies of the transitional modes, i.e. of those modes which change from vibrations into free rotations of the fragments relative to each other. Often, an exponential decay of the transitional mode frequencies was observed, such as described approximately by

\[
v = v(r_e) \exp \left[ -\alpha_e (r - r_e) \right] \tag{3}
\]

For reaction R1 and its degenerate transitional mode, the parameters \( v(r_e) = 516 \text{ cm}^{-1} \) and \( \alpha_e = 0.89 \text{ Å}^{-1} \) were fitted such that \( \alpha_e/\beta_e = 0.54 \). A ratio of \( \alpha_e/\beta_e \) much larger than unity would correspond to “loose activated complex” transition state theory (TST), i.e., to “phase space theory” (PST), whereas normal (and rigid) activated complex TST corresponds to smaller values of \( \alpha_e/\beta_e \).

The ratio of \( \alpha_e/\beta_e = 0.54 \) determined for reaction R1 is close to the average value of 0.5 found empirically for many simple bond dissociation processes in.\(^{14}\) Table 1 compares a series of quantum-chemically determined ratios \( \alpha_e/\beta_e \) for reactions R1–R4 and recombination reactions with other C–F bonds. The shown values on average amount to \( \alpha_e/\beta_e = 0.47 \pm 0.04 \), indeed being close to 0.5, although some deviations are also observed.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \alpha_e/\text{Å}^{-1} )</th>
<th>( \beta_e/\text{Å}^{-1} )</th>
<th>( \alpha_e/\beta_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF(_3) + F</td>
<td>0.89</td>
<td>1.66</td>
<td>0.54</td>
</tr>
<tr>
<td>CF(_3) + Cl</td>
<td>0.75</td>
<td>1.65</td>
<td>0.46</td>
</tr>
<tr>
<td>CF(_3) + Br</td>
<td>0.69</td>
<td>1.60</td>
<td>0.43</td>
</tr>
<tr>
<td>CF(_3) + I</td>
<td>0.60</td>
<td>1.45</td>
<td>0.41</td>
</tr>
<tr>
<td>CF(_3) + F</td>
<td>0.53</td>
<td>1.76</td>
<td>0.30</td>
</tr>
<tr>
<td>CF + F</td>
<td>0.97</td>
<td>1.71</td>
<td>0.57</td>
</tr>
<tr>
<td>CF(_2) + F</td>
<td>1.74</td>
<td>2.90</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Besides eqs. (2) and (3), also the dependence of the effective rotational constant \( (B + C)/2 \) of the reacting species along the minimum energy path (MEP) of the dissociating bond is of relevance. A fit in the form

\[
(B + C)/2 = \{ (B^* + C^*)/2 \} \{ 1 + b_1 (r - r_e) + b_2 (r - r_e)^2 \} \tag{4}
\]

was found to be appropriate (for reaction R1 with the parameters \( (B^* + C^*)/2 = 0.190 \text{ cm}^{-1}, \) \( b_1 = 0.374, \) and \( b_2 = 0.19; \) \( r \) and \( r_e \) in Å; for reactions R2–R4, see the SI). Together with eqs. (2) and (3), eq. (4) serves for the determination of the minimum threshold energies \( E_{th}^{(J)} \) as a function of the total angular momentum (quantum number \( J \)), i.e. the centrifugal maxima of the PES. The \( E_{th}^{(J)} \) are required at various places of the calculations, for instance for the calculation of rate constants in the PST - limit. Eqs. (2)–(4) characterize those properties of the PES which enter the calculation of thermal rate constants in a dominant way, while finer details are mostly averaged out and appear only of minor importance.

2.2 Determination of Limiting High-Pressure Rate Constants

The high-pressure range of recombination corresponds to a capture situation where all encounters of reactants A and B lead to the formation of complexes AB to be stabilized by collisions. It, therefore, appears reasonable to express the limiting high-pressure recombination rate constants \( k_{\text{rec,}\text{c}} \) in terms of simple hard-sphere collision theory, with rate constants \( k_{\text{coll, HS}} \) given by\(^{15}\)

\[
k_{\text{coll, HS}} = f_d \ d_{\text{AB}}^2 \ (8 \ \pi \ kT/\mu_{\text{AB}})^{1/2} \tag{5}
\]

