RESEARCH PAPER

The kinetics of the $CF_3 + CF_3$ and $CF_3 + F$ combination reactions at 290 K and at He-pressures of ≈ 1–6 Torr

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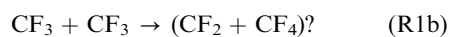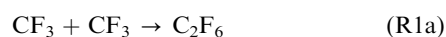[b] *IMEC, Kapeldreef 75, B-3001 Leuven, Belgium. E-mail: Johan.Vertommen@imec.be*

The rate constants for the combination reactions $CF_3 + CF_3$ and $CF_3 + F$ at 290 K and helium pressures of ≈ 1–6 Torr have been determined, using clean chemical sources of CF_3, by means of discharge flow-molecular beam sampling-threshold ionisation mass spectrometry (DF/MB-TIMS). For the mutual reaction of CF_3, no pressure dependence could be observed over the 1–6 Torr pressure range, indicating that the obtained rate constant of $k_1^\infty = (1.8 \pm 0.6) \times 10^{-12}$ cm^3 s^{-1} is the high pressure limit. This result, which agrees with the lowest values in literature but is *ca.* five times smaller than the most recent data, is fully in line with the known trend in the mutual reaction rate constant for the series CH_3; CH_2F; and CHF_2. The reaction of CF_3 with F was found to exhibit a clear pressure dependence in the 0.5 to 6 Torr range. Using a Troe fall-off formalism, the low-pressure limit rate constant was determined as k_2^0(He) $= (1.47 \pm 0.24) \times 10^{-28}$ cm^6 s^{-1}, differing substantially from the only available previous determination; a variational transition state theoretical treatment is shown to support our data.

Introduction

CF_3 is a key intermediate in the chemistry of fluorocarbon etching plasmas in the manufacture of integrated circuits. Its major plasma reactions

$$CF_3 + CF_3 \rightarrow C_2F_6 \qquad \text{(R1a)}$$

$$CF_3 + CF_3 \rightarrow (CF_2 + CF_4)? \qquad \text{(R1b)}$$

$$CF_3 + F \rightarrow CF_4 \qquad \text{(R2)}$$

have received wide attention from various research groups.[1–19] However, the reported kinetic data show a wide spread. Regarding the mutual reaction of CF_3, the available rate constant k_1 data at room temperature range from 2.2×10^{-12} to 1.5×10^{-11} cm^3 s^{-1}. This may be partly due to the wide range of experimental conditions (gas composition, pressure) and in some cases to the extrapolation of data to ambient pressure and/or room temperature conditions. To cite only the more recent determinations at room temperature, Pagsberg *et al.*[17] reported $k_1 = (10.4 \pm 1.2) \times 10^{-12}$, Vakhtin[16] $(3.9 \pm 1.3) \times 10^{-12}$, Skorobogatov *et al.*[14] $(11 \pm 4) \times 10^{-12}$, Robertson *et al.*[13] 4.7×10^{-12}, Brown *et al.*[11] $(2.2 \pm 0.5) \times 10^{-12}$, Selamoglu *et al.*[10] $(4.0 \pm 0.5) \times 10^{-12}$ and Plumb and Ryan[9] 8.3×10^{-12} cm^3 s^{-1}. The cited data of Robertson *et al.* and Selamoglu *et al.* have been corrected for the pressure effect $k^\infty / k = 1.33$ as determined by these authors for their low-pressure conditions ($p = 10$ mtorr and room temperature). It was our goal to determine the $CF_3 + CF_3$ rate constant using a clean source of CF_3, in the absence of any other radical, so as to avoid interference by other CF_3-removal reactions, and hence to clarify this situation.

Data on the $CF_3 + F \rightarrow CF_4$ reaction, on the other hand, are scarce: quite surprising since it is one of the most important reactions in a plasma etching system, acting as a major radical sink and removal pathway of the main etching species, namely F atoms. Butkovskaya *et al.*[18] determined the bimolecular rate constant at 2 and 7 Torr Ar: $k_2(2 \text{ Torr}) = (1.0 \pm 0.2) \times 10^{-11}$ and $k_2(7 \text{ Torr}) = (4.4 \pm 1) \times 10^{-11}$ cm^3 s^{-1}, respectively. According to the authors this corresponds to a third order rate constant k_2^0(Ar) $= (1.6 \pm 0.4) \times 10^{-28}$ cm^6 s^{-1}. They also conclude that at 7 Torr the reaction is still in its lower pressure limit. Plumb and Ryan[19] on the other hand measured the 295 K rate coefficient at pressures between 0.7 and 7 Torr He. Over this pressure range only a slight increase in the rate constant was observed from 1.1×10^{-11} to 1.69×10^{-11} cm^3 s^{-1}. By fitting their data to Troe's formalism[34] they obtained the following parameters: k_2^0(He) $= 3.80 \times 10^{-27}$ cm^6 s^{-1}, $k_2^\infty = 1.99 \times 10^{-11}$ cm^3 s^{-1}, with the broadening factor $F_C = 0.54$. Given the large discrepancy between Butkovskaya's and Plumb's data—all the more significant since k^0 values are generally higher for Ar than He—we also re-examined the kinetics of this important combination process.

It should be noted that a reaction channel $CF_3 + F \rightarrow CF_2(X~^1A_1) + F_2$ can be disregarded as it is endothermal by ≈ 251 kJ mol^{-1}.

Experimental setup

The discharge-flow/molecular beam sampling mass spectrometer technique (DF/MB-MS) applied in this work has been previously described in detail;[20,21] only a brief summary will be given here. The flow reactor consists of a cylindrical quartz tube ($d = 2.8$ cm) equipped with two discharge side arms, two concentric axially movable central injector tubes, and two additional side inlets. *Via* these various inlets, continuous flows of gases can be added to the flow reactor. The flow rates were regulated and measured by calibrated mass flow controllers (MKS). Species concentrations in the reactor were determined from the fractional flows, the total pressure and the temperature. CF_3 radicals are formed by the reaction of CF_3H or CF_3I with F atoms, which are generated far upstream by passing a flow of F_2 diluted in He through a 75 W microwave discharge

in an Al_2O_3 side-arm ($\geq 90\%$ dissociation). The reactor wall was treated with a 10% HF solution on a regular basis to passivate the walls and suppress F atom recombination. Doing so, the position of the inner reactor tubes, and hence the total wall surface area exposed to F atoms, did not influence the observed recombination yield. All experiments were carried out at 290 K and over a pressure range between 0.5 and 6 Torr in He. The flow velocities typically ranged from 600 to 1800 cm s^{-1} and the corresponding maximum reaction times from 14 to 40 ms.

