**Shock wave and modelling study of the dissociation pathways of (C\textsubscript{2}F\textsubscript{5})\textsubscript{3}N**

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The thermal decomposition of perfluorotriethylamine, (C\textsubscript{2}F\textsubscript{5})\textsubscript{3}N, was investigated in shock waves by monitoring the formation of CF\textsubscript{2}. Experiments were performed over the temperature range of 1120–1450 K with reactant concentrations between 100 and 1000 ppm of (C\textsubscript{2}F\textsubscript{5})\textsubscript{3}N in the bath gas Ar and with [Ar] in the range of (0.7–5.5) × 10\textsuperscript{-5} mol cm\textsuperscript{-2}. The experiments were accompanied by quantum-chemical calculations of the energies of various dissociation paths and by rate calculations, in particular for the dissociation of C\textsubscript{2}F\textsubscript{5} via C\textsubscript{2}F\textsubscript{5} → CF\textsubscript{3} + CF\textsubscript{2}. The overall reaction can proceed in different ways, either by a sequence of successive C–N bond ruptures followed by fast C\textsubscript{2}F\textsubscript{5} decompositions, or by a sequence of alternating C–C and C–N bond ruptures. A cross-over between the two pathways can also take place. At temperatures below about 1300 K, yields of less than one CF\textsubscript{2} per (C\textsubscript{2}F\textsubscript{5})\textsubscript{3}N decomposed were observed. On the other hand, at temperatures around 2000 K, when besides the parent molecule, CF\textsubscript{3} also dissociates, yields of six CF\textsubscript{2} per (C\textsubscript{2}F\textsubscript{5})\textsubscript{3}N decomposed were measured. The rate-delays of the dissociation mechanism at intermediate temperatures were suggested to be the processes (C\textsubscript{2}F\textsubscript{5})\textsubscript{3}NCF\textsubscript{3} → (C\textsubscript{2}F\textsubscript{5})\textsubscript{3}N + CF\textsubscript{3} and (CF\textsubscript{3})\textsubscript{3}N → N + CF\textsubscript{2}. The reduction of the CF\textsubscript{2} yields at low temperatures was tentatively attributed to a branching of the mechanism at the level of (C\textsubscript{2}F\textsubscript{5})\textsubscript{3}NCF\textsubscript{3}, from where the cyclic final product perfluoro-N-methylpyrrolidine, (C\textsubscript{4}F\textsubscript{8})NCF\textsubscript{3}, is formed which was identified in earlier work from the literature.

1. Introduction

Perfluorotriethylamine, (C\textsubscript{2}F\textsubscript{5})\textsubscript{3}N, has a number of interesting properties. On the one hand, it may serve as a benign liquid reaction medium for Lewis acid-catalyzed organic reactions\textsuperscript{1} and other preparative applications. On the other hand, its structure is remarkable, being characterized by a nearly planar C\textsubscript{3}N skeleton with CNC angles near to 120°.\textsuperscript{2} This skeleton is surrounded by an “inner shell” of CF\textsubscript{2} groups and an “outer shell” of CF\textsubscript{3} groups. The structure of (C\textsubscript{2}F\textsubscript{5})\textsubscript{3}N has been discussed in relation to that of other fluorinated triamines such as (CF\textsubscript{3})\textsubscript{3}N,\textsuperscript{3} (CH\textsubscript{3}CF\textsubscript{3})\textsubscript{3}N,\textsuperscript{4} and (SF\textsubscript{3})\textsubscript{3}N.\textsuperscript{5} Because of its favorable properties, (C\textsubscript{2}F\textsubscript{5})\textsubscript{3}N has also been considered as an alternative to environmentally more harmful halons.\textsuperscript{6} In a study of the thermal decomposition of undiluted gaseous (C\textsubscript{2}F\textsubscript{5})\textsubscript{3}N in a flow system, by employing gas chromatography (GC) and GC/mass spectrometry (MS) analyses of the final products, perfluoro-N-methylpyrrolidine, (C\textsubscript{4}F\textsubscript{8})NCF\textsubscript{3}, was identified.\textsuperscript{6} In order to shed more light on the elementary steps of the pyrolysis, shock wave studies of the thermal decomposition of (C\textsubscript{2}F\textsubscript{5})\textsubscript{3}N diluted in Ar appeared promising. As the decomposition may proceed through different pathways, however, the interpretation of the experiments had to be accompanied by quantum-chemical calculations of the energetics of the reactions involved. That is the subject of the present article.

At sufficiently high temperatures, an overall decomposition

\[
(C\textsubscript{2}F\textsubscript{5})\textsubscript{3}N \rightarrow C\textsubscript{2}F\textsubscript{5} + N \quad \Delta H_{298}^\circ = 905 \text{ kJ mol}^{-1} \tag{1}
\]