(with hard-sphere collision diameter \( d_{\text{AB}} \) and reduced mass \( \mu_{\text{AB}} \) of the reactants A and B). An electronic weight factor \( f_d = Q_d(AB)Q_d(A)Q_d(B) \) with the respective electronic partition functions \( Q_d \) indicates which fraction of encounters leads into the relevant electronic state of AB. While \( k_{\text{coll, HS}} \) is well defined for a hard-sphere potential with contact distance \( d_{\text{AB}} \) between the reactants, the treatment changes for more complicated potentials like the Morse-potential of eq. (2). In this case, classical trajectory (CT) calculations allow one to determine rate constants \( k_{\text{cap}} \) for capture of the reactants. Systematic CT calculations have been made in\(^{16}\) (for atoms combining with linear rotors) and\(^{17}\) (for linear rotors combining with linear rotors) considering a variety of adduct geometries. The calculations led to approximate analytical expressions for a quantity defined by

\[
Y(X) = k_{\text{cap, PST}} \ (8 \ \pi \ kT/\mu_{\text{AB}})^{-1/2} \beta_e^2 \tag{6}
\]

which corresponds to the ratio \( k_{\text{cap, PST}}/k_{\text{coll, HS}} \) (\( f_d \) here is put equal to unity). The derived expressions were found to be of the form

\[
Y(X) \approx a_0 + a_1 \ X + a_2 \ X^2 \tag{7}
\]
with $X$ defined by $X = \ln (kT/D_e) - \beta E_e$ and the coefficients determined as $a_0 = -15.7706$, $a_1 = -8.6364$, and $a_2 = 0.9975$ (often the equilibrium center-of-mass distance between the reactants A and B in the adduct AB may be used for $r_e$). It should be mentioned that accounting for the change of the rotational constant of the adduct along the MEP as described by eq. (4) has only a minor influence on eq. (7). On the other hand, the anisotropy of the potential described by eq. (3) reduces the capture rate constant $k_{cap}$ to values smaller than $k_{cap}^{PST}$. We characterize this effect by a “rigidity factor” $f_{rigid}$ defined by

$$f_{rigid} = k_{rec,e}^{PST}/k_{rec,e}$$

As long as $f_{rigid} < 0.8$,

$$f_{rigid} \approx 8^{1/2} \left(\frac{B_e + C_e}{2}\right) D_e / \{h\nu(r_e)\}^2$$

provides a useful approximation to the results of the CT calculations (for more detailed expressions, see[16] and[17]). One should also note that the results from the CT calculations coincide with results from the Statistical Adiabatic Channel Model (SACM)[18] such that the method is denoted by “SACM/CT”. In the present work we have compared SACM/CT calculations of $k_{cap} = k_{rec,e}$ with $k_{cap}^{PST} = k_{rec,e}^{PST}$ (both from SACM/CT and classical PST calculations). Table 2 shows results for $k_{rec,e}^{PST}$, $f_{rigid}$ and $k_{rec,e} = f_{rigid} k_{rec,e}^{PST}$, for reactions R1–R4 and at temperatures between 300 and 4000 K. The various contributing molecular parameters (see the SI) according to eqs. (6)–(9) partly compensate each other such that specific trends are difficult to recognize.

### Table 2. Modelled high-pressure recombination rate constants for reactions R1–R4 in phase space theoretical limit, $k_{rec,e}^{PST}$ (see text, upper third of the table, in $10^{-2} cm^3 mol^{-1} s^{-1}$), $k_{rec,e}$ (see text, lower third of the table, also in $10^{-2} cm^3 mol^{-1} s^{-1}$), and rigidity factors $f_{rigid} = k_{rec,e}/k_{rec,e}^{PST}$ (middle third of the table; the given $f_{rigid}$ account for minor rotational contributions; $f_{rigid}$ was included in all calculations).}

<table>
<thead>
<tr>
<th>T/K</th>
<th>CF$_1$ + F</th>
<th>CF$_1$ + Cl</th>
<th>CF$_1$ + Br</th>
<th>CF$_1$ + I</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>67.6</td>
<td>54.9</td>
<td>47.6</td>
<td>41.7</td>
</tr>
<tr>
<td>1000</td>
<td>79.0</td>
<td>69.4</td>
<td>66.8</td>
<td>59.5</td>
</tr>
<tr>
<td>2000</td>
<td>87.0</td>
<td>75.8</td>
<td>80.7</td>
<td>71.5</td>
</tr>
<tr>
<td>4000</td>
<td>96.2</td>
<td>83.6</td>
<td>94.0</td>
<td>84.0</td>
</tr>
</tbody>
</table>

$$f_{rigid} \approx 8^{1/2} \left(\frac{B_e + C_e}{2}\right) D_e / \{h\nu(r_e)\}^2$$

In summary, we found that the calculated values of $k_{rec,e}$ generally agree with the most probable experimental values within about a factor of two. As many parameters contribute to the high pressure rate constants, one cannot expect simple behavior, like simple temperature dependences.