Qualitative and quantitative analysis was carried out by molecular beam sampling and threshold-ionization mass spectrometry. At the reactor exit, the gas is sampled through a 0.3 mm pinhole in a quartz cone giving access to the first of three differentially pumped low-pressure chambers. The ensuing gas jet is mechanically chopped in the second chamber to allow phase-sensitive detection. The resulting modulated molecular beam finally enters the third chamber, which houses a co-axial electron-impact ionizer and an extranuclear quadrupole mass spectrometer. A lock-in amplifier, tuned in phase with the beam modulation, allows distinction between the beam and background ions. In order to suppress signal contamination by fragment-ions, the nominal electron energies E_{el} were only a few eV above the ionization potentials (IP) of the species being monitored (CF_3 at 12.7 eV, C_2H_6 at 21.5 eV, CH_3 at 12.3 eV). In the case of CF_3 measurements in the presence of excess CF_3H, the CF_3^+ signal intensities were duly corrected for any residual CF_3^+ signal contribution from CF_3H fragment-ions, based on the signal ratio $i(CF_3^+)/i(CF_3H^+)$ measured separately in the absence of F atoms and on the actual $i(CF_3H^+)$ signal.

Methodology

(a) Determination of $[F]_0$

A prerequisite for the accurate determination of the $CF_3 + CF_3$ and $CF_3 + F$ rate constants is a reliable method for determining the initial absolute F atom concentration since it either directly determines the initial CF_3 concentration or is directly involved as reaction partner in large excess. Fluorine atoms are formed upstream, in a 75 W microwave discharge through ($\geq 90\%$) dissociation of F_2, diluted in He. The discharged fluorine/He mixture is mixed with CF_3H or CF_3I after flow times through the silica reactor of ≥ 0.1 s. Most often, the concentration of atoms formed from a parent diatom in a discharge is determined by switching the discharge on and off while following the concentration change of the diatomic precursor. However, due to the corrosive nature of F_2, one cannot safely rely on the F_2/He mixture ratio in the gas cylinder as specified by the supplier. Therefore the initial F atom content $[F]_0$ of the discharged mixture was determined by admixing a very large excess of CH_4 (instead of CF_3H) through the central injector, resulting in the sequence:

$$CH_4 + F \rightarrow CH_3 + HF \quad (R3)$$

$$CH_3 + CH_3 (+ M) \rightarrow C_2H_6 (+ M) \quad (R4)$$
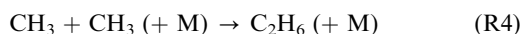
By using a sufficiently high CH_4 concentration and given the large k_3 of $(6.3 \pm 0.15) \times 10^{-11}$ cm^3 s^{-1},[22] conversion of F to CH_3 should be quasi-quantitative in less then 1 ms. Then, stoichiometry dictates that
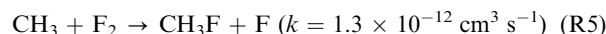
$$[F]_0 = [CH_3] + 2[C_2H_6] \quad (1)$$

or

$$[F]_0 = \frac{i(CH_3^+)}{S(CH_3)} + 2\frac{i(C_2H_6^+)}{S(C_2H_6)} \quad (2)$$

where $i(X^+)$ represents the measured signal and $S(X) \equiv i(X^+)/[X]$ the mass spectrometric sensitivity. Removal of CH_3

through the slow reaction with undissociated molecular fluorine ($\leq 10\%$),[23]

$$CH_3 + F_2 \rightarrow CH_3F + F \quad (k = 1.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}) \quad (R5)$$

forms again F atoms which—under our conditions of large excess CH_4—will immediately regenerate CH_3 via reaction (3). The overall net result of this reaction sequence is thus

$$CH_4 + F_2 \rightarrow CH_3F + HF \quad (R6)$$

and hence does not affect the stoichiometry eqn. (1) in any way.

Thus, plotting $2 \times i(C_2H_6^+)$ as a function of $i(CH_3^+)$ for various reaction times should yield a straight line with

$$\text{Slope} = -\frac{S(C_2H_6)}{S(CH_3)} \text{ and intercept} = S(C_2H_6)[F]_0 \quad (3)$$

as exemplified in Fig. 1. The CH_3^+ signals, at $E_{el} = 12.3$ eV, were corrected for fragment-ion contribution from CH_4. The intercept, combined with the sensitivity $S(C_2H_6)$ as determined using a certified C_2H_6/He gas mixture, yields the initial $[F]_0$. As an additional verification of this technique, the CH_3 sensitivity $S(CH_3)$ was determined from the slope of these plots. Using this value, the rate constant of reaction (4) could be determined from the experimental CH_3 decay profiles: $k_4 = [S(CH_3)/2t] \times [1/i(CH_3^+)_0 - 1/i(CH_3^+)_t]$. Our k_4 results at 2 Torr He and 290 K ranged between 5.0 and 5.4×10^{-11} cm^3 s^{-1}, which is in good agreement with the most recent available literature data ($5.5 \pm 0.3 \times 10^{-11}$ cm^3 s^{-1}).[24]

The alternative $[F]_0$ determination method based on the titration of F with H_2

$$F + H_2 \rightarrow HF + H \quad (R7)$$

did not provide satisfactory results due to the uncertain fate of the H atoms formed in this reaction. They can either react with undissociated F_2, forming a new F atom, or combine with F atoms on the reactor wall.

$$H + F_2 \rightarrow HF + F \quad (R8)$$

$$H + F \rightarrow HF \quad (R9)$$

Depending on the impact of the latter reaction, the equivalence point will range between:

$$[H_2]_{eq} = [F_2]_0 + [F]_0 \text{ and } [H_2]_{eq} = 0.5[F]_0 \quad (4)$$

As with the analogous $Cl + H$ reaction, the wall reaction between H atoms and F was observed indeed to be significant,
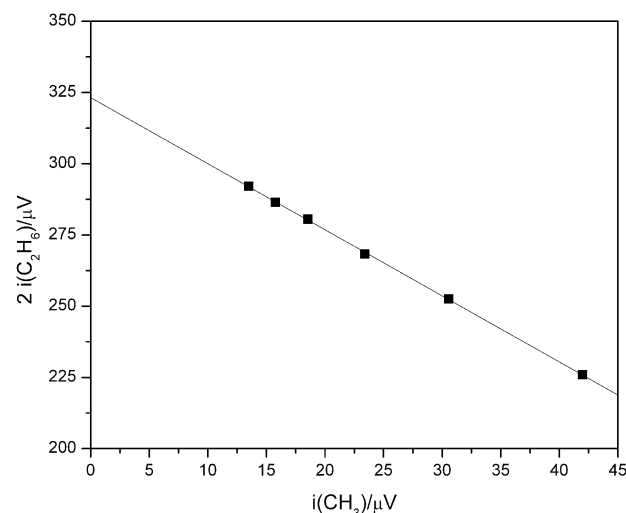
Fig. 1 Determination of $[F]_0$ by the reaction of F with CH_4: plot of $2 i(C_2H_6^+)$ measured at 21.5 eV as a function of $i(CH_3^+)$, measured at 12.3 eV. The intercept corresponds to the initial F atom concentration as described by eqn. (2).

and the H_2-titration method was found to be unreliable and to generally yield too high values for the initial F concentration.