#### 2.3 Determination of Limiting Low-Pressure Rate Constants

After the calculation of limiting high-pressure rate constants $k_{rec,e}$ has been described in Section 2.2, limiting low-pressure rate constants $k_{rec,0}$ are considered in the following. By solving master equations for collisional activation/deactivation and assuming steady-state for the populations of excited states,[19] expressions for $k_{rec,0}$ could be represented in the form

$$k_{rec,0} = [M] Z_{D1} \beta \rho_{vib,h}(E_0) kT F_{anh} F_E F_{rot} \left[\frac{\hbar}{T} f_{trans}/Q_v(A) Q_{vib}(B)\right].$$

$Z_{D1}$ here denotes the Lennard-Jones collision frequency between excited AB and M, $\rho_{vib,h}(E_0)$ is the harmonic vibrational density of states of excited AB at the dissociation energy $E_0$. $F_{anh}$, $F_E$, and $F_{rot}$ are correction factors for anharmonicity, for the used expressions of the energy dependence of the vibrational density of states, and for rotation, respectively. $f_{trans}$ is as given above; $f_{trans}$ and $f_{rot}$ are the relevant ratios of translational and rotational partition functions in $k_{vib}$; $Q_{vib}$ and $Q_{rot}$ are vibrational and rotational partition functions, respectively; The collision efficiency $\beta_v$ is related to the average (total) energy $\langle \Delta E \rangle_{total}$ transferred per collision through

$$\beta_v (1 - \beta_v^{1/2}) \approx - \langle \Delta E \rangle_{total}/h c (F_E kT)$$

(one should note that $\langle \Delta E \rangle_{total}$ is a negative quantity). For large values of the ratio $- \langle \Delta E \rangle_{total}/hc (F_E kT)$, one has “strong collisions”, i.e. $\beta_v$ approaches unity. In the case $\beta_v < 1$, one speaks of “weak collisions”. The various molecular parameters enter the expression for $k_{rec,0}$ in an intricate manner. This is illustrated in Table 3, where some of the factors entering eq. (10) are compared for reactions R1–R4. The table shows that the decrease of $k_{rec,0}/[Ar]$ from reaction R1 to reaction R4 is dominated by the decrease of $\rho_{vib,h}(E_0)$ which, in turn, is related to the decrease of $E_0$. As compact expressions for $\rho_{vib,h}(E_0)$ are available (see e.g.[21]), the trend of $k_{rec,0}$ within the considered group of reactions can well be quantified and be attributed mostly to the trend of $\rho_{vib,h}(E_0)$. At present, the largest uncertainty for the calculation of $k_{rec,0}$ appears to be the value of $\langle \Delta E \rangle_{total}$ and, hence, of $\beta_v$. It is often used as an empirical fit parameter to be chosen of reasonable magnitude. However, theoretical calculations are also becoming possible (see e.g.[22]). Values of $- \langle \Delta E \rangle_{total}/hc = 100 cm^{-1}$ have been chosen for the calculations of Table 3, while an experimentally fitted value of 500 cm$^{-1}$ was preferred in Figure 1 (further considerations are given below).
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Table 3. Contributions to low-pressure rate constants $k_{rec,0}$ expressed by eq. (10) (modelling according to[26] for M=Ar and $T=300$ K with $E_0$ in kJ mol$^{-1}$, $Z_{ij}$ in 10$^{14}$ cm$^{-1}$ mol$^{-1}$ s$^{-1}$, $\rho_{abh}(E_0)$ in 10$^8$(kJ mol$^{-1}$)$^{-1}$, and $k_{rec}/[Ar]$ in 10$^{10}$ cm$^{-3}$ mol$^{-1}$ s$^{-1}$; estimates of the collision efficiency $\beta_c$ have been made through eq. (11) with $-\langle \Delta E \rangle_{total}/hc = 100$ cm$^{-1}$.

|                  | $CF_1+F$ (+Ar) | $CF_1+Cl$ (+Ar) | $CF_1+Br$ (+Ar) | $CF_1+I$ (+Ar) |
|------------------|----------------|----------------|
| $E_0$            | 542            | 361            | 293            | 225            |
| $Z_{ij}$         | 1.7            | 1.8            | 1.8            | 1.8            |
| $\rho_{abh}(E_0)$ | 7.5            | 1.4            | 0.68           | 0.15           |
| $F_{rec}$        | 1.8            | 1.2            | 1.2            | 1.2            |
| $F_{f_r}$        | 1.04           | 1.05           | 1.06           | 1.08           |
| $F_{n_r}$        | 15.5           | 16.2           | 19.1           | 16.6           |
| $\beta_c$        | 0.24           | 0.24           | 0.23           | 0.23           |
| $k_{rec}/[Ar]$   | 9.7            | 5.4            | 2.5            | 0.49           |