(b) $CF_3 + CF_3$

The mutual reaction of CF_3 was studied in a CF_3H/F system at large excess of CF_3H over F. While the alternative $CF_3I + F$ reaction as CF_3 source benefits from a much higher rate coefficient (1.6×10^{-10} cm^3 s^{-1})[25] than the $F + CF_3H$ reaction (1.5×10^{-13} cm^3 s^{-1}),[26] the difference between the ionisation potential of CF_3 (9.3 eV) and the appearance potential of CF_3^+ from CF_3I (10.9 eV) is so small[27] that CF_3I cannot be used in systems where it has to be in excess to the co-reactant F, and its use is therefore restricted to the study of the $CF_3 + F$ reaction.

The concentration of CF_3H (3 to 6×10^{15} cm^{-3}) was in very large excess to F ($\approx 5 \times 10^{13}$ cm^{-3}) and in these conditions the F decay rate is ≈ 600 s^{-1}, which guarantees a 95% conversion of F atoms after 5 ms.

$$CF_3H + F \rightarrow CF_3 + HF \qquad (R10)$$

The hundredfold excess of CF_3H also ensures a negligible loss of F and CF_3 by the secondary reaction

$$CF_3 + F \rightarrow CF_4 \qquad (R2)$$

and hence a quasi-quantitative conversion of F into CF_3. The gas flow rates were varied between 600 and 1400 cm s^{-1} in order to obtain an as large as possible total reaction time (up to 40 ms). After the rapid conversion of F atoms into CF_3, only the mutual reaction of CF_3 can occur, no other reactive species being present:

$$CF_3 + CF_3 (+ M) \rightarrow C_2F_6 (+ M) \qquad (R1a)$$

$$CF_3 + CF_3 \rightarrow CF_4 + CF_2 \qquad (R1b)$$

Reaction path 1b, which is seldom considered in reaction models, is thermochemically accessible: $\Delta H_r = -46$ kcal mol^{-1},[28] but then only for the formation of CF_2 in its (quasi un-reactive) singlet ground state.[29]

The value of k_1, the mutual CF_3 reaction rate constant, can be obtained directly from the CF_3 decay. As soon as all F atoms are converted into CF_3, i.e. after ≈ 8 ms in our conditions, CF_3 removal can occur only by reaction (1), obeying:

$$\frac{d[CF_3]}{dt} = -2(k_{1a} + k_{1b})[CF_3]^2 = -2k_1[CF_3]^2 \qquad (5)$$

which results in:

$$[CF_3]^{-1} = [CF_3]_0^{-1} + 2k_1t \qquad (6)$$

Plotting $[CF_3]^{-1}$ as a function of time results in a straight line with a slope equal to $2 \times k_1$. In order to successfully apply this method, it is imperative to measure the absolute concentration of CF_3. The mass spectrometric sensitivity to CF_3 is determined through the initial F atom concentration $[F]_0$ via the stoichiometry equation, valid after disappearance of all F atoms:

$$[F]_0 = [CF_3] + 2[C_2F_6] + 2[CF_4] \qquad (7)$$

using the ratio $k_{1a}/k_{1b} = [C_2F_6]/[CF_4]$, this can be rewritten to:

$$[F]_0 = [CF_3] + 2[C_2F_6]\left(1 + \frac{k_{1b}}{k_{1a}}\right) \qquad (8)$$

Converting concentrations into signal intensities yields:

$$i(CF_3^+) = [F]_0 S(CF_3)$$
$$- 2\frac{i(C_2F_5^+)}{S(C_2F_5^+/C_2F_6)} S(CF_3)\left(1 + \frac{k_{1b}}{k_{1a}}\right) \qquad (9)$$

with $i(CF_3^+)$ and $i(C_2F_5^+)$ the signal intensities of CF_3^+ (corrected for any $CF_3H \rightarrow CF_3^+$-fragment ion contribution) and of the $C_2F_5^+$ fragment ion from C_2F_6, respectively. $S(CF_3)$

and $S(C_2F_5^+/C_2F_6)$ are the respective sensitivities for CF_3 and for C_2F_6 (based on the more abundant $C_2F_5^+$ fragment ion). Plotting $i(CF_3^+)$ as a function of $2i(C_2F_5^+)$ for various reaction times after F-disappearance thus yields a straight line with an intercept equal to $[F]_0 S(CF_3)$. After the separate determination of the initial $[F]_0$ concentration (see above), the mass spectrometric sensitivity $S(CF_3)$ and thus the absolute CF_3 concentration during its decay can be readily derived.

(c) $CF_3 + F$

The reaction of CF_3 radicals with F atoms was studied in a CF_3I/F system in which the concentration of F (≈ 1.0 to 3.5×10^{13} cm^{-3}) was on average in 10-fold excess over CF_3I. The resulting pseudo-first order rate constant of more then 2000 s^{-1} guarantees a 95% conversion of CF_3I after 1.5 ms. The 9-fold excess of F atoms over CF_3 suppresses the contribution of the slow mutual CF_3 reaction to the overall CF_3 removal. Even with the lowest rate constant of the $CF_3 + F$ reaction found in the literature,[18] at most 3% of the total initial CF_3 will be removed by mutual reaction in our conditions. The reaction of CF_3 with F_2 can be neglected as the maximum concentration of F_2 molecules is at least a factor 40 smaller then that of F atoms. Furthermore, the rate constant of $CF_3 + F_2$, according to Plumb et al.,[19] is about 10 times less then that of $CF_3 + F$.

$$CF_3I + F \rightarrow CF_3 + IF \qquad (R11)$$

$$CF_3 + F (+ M) \rightarrow CF_4 (+ M) \qquad (R2)$$

Thus, for a given, quasi-constant [F], the removal rate is

$$\frac{d[CF_3]}{dt} = -k_2[CF_3][F] = -k_2'[CF_3] \qquad (10)$$

where $k_2' = k_2[F]$
or

$$i(CF_3^+) = i(CF_3^+)_0 \exp(-k_2't) \qquad (11)$$

In order to avoid contribution to the CF_3^+ signal from fragmentation of CF_4, the ionizing-electron energy was set at 12.7 eV, which is 3.4 eV above the ionisation potential of CF_3 and 2.8 eV below the appearance potential of CF_3^+ from CF_4.[27] Plotting the logarithm of the experimental CF_3^+-signals as a function of time yields the pseudo-first order rate constant k_2' (see for example Fig. 2). Repeating these experiments for various excess F atom concentrations and plotting the obtained k_2' values in function of [F], will yield the $CF_3 + F$ rate constant k_2 (see for example Fig. 5).
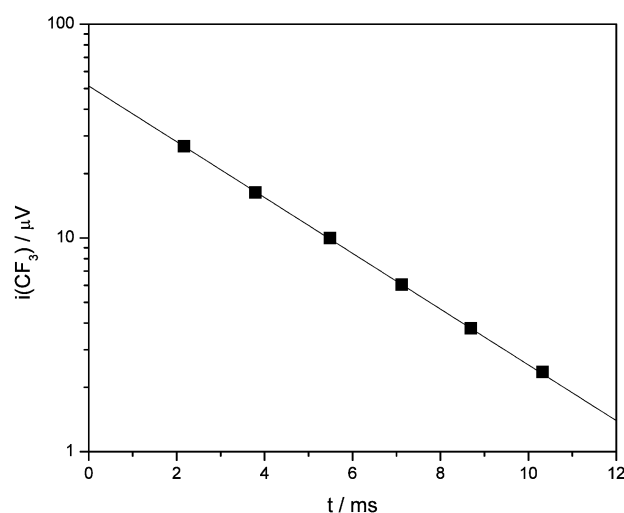
Fig. 2 Determination of the pseudo-first order rate constant k_2' of the $CF_3 + F$ reaction: typical semi-log plot of $i(CF_3^+)$ versus reaction time t.
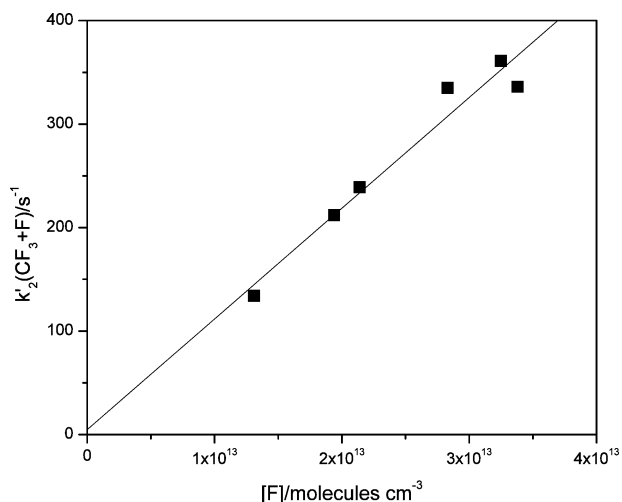
Fig. 3 Plot of the pseudo-first order rate constants k_2' as a function of [F] at 290 K and 2 Torr He. The slope yields the bimolecular rate constant $k_2(CF_3 + F)$. The negligible (4.7 ± 31) s^{-1} intercept shows that additional CF_3 removal processes, such as wall loss, are negligible.
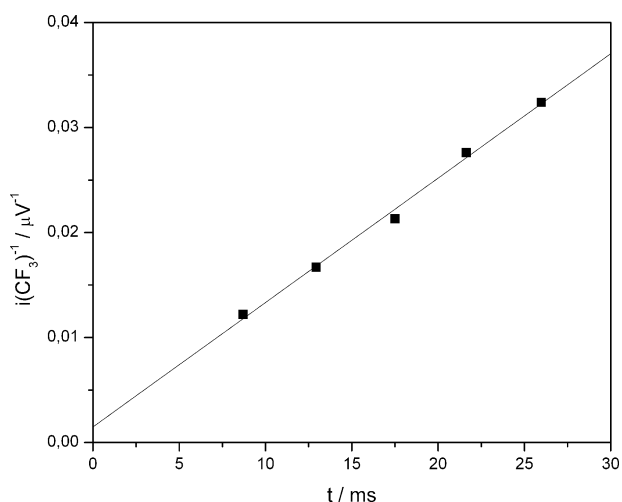
The mutual CF_3 reaction

(a) Experimental results

The absolute bimolecular rate constants k_1 for the mutual CF_3 reaction were derived from plotting $1/i(CF_3^+)$ as a function of time. (See example in Fig. 4). The product of the gradient of these plots with the sensitivity $S(CF_3)$ represent $2 \times k_1$. The rate coefficients were determined at 290 K at four pressures between 1 and 6 Torr. At each pressure, k_1 was measured for a range of initial CF_3 concentrations between 2 and 8×10^{13} cm^{-3}; the mean values are listed in Table 1 and displayed in Fig. 5. The combined repeatability and statistical errors of the k_1 determinations ranged typically around 10%. The stated errors in Table 1, amounting to about 20%, include estimated possible systematic errors that could result from inaccuracies in the absolute reactant concentration.

The differences between the obtained k_1 values at different pressures is smaller then the errors on the individual data points. This leads us to the conclusion that the rate constant is independent of pressure in the 1–6 Torr pressure range covered. The obtained rate constant therefore corresponds to the high pressure limit:

$$k_1^\infty = (1.8 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$

Fig. 4 Determination of the rate constant k_1 of the mutual CF_3 reaction: Plot of $i(CF_3^+)^{-1}$ as a function of reaction time. The initial F concentration was 4.13×10^{13} cm^{-3}.
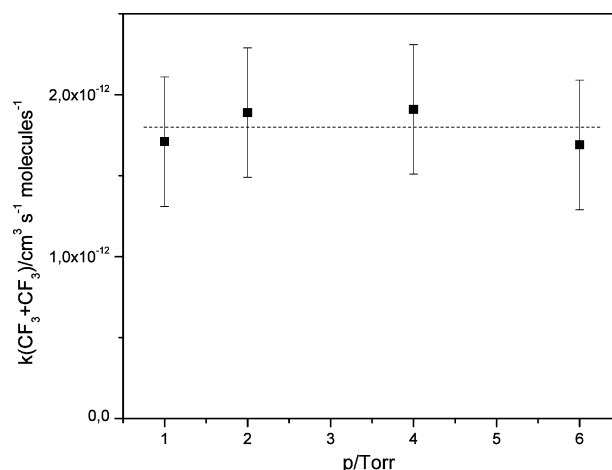
Fig. 5 Rate coefficients $k_1(CF_3 + CF_3)$ at 290 K as a function of pressure. --: average value.

as the mean of our data over the entire pressure range. Experiments at pressures below 1 Torr could not be adequately performed due to the low achievable maximum flow rates at these pressures. This resulted in too rapid CF_3 decays compared to the time scale of our measurements.