2.4 Falloff Curves

The calculation of the limiting high- and low-pressure rate constants ($k_{rec,c}$ or $k_{dis,c}$ and $k_{rec,0}$ or $k_{dis,0}$) by eqs. (5)–(11) allows one to locate the position of the falloff curves along the scale of bath gas concentrations [M]. The most important quantity in this respect is that value of [M], denoted by $[M]_{cent}$, for which the extrapolated $k_{rec,c}$ ([M]) or $k_{dis,0}$ ([M)]) is equal to $k_{rec,0}$ (or $k_{dis,0}$); i.e., $[M]_{cent}$ is defined by

$$[M]_{cent} = k_{rec,0}/k_{rec,c} = k_{dis,0}/k_{dis,c}. \quad (12)$$

The results described in sections 2.2 and 2.3 lead to important conclusions on $[M]_{cent}$. First, one notes that $[M]_{cent}$ markedly increases with increasing temperature. This is illustrated, e.g., in Figure 1 where $[Ar]_{cent}$ increases from $[Ar]_{cent}$ ≈ 2 × 10$^{-11}$ cm$^{-3}$ at 300 K to $[Ar]_{cent}$ ≈ 2 × 10$^{-4}$ cm$^{-3}$ at 3000 K. Second, one observes some dependence on the chosen value of $-\langle \Delta E \rangle_{total}$. E. g., at 3000 K one has $[Ar]_{cent}$ ≈ 7 × 10$^{-4}$ cm$^{-3}$ for $-\langle \Delta E \rangle_{total}/hc = 100$ cm$^{-1}$ while $[Ar]_{cent}$ ≈ 7 × 10$^{-5}$ cm$^{-3}$ for $-\langle \Delta E \rangle_{total}/hc = 2000$ cm$^{-1}$.

While the value of $[M]_{cent}$ is of central importance, one also has to consider the shape of the falloff curves, i.e. the type of transition from $k_{rec,0}$ to $k_{rec,c}$ (or from $k_{dis,0}$ to $k_{dis,c}$). In the simple Lindemann-Hinshelwood model of competing single-step inter- and intra- molecular processes, it would be given by

$$k_{rec}/k_{rec,c} = x/(1+x) \quad (13)$$

where $x = k_{rec,0}/k_{rec,c}$ or $x = k_{dis,0}/k_{dis,c}$. The results of more detailed treatments, like the RRKM (Rice – Ramsperger–Kassel – Marcus) model, however, require modifications of this result. These may be represented by an additional “broadening factor” $F(x)$ to be multiplied with the right-hand side of eq. (13).[25] $F(x)$ can be interpreted in terms of an “effective number of oscillators” of the system, and it can be estimated for strong collisions (superscript sc) as well as weak collisions (superscript we). One has $F(x) \approx F(x)^{\text{sc}} F(x)^{\text{we}}$ where $F(x)^{\text{sc}}$ can be estimated with the methods of[26] while $F(x)^{\text{we}}$ can be expressed by the collision efficiency $\beta_c$.[26,24,25]

Most importantly, $F(x)$ is characterized by a “central broadening factor”, defined by $F_{cent} = F(x=1)$. With this value, $F(x)$ can roughly be approximated by $[26]$

$$\log F(x) \approx \{1/[1+(\log x/N)^2]\} \log F_{cent} \quad (14)$$

where

$$N \approx 0.75 - 1.27 \log F_{cent} \quad (15)$$

In case of very broad falloff curves (small $F_{cent}$), a more refined, alternative expression has been proposed in [24, 25]. It is of the form

$$F(x) = (1 + x/x_0)^n/[1 + (x/x_0)^n] \quad (16)$$

where $x_0$ has been found in the range 0.9–1. $N$ is related to $F_{cent}$ by

$$n = \ln 2/\ln(2/F_{cent}) \quad [1-b + b (x/x_0)^n] \quad (17)$$

where $q = (1+F_{cent}-1)/\ln(F_{cent}/10)$ and $b$ has been found in the range 0.1–0.25. For simplicity, we mostly used $x_0 = 1$ and $b = 0.2$.