When examining the signal intensities of the various possible reaction products, we observed large $C_2F_5^+$ signals, confirming the importance of channel 1a. The signal of CF_2^+ on the other hand did not significantly rise above the (small) background CF_2^+ fragment ion contribution from CF_3H (while CF_4 could not be observed since it has no parent ion). Reaction channel 1b therefore appears to be minor, if not negligible.

(b) Discussion

Our $k_1^\infty(CF_3 + CF_3)$ result at 290 K is in accord with the lowest literature value at room temperature, $(2.2 \pm 0.5) \times 10^{-12}$ cm^3 s^{-1},[11] and is also within the combined 2σ error range of a few other determinations,[10,16] but is clearly at odds with the high k_1 values ($\approx 1.0 \times 10^{-11}$ cm^3 s^{-1}) reported by some other groups.[14,17]

A significant underestimation of k_1 on our part is only conceivable if a fast regeneration of CF_3 were to occur in our system. However, our $(1/[CF_3])(t)$ data do not show at all the leveling-off at larger t that is expected in case of CF_3-regeneration. Moreover, the only possible CF_3-regeneration path in our system is a reaction of the (at best minor) product $CF_2(X\ ^1A_1)$ with CF_3H. However, all $CF_2(X)$ reactions with closed-shell molecules are very slow, with $k(300\ K)$ rate coefficients well below 10^{-15} cm^3 s^{-1}.[29] Even for $k(CF_3H + CF_2) = 10^{-15}$ and k_{1b}/k_1 as high as 0.2, at most 1% of the CF_3 could be regenerated over 10 ms in our conditions.

Possible reasons for too high rate constant values reported in the literature are CF_3-removal by other reactions or erroneous absolute $[CF_3]$ or $[F]_0$ values. To prevent the first source of errors we have used an as straightforward and clean as possible CF_3 generation method in order to eliminate all possible side reactions, whereas in the more complex systems used by some other authors, CF_3 removal by other reactive species cannot be

Table 1 The $k_1(CF_3 + CF_3)$ rate coefficients at 290 K as a function of pressure

p/Torr	k_1/cm^3 s^{-1}
1	$(1.71 \pm 0.4) \times 10^{-12}$
2	$(1.89 \pm 0.4) \times 10^{-12}$
4	$(1.91 \pm 0.4) \times 10^{-12}$
6	$(1.69 \pm 0.4) \times 10^{-12}$

Table 2 k^{∞} of the mutual reactions of the series $CH_{3-n}F_n$ and $CH_{3-n}Cl_n$, $n = 0–3$, at 298 K

Reaction	k^{∞}(298 K)/cm³ s⁻¹	Refs.
$CH_3 + CH_3$	$(5.5 \pm 0.3) \times 10^{-11}$	24
$CH_2F + CH_2F$	$(1.2 \pm 0.13) \times 10^{-11}$	30
$CHF_2 + CHF_2$	$(4.4 \pm 1.3) \times 10^{-12}$	30
$CF_3 + CF_3$	$(2.2 \pm 0.5) \times 10^{-12}$	11
	$(1.8 \pm 0.6) \times 10^{-12}$	This work
	$(11 \pm 4.0) \times 10^{-12}$	14
	$(10.4 \pm 1.2) \times 10^{-12}$	17
$CH_2Cl + CH_2Cl$	$(2.8 \pm 0.3) \times 10^{-11}$	31
$CHCl_2 + CHCl_2$	$(9.3 \pm 1.7) \times 10^{-12}$	31
$CCl_3 + CCl_3$	$(3.3 \pm 0.8) \times 10^{-12}$	32

Table 3 $k_2(CF_3 + F)$ at 290 K as a function of pressure

p/Torr	k_2/cm³ s⁻¹
0.5	$(2.06 \pm 0.4) \times 10^{-12}$
0.75	$(2.29 \pm 0.5) \times 10^{-12}$
1.0	$(5.20 \pm 1.0) \times 10^{-12}$
1.5	$(6.98 \pm 1.4) \times 10^{-12}$
2.0	$(1.06 \pm 0.2) \times 10^{-11}$
3.0	$(1.06 \pm 0.2) \times 10^{-11}$
4.0	$(1.51 \pm 0.3) \times 10^{-11}$
5.0	$(1.50 \pm 0.3) \times 10^{-11}$
6.0	$(1.74 \pm 0.3) \times 10^{-11}$

excluded. We have also found the $[F]_0$ determinations by the $F + H_2 \rightarrow HF + H$ titration reaction, used by some authors, to be unreliable.

Moreover, it is highly instructive to compare the high[14,17] and low data[10,11,16,this work] on $k_1^{\infty}(CF_3 + CF_3)$ with the literature data for the series $k^{\infty}(CH_3 + CH_3)$,[24] $k^{\infty}(CH_2F + CH_2F)$[30] and $k^{\infty}(CHF_2 + CHF_2)$,[30] all listed in Table 2.

The CH_3 recombination coefficient is now well established[24] with $k^{\infty}(290 \text{ K}) = (5.5 \pm 0.3) \times 10^{-11}$ cm³ s⁻¹. Note that our 2 Torr He result of $(5.2 \pm 0.5) \times 10^{-11}$ cm³ s⁻¹ is in agreement with the most recent literature value of $(4.5 \pm 0.5) \times 10^{-11}$ cm³ s⁻¹,[24] attesting to the validity of our $[F]_0$ determination method (see above), which is of critical importance for the reliability of our $k^{\infty}(CF_3 + CF_3)$ value. The $k^{\infty}(CH_2F + CH_2F)$ and $k^{\infty}(CHF_2 + CHF_2)$ data, from Hack's group, have become available recently;[30] interestingly, for the latter, they report a positive T-dependence: $k_{CHF_2}^{\infty} = 2.8 \times 10^{-11} \exp(-555/T)$, suggesting a small effective barrier.

The Table 2 data shows a manifest trend for the first three reactions: the bimolecular k^{∞} rate coefficient for the mutual reaction of (F-substituted) methyl radicals $CH_{3-n}F_n$ decreases sharply with increasing number n of F-substituent atoms. Extrapolation to CF_3 strongly suggest a rate coefficient in the low 10^{-12} cm³ s⁻¹ range, consistent with the results of Brown et al.[11] and of this work, but in disaccord with the $\approx 10^{-11}$ cm³ s⁻¹ data of Pagsberg et al.[17] and Skorobogatov et al.[14] From a fundamental point of view, the sharp decrease of $k^{\infty}(CH_{3-n}F_n)$ with increasing n can be interpreted in terms of the increasingly repulsive or screening effects by the negatively charged F atoms on the spatially-averaged potential energy of two approaching $CH_{3-n}F_n$ radicals. A similar, but somewhat less pronounced, trend is manifest for the analogous $CH_{3-n}Cl_n$ series (see Table 2).

In any case, according to our results, current plasma etching models that use the average of all k_1 literature data may substantially overestimate the $CF_3 + CF_3$ combination rate.

The reaction of CF_3 with F

(a) Experimental results

The decay rates k_2' for CF_3 removal at a given excess $[F]$ were derived from the semi-log $i(CF_3^+)$ vs. t fits (see for example Fig. 2) and plotted as a function of $[F]$ (varied between 1.0 and 3.5×10^{13} cm⁻³; see Fig. 3). The gradients of these plots represent the absolute bimolecular rate coefficients k_2 of $CF_3 + F$. The k_2 determined at nine pressures between 0.5 and 6 Torr are listed in Table 3. Contrary to the mutual CF_3 reaction, reaction (2) is in its fall-off region in this pressure range. Measurements at 0.5 Torr were feasible for this reaction, as the decrease in flow rate at low pressures was compensated by the decrease of the overall rate constant. However, at the lowest pressures a correction had to be made for the increased

importance of axial diffusion; at 0.5 Torr the underestimation of the rate constant was about 10%, while at 2 Torr less than 1%. The measured pressure dependence of k_2 displayed in Fig. 6 has the characteristic shape expected from theory. The combined repeatability and statistical errors of the present k_2 determinations were typically around 10%. The stated errors in Table 3, amounting to about 20%, include estimated possible systematic errors that could result from inaccuracies in the absolute concentration of the F reactant.

(b) Discussion

At pressures of 4 Torr and higher our k_2 data are near-identical with Plumb and Ryan's data.[19] However, at lower pressures our data reveal a quite different fall-off behaviour. Our 2 Torr result is $\approx 75\%$ of the Plumb and Ryan value, dropping to $\approx 45\%$ at 1 Torr. According to our data (Fig. 6) the high pressure limit is far from attained at 6 Torr. The clear curvature throughout the 0.5–6 Torr range indicates that the rate constants are still in the intermediate fall-off region. The fall-off behaviour was fitted by using the semi-empirical Troe formalism[33] as expressed by eqn. (12):

$$k/k^{\infty} = \frac{k^0[M]/k^{\infty}}{1 + k^0[M]/k^{\infty}} F_C^{\{1+(\log(k^0[M]/k^{\infty}))^2\}^{-1}} \qquad (12)$$

In this equation, k^{∞} is the rate constant in the high pressure limit, $k^0[M]$ the rate coefficient at the low pressure limit, $[M]$ the bath gas concentration, and F_C a broadening factor which expresses the departure of the fall-off curve from that predicted by the Lindemann–Hinshelwood equation.

We found it impossible to perform a precise three-parameter determination (k^{∞}, k^0 and F_C) from the data, as the strong coupling of F_C and k^{∞} produces large inversely correlated
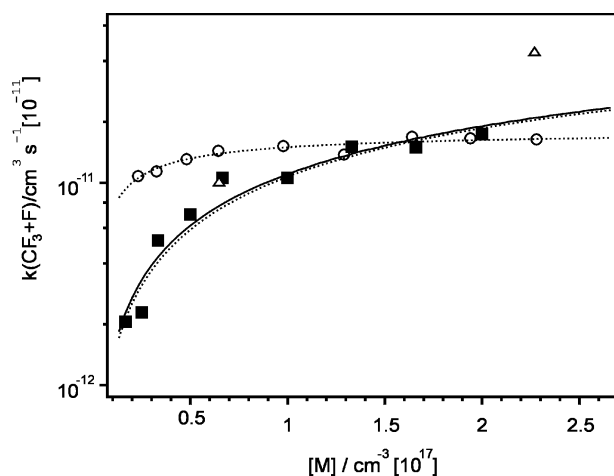
Fig. 6 Plot of the $CF_3 + F$ rate constants k_2 as a function of the bath gas number density, $[M]$. ■ our data (He); ○ Plumb and Ryan (He);[19] △ Butkovskaya et al. (Ar).[18] The Troe-fits are represented by the dotted lines while the full line represents the MVIPF calculations.

errors on these two parameters. This is attributable entirely to the high-end limit of the experimental pressure range, which is too low to allow reliable extrapolation to the high-pressure regime. We then used the method proposed by Troe[33,34] to predict the broadening factor F_C, and used this F_C as a fixed value in two-parameter Troe fits of our experimental data. Since an accurate prediction of F_C requires the *a priori* knowledge of some parameters, *e.g.* the collisional efficiency factor β_{coll}, we varied the F_C value used in these 2-parameter fits between 0.40 to 0.60, to account for any uncertainties in the derivation of our predicted F_C; this range includes the $F_C = 0.54$ adopted by Plumb and Ryan, and agrees with typical results for strongly bonded, tight product molecules. The Troe fit with $F_C = 0.50$ is displayed in Fig. 6. The value for k^{∞} remains strongly correlated with the adopted value of F_C and the statistical weighting of the data points, varying from 8×10^{-11} to 3×10^{-10} cm^3 s^{-1} for the range of F_C values mentioned higher. As such, a reliable estimate for this parameter is not possible, though our results seem to indicate a somewhat higher k_2^{∞} than Plumb and Ryan's[19] k_2^{∞} of 2.0×10^{-11} cm^3 s^{-1}. On the other hand, k^0 was found to be nearly independent of the value of F_C used, ranging from 1.51 to 1.44×10^{-28} cm^6 s^{-1} and with statistical errors of about 15%, and furthermore remained very close to the results of the three-parameter fits; k^0 can therefore be reliably estimated from our experimental data, with:

$$k_2^0 = (1.47 \pm 0.24) \times 10^{-28} \text{ cm}^6 \text{ s}^{-1}$$

This value of k^0 is significantly different from the value obtained by Plumb and Ryan, $k_2^0 = 3.80 \times 10^{-27}$ cm^6 s^{-1}.