Using $-\langle \Delta E \rangle_{total}/hc = 500$ cm$^{-1}$ (see the following section), sets of falloff curves for the recombination reactions R2–R4 have been calculated. Figures 2–4 show the results. The shapes of the curves are all quite similar to that shown in Figure 1 for reaction R1. However, because of different $[Ar]_{cent}$ (mostly caused by different $\rho_{abh}(E_0)$, due to different $E_0$), the position of the curves along the scale of $[Ar]$ are different. In practice it matters more that the reactions in the dissociation direction are studied at different temperatures. Reaction R1 in the dissociation direction, e.g., in our laboratory has been studied at temperatures around 2500 K,[26] while the corresponding dissociation experiments for reaction R4 have been made at half that temperature.[27—29]

3. Practical Problems

The dependence of the reaction order on the nature of the bath gas M and on the temperature T, such as illustrated in Figures 1–4, poses a challenge to applications. In order to determine the reaction order, one either has to perform experiments over a sufficiently broad pressure range, which may be difficult to do, or one may try to compare measurements with modelled falloff curves, which is hampered by uncertainties in the input quantities (to a small extent of the reaction enthalpy $\Delta H^0$ and to a much larger extent of the energy transfer parameter $-\langle \Delta E \rangle_{total}$). Further difficulties may arise when the composition of the bath gas, during an

experiment, changes with time. The effects of uncertainties in $\Delta H_0$ and $\langle \Delta E \rangle_{\text{total}}$ may be difficult to disentangle (the value of $\langle \Delta E \rangle_{\text{total}}/hc = -500 \text{ cm}^{-1}$ used in the modelling of Figures 1–4 has been taken from the analysis of dissociation experiments of CF$_4$ in Ar near 2500 K$^{[26]}$ assuming an only weak temperature dependence of $\langle \Delta E \rangle_{\text{total}}$, see$^{[31]}$).

The situation looks simplest for recombination experiments near room temperature. For bath gas pressures near to 1 Torr (corresponding to [M] $\approx 5 \times 10^{-8} \text{ mol cm}^{-3}$), Figures 1–4 indicate that $k_{\text{rec}}$ for all reactions R1–R4 is close to their high-pressure second-order limit. Replacing M=Ar by M=He changes the situation only slightly. Nevertheless, a small drop
of $k_{\text{rec}}$ with decreasing [He] for reaction R1 was reported in [8]. It was shown in [30] that this is compatible with modelling results. On the other hand, the stronger dependences of $k_{\text{rec}}$ on [M] reported in [32, 33] appear less probable and call for a re-analysis of the experiments. A representation as a third-order process certainly does not appear justified. Studies of the thermal dissociation of CF$_4$ at temperatures between 2000 and 3000 K and [Ar] between $5 \times 10^{-6}$ and $10^{-4}$ mol cm$^{-3}$ in [26, 34], according to Figure 1 locate the reaction between a second-order and a first-order process. The analogous applies to dissociation experiments for CF$_3$Cl [35]. For the dissociation of CF$_3$Br (see e.g. [35–37]), and even more that of CF$_3$I, [27–29, 35] the intermediate reaction order had to be accounted for. A representation as a first-order process here did not appear justified at all. Instead, rate constants $k_{\text{dis}}$ had to be reported for a fixed pressure (or [M]) such as done in [6], or full falloff curves have to be determined and rate constants represented accordingly. Experimental and modelling studies of the thermal dissociations of CF$_3$Cl, CF$_3$Br, and CF$_3$I at low bath gas pressures (corresponding to $10^{-6}$ mol cm$^{-3}$) have all been represented as second-order processes. While this appears realistic for the temperatures near 2000 K as applied in the studies of CF$_3$Cl and CF$_3$Br, for the lower temperatures (near 1000 K) employed for the dissociation of CF$_3$I, deviations due to the transition to first-order behavior according to Figure 4 have to be expected. A re-analysis of the available results with full falloff curves thus appears advisable.

In any case, it is not possible to model dissociation pathways of SF$_6$-alternatives like perfluoroketones or perfluoronitriles by sequences of first-order processes characterized by simple Arrhenius expressions of their rate constants. It may be more appropriate to assume second-order dissociation behavior with effective rate constants taken from falloff curves at the relevant pressures. The falloff curves for $k_{\text{rec}}$ shown in Figures 1–4 may serve for this purpose.

**Acknowledgements**

The authors are grateful to Professor Helmut Schwarz for his long-standing encouragement of kinetic work and his inspiring suggestions of applications. Support by the Deutsche Forschungsgemeinschaft (Project TR69/21-3) is also gratefully acknowledged. Open Access funding enabled and organized by Projekt DEAL.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**References**


Research Article


Manuscript received: January 16, 2023
Revised manuscript received: February 22, 2023
Version of record online: March 14, 2023