To further investigate this discrepancy, the pressure-dependent rate coefficient for recombination of CF$_3$ + F was also calculated by applying the microcanonical variational (microcanonical variational theory of radical recombination by inversion of interpolated partition function, MVIPF) method described by Forst[35] to the CF$_4 \rightarrow$ CF$_3$ + F dissociation reaction, and multiplying this dissociation rate coefficient[35] by the CF$_4 \leftrightarrow$ CF$_3$ + F equilibrium constant K_{eq} (290 K) of 6×10^{69} cm^3 as derived from thermochemical data available from JANAF.[36] The MVIPF method essentially describes the transition state for barrierless dissociation as an activated complex with properties—and hence a partition function—intermediate between the reactant CF$_4$ and the products CF$_3$ + F. The energy-dependent sum of states for the TS is derived from an inverse Laplace transform of that intermediate's partition function; the rate-limiting minimal sum of states along the reaction coordinate is located microcanonically as a function of E and J. Rotational effects as a function of J are incorporated by describing the dissociating molecule as a quasi-diatom 2D molecular rotor, while rotation along the third molecular axis is considered as an active 1D internal rotor with no J-dependent restrictions on quantum number K. The MVIPF method requires input of the molecular properties of CF$_4$, CF$_3$ and F to calculate the partition functions for products and reactant; we used the same vibrational wave numbers and rotational constants for CF$_4$ and CF$_3$ as used by Plumb and Ryan in their RRKM analysis.[19] The rate of change from reactant-like to product-like properties and partition functions along the reaction coordinate is controlled by a switching function $\exp[-c_{adj} \times (r - r_e)^2]$ as a function of the length r of the dissociating C–F bond compared to the equilibrium bond length r_e in CF$_4$. The constant c_{adj} is an adjustable parameter controlling the 'looseness' of the transition state and is derived by fitting the predicted rate coefficients to experimental rate data. In addition, the efficiency-corrected collision number $\beta_{coll} \times Z_{LJ}$ can be used as an adjustable parameter to control the fall-off behavior of the rate coefficients to obtain an optimal fit to the available data. The high-pressure limit rate coefficient k^{∞} is not sensitive to $\beta_{coll} \times Z_{LJ}$, but is controlled solely by the value of c_{adj}.

A good MVIPF fit of the experimental data points reported in this work can be obtained using an adjustable parameter c_{adj} of 0.24 to 0.5 Å^{-2}, with values for $\beta_{coll} \times Z_{LJ}$ of 1.6×10^{-11} to 1.4×10^{-11} cm^3 s^{-1}, respectively. Fig. 6 shows the MVIPF recombination rate coefficients for the experimental pressure range, computed using c_{adj} and $\beta_{coll} \times Z_{LJ}$ of 0.31 Å^{-2} and 1.42×10^{-11} cm^3 s^{-1}, respectively, showing a good agreement with our experimental data. Similar to the Troe fits described earlier, a more precise estimate of c_{adj} and hence k^{∞} is not possible due to the low experimental pressures, with k^{∞} varying from 1×10^{-10} to 2×10^{-10} cm^3 s^{-1} over the parameter range mentioned. The low-pressure rate coefficient k^0 is much less sensitive to the value of the adjustable parameters, changing only from 1.58×10^{-28} to 1.67×10^{-28} cm^3 s^{-1} between the extreme fitting parameter values; such results are in very good agreement with those from the Troe fits. The efficiency-corrected collision numbers $\beta_{coll} \times Z_{LJ}$ of $(1.4–1.6) \times 10^{-11}$ cm^3 s^{-1} correspond to a weak-collision efficiency β_{coll} of 0.06 to 0.07, assuming a reasonable collision number Z_{LJ} of 2.3×10^{-10} cm^3 s^{-1} (M = He); this translates to an average downward collisional energy transfer $\langle \Delta E_{down} \rangle$ of about 65 to 72 cm^{-1} when assuming an exponential energy-down model. The value of the parameter c_{adj} is directly comparable to values found for similar recombination reactions,[35] while the energy transfer parameter $\langle \Delta E_{down} \rangle$ for M = He is in good agreement with commonly accepted energy transfer parameters.[37]

Reproducing the high-pressure and low-pressure limits as reported by Plumb and Ryan[19] proved less straightforward. Their high-pressure limit of k^{∞}(290 K) of 2×10^{-11} cm^3 s^{-1} could only be reproduced using a c_{adj} of 0.152 Å^{-2}; this latter value is well outside the range of values found for similar reactions[35] and corresponds to an unlikely tight transition state. Furthermore, using this c_{adj}, we could only reproduce Plumb and Ryan's[19] low-pressure k_2^0(290 K) of 3.8×10^{-27} cm^3 s^{-1} by adopting an efficiency-corrected collision number $\beta_{coll} \times Z_{LJ}$ of 6.2×10^{-10} cm^3 s^{-1}; even when assuming a strong-collision system with $\beta_{coll} = 1$ this implies an unphysically high collision number Z_{LJ}.

The cause of the marked difference between our experimental results and Plumb and Ryan's is an open question, especially since our k(CF$_3$ + O$_2$) measurements,[38] using the same method, are in good agreement with their and other literature data. However, the reproduction of Plumb and Ryan's data requires the adoption of unlikely parameters in the MVIPF formalism. The parameters for our results, on the other hand, are in the ranges reported in the literature. Although this strongly suggests that our data provide a more accurate description of the chemical kinetics, independent third-party measurements of this important reaction are certainly welcome. In particular, measurements at higher pressures would significantly improve the Troe fits and MVIPF treatment to determine k^{∞}, and concomitantly the fall-off parameter F_C and/or $\beta_{coll} \times Z_{LJ}$.

Conclusions

We have determined the rate constants of the combination reactions of CF$_3$ with CF$_3$ and F over an extended pressure range. Our results clearly show that k(CF$_3$ + CF$_3$) is in the high pressure limit at pressures above 1 Torr He while the rate constant of CF$_3$ + F is in the fall-off region at pressures of 0.5 to 6 Torr He. Our k(CF$_3$ + CF$_3$) value of $(1.8 \pm 0.6) \times 10^{-12}$ cm^3 s^{-1} is in close accord with the lowest literature value and is also compatible with several other determinations, but clearly diverges from the high k values ($\geq 1.0 \times 10^{-11}$ cm^3 s^{-1}) reported by some other groups. Our CF$_3$ + CF$_3$ data are fully in line with the sharp decrease in the rates of the mutual reactions of methyl radicals upon increasing F-substitution (CH$_3$; CH$_2$F; CHF$_2$). Our rate data on the CF$_3$ + F reaction, backed by variational transition state MVIPF calculations,

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provide evidence for a much lower k^0 value, as well as a fall-off region extending to higher pressures than indicated by earlier literature data.[19]

References

1   P. B. Ayscough, *J. Chem. Phys.*, 1956, **24**, 944.
2   T. Ogawa, G. A. Carlson and G. C. Pimentel, *J. Phys. Chem.*, 1970, **74**, 2090.
3   N. Basco and F. G. M. Hathorn, *Chem. Phys. Lett.*, 1971, **8**, 291.
4   R. Hiatt and S. W. Benson, *Int. J. Chem. Kinet.*, 1972, **4**, 479.
5   G. A. Skorobogatov, V. G. Seleznev and O. N. Slesar, *Dokl. Phys. Chem.*, 1976, **231**, 1292.
6   M. Rossi and D. M. Golden, *Int. J. Chem. Kinet.*, 1979, **11**, 775.
7   K. Glanzer, M. Maier and J. Troe, *J. Phys. Chem.*, 1980, **84**, 1681.
8   A. M. Velichko, E. B. Gordon, A. A. Nedelkin, A. I. Nikitin and V. L. Tal'roze, *High Energy Chem.*, 1985, **19**, 58.
9   I. C. Plumb and K. R. Ryan, *Plasma Chem. Plasma Proc.*, 1986, **6**, 205.
10 N. Selamoglu, M. J. Rossi and D. M. Golden, *Chem. Phys. Lett.*, 1986, **124**, 68.
11 C. E. Brown, J. J. Orlando, J. Reid and D. R. Smith, *Chem. Phys. Lett.*, 1987, **142**, 213.
12 G. A. Skorobogatov, B. P. Dymov, V. N. Lebedev and V. K. Khripun, *Kinet. Katal.*, 1987, **28**, 682.
13 R. M. Robertson, D. M. Golden and M. J. Rossi, *J. Phys. Chem.*, 1988, **92**, 5338.
14 G. A. Skorobogatov, O. N. Slesar and N. D. Torbin, *Vestn. Leningr. Univ. Ser. Fiz. Khim.*, 1988, **4**, 30.
15 Y. Hidaka, T. Nakamura and H. Kawano, *Chem. Phys. Lett.*, 1989, **154**, 573.
16 A. B. Vakhtin, *Int. J. Chem. Kinet.*, 1996, **28**, 443.
17 P. Pagsberg, J. T. Jodkowski, E. Ratajczak and A. Sillesen, *Chem. Phys. Lett.*, 1998, **286**, 138.
18 N. I. Butkovskaya, M. N. Larichev, I. O. Leipunskii, I. I. Morozov and V. L. Tal'roze, *Kinet. Katal.*, 1980, **21**, 343.
19 I. C. Plumb and K. R. Ryan, *Plasma Chem. Plasma Proc.*, 1986, **6**, 11.
20 C. Vinckier and W. Debruyn, *Symp. (Int.) Combust., [Proc.]*, 1979, **17**, 623.
21 W. Boullart, K. Devriendt, R. Borms and J. Peeters, *J. Phys. Chem.*, 1996, **100**, 998.
22 R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi and J. Troe, *Gas Kinetic Data for Atmospheric Chemistry*, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, Centre for Atmospheric Science, University of Cambridge, UK, http://www.iupac-kinetic.ch.cam.ac.uk.
23 C. M. Moore, I. W. M. Smith and D. W. A. Stewart, *Int. J. Chem. Kinet.*, 1994, **26**, 813.
24 B. Wang, H. Hou, L. M. Yoder, J. T. Muckerman and C. Fockenberg, *J. Phys. Chem. A*, 2003, **107**, 11414, and references cited therein.
25 R. S. Iyer and F. S. Rowland, *J. Phys. Chem.*, 1981, **85**, 2493.
26 F. Louis and J. P. Sawerysyn, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 1437.
27 H. M. Rosenstock, K. Draxl, B. W. Steiner and J. T. Herron, *J. Phys. Chem. Ref. Data*, 1977, **6**, Suppl. 1.
28 R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, M. J. Rossi and J. Troe, *J. Phys. Chem. Ref. Data*, 1997, **26**, 1329.
29 (*a*) W. Hack, M. Wagner and K. Hoyermann, *J. Phys. Chem.*, 1995, **99**, 10847; (*b*) A. P. Modica, *J. Chem. Phys.*, 1967, **46**, 3663; (*c*) J. Edelbuttel-Einhaus, K. Hoyermann, G. Rohde and H. Gg. Wagner, *Ber. Bunsen-Ges. Phys. Chem.*, 1989, **93**, 1413; (*d*) F. W. Dalby, *J. Chem. Phys.*, 1964, **41**, 2297.
30 T. Beiderhase, W. Hack, K. Hoyermann and M. Olzmann, *Z. Phys. Chem.*, 2000, **214**, 625.
31 P. B. Roussel, P. D. Lightfoot, F. Caralp, V. Catoire, R. Lesclaux and W. Forst, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2367.
32 F. Danis, F. Caralp, B. Veyret, H. Loirat and R. Lesclaux, *Int. J. Chem. Kinet.*, 1989, **21**, 715.
33 K. A. Holbrook, M. J. Pilling and S. H. Robertson, *Unimolecular Reactions*, Wiley, Chichester, 2nd edn., 1996.
34 W. C. Gardiner, Jr., *Combustion Chemistry*, Springer-Verlag, New York, 1984.
35 W. Forst, *Unimolecular Reactions*, Cambridge University Press, Cambridge, 2003.
36 M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald and A. N. Syverud, *J. Phys. Chem. Ref. Data*, 1985, **14**, 1–1856, Suppl. 1 [JANAF Thermochemical Tables, (3rd edn.)].
37 I. Oref and D. C. Tardy, *Chem. Rev.*, 1990, **90**, 1407.
38 J. Vertommen, PhD Thesis, K. U. Leuven, 1992.