(with \(\Delta H_{298}^\circ (C\textsubscript{2}F\textsubscript{5})\textsubscript{3}N = -3138 \text{ kJ mol}^{-1}\) from ref. 7, \(\Delta H_{298}^\circ (C\textsubscript{2}F\textsubscript{3}) = -901.9 \text{ kJ mol}^{-1}\) and \(\Delta H_{298}^\circ (N) = 472.7 \text{ kJ mol}^{-1}\) from ref. 8; values for 298 K) would be accompanied by the dissociation of C\textsubscript{2}F\textsubscript{5},\textsuperscript{9,10}

\[
C\textsubscript{2}F\textsubscript{5} \rightarrow CF\textsubscript{3} + CF\textsubscript{2} \quad \Delta H_{298}^\circ = 243.8 \text{ kJ mol}^{-1} \tag{2}
\]

which then could be followed by CF\textsubscript{3} dissociation\textsuperscript{11,12}

\[
CF\textsubscript{3} \rightarrow CF\textsubscript{2} + F \quad \Delta H_{298}^\circ = 355.5 \text{ kJ mol}^{-1} \tag{3}
\]

and, finally, by CF\textsubscript{2} dissociation

\[
CF\textsubscript{2} \rightarrow CF + F \quad \Delta H_{298}^\circ = 517.6 \text{ kJ mol}^{-1} \tag{4}
\]

(unless stated differently, enthalpies in this work are from ref. 8).
In more detail, the dissociation (1) could proceed by a sequence of C–N bond ruptures

\begin{align*}
(C_2F_5)_2N &\rightarrow (C_2F_5)N + C_2F_3 \\
(C_2F_5)_2N &\rightarrow (C_2F_5)N + C_2F_5 \\
(C_2F_5)_N &\rightarrow N + C_2F_5
\end{align*}

(5) (6) (7)

which would be followed by C2F5 dissociations (2) (and, at a slower rate, by CF3 dissociations (3)). Because of the compact structure of (C2F5)N, also a dissociation sequence of alternating C–C and C–N bond ruptures

\begin{align*}
(C_2F_5)_2N &\rightarrow (C_2F_5)_2NCF_2 + CF_3 \\
(C_2F_5)_2NCF_2 &\rightarrow (C_2F_5)_2N + CF_2 \\
(C_2F_5)_NCF_2 &\rightarrow (C_2F_5)NCF_2 + CF_3 \\
(C_2F_5)_2N &\rightarrow (C_2F_5)N + CF_2 \\
(C_2F_5)_N &\rightarrow CF_2N + CF_3 \\
(CF_2)_N &\rightarrow N + CF_2
\end{align*}

(8) (9) (10) (11) (12) (13)

appears possible. At the level of (C2F5)3N and (C2F5)2N a cross-over between the C–N and the C–C bond-breaking pathways would be possible.

(C2F5)3N has a low vapour pressure which, nevertheless, allows for the preparation of gaseous reactant/Ar mixtures suitable for shock wave experiments. The progress of the decomposition then can conveniently be followed by recording time-resolved UV absorption signals from CF2 near 248 nm (see ref. 13 and 14 for high-temperature absorption coefficients of CF2). Additional observations near 200 nm might be considered for the detection of CF3.15 At temperatures where CF2 becomes unstable, also absorption signals from CF might become observable.16 By analyzing absorption-time profiles, at first, the CF2 yields are of relevance. Second, the time dependence of the CF2 signals would be analyzed with respect to the sequence (5)–(7) followed by reactions (2) and (3) or the sequence (8)–(13) with the possibility of cross-over between the two pathways. Some speculations about the ultimate formation of (C2F5)NCF2 in the present work were also made. In high temperature experiments, finally, the kinetics of N/F/CF2 mixtures of known composition becomes accessible.

In the following, the description of experimental results is preceded by quantum-chemical calculations which facilitate the interpretation of the recorded CF2 yields and of the time dependence of the recorded concentration profiles of CF2. As the decomposition of C2F5 via reaction (2) represents an important intermediate step of the mechanism and as only controversial information on its rate is available,9,10 a modelling of this rate also appeared desirable.

2. Quantum-chemical calculations of reaction energies

The enthalpies of reactions (2) and (5)–(13) (at 0 K) were determined by using a variety of DFT models, combined with a 6-311+G(3df) basis set, and using the Gaussian set of codes.17 In detail, B3LYP,18,19 M06-2X,20 BMK,21 and oB97X-D22 models were used. The quality of the DFT results was tested for the dissociation of (C2F5)N in reactions (7) and (12) by also performing high-level ab initio CBS-QB323 and G424 calculations. As the agreement between the DFT and the ab initio calculations for the (C2F5)N dissociations appeared satisfactory, only DFT calculations were made for the dissociation of larger species. A comparison of the results obtained by using the various models is given in the ESI.†

\[ \Delta H^0 \]

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(C_2F_5)_3N &\rightarrow (C_2F_5)N + CF_2 \\
(C_2F_5)_N &\rightarrow CF_2N + CF_3 \\
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our earlier work (see, e.g. ref. 13, 15 and 16; for more details, see the ESI†). The results are shown in Fig. 2. The calculation of individual rate constants for other reaction steps of the pathway was beyond the scope of the present work. Likewise, the complex rearrangement processes leading to the final cyclic product (C₄F₈)NCF₃ were not further investigated here.

3. Experimental technique and results

Our shock wave technique has been described before (for details, see, e.g. ref. 12–16). Mixtures of (C₂F₅)₃N (from Fluorochem, purity 96%) and Ar (from Air Liquide, purity 99.9999%) were prepared in mixing vessels outside the shock tube and then introduced into the tube. Usually, low-concentration mixtures of about 200 ppm of (C₂F₅)₃N in Ar were used, but higher concentrations (up to about 1000 ppm (C₂F₅)₃N) were also employed. The experimental conditions behind incident and reflected shock waves are included in Table 2 (and given in the figure captions). UV absorption signals were recorded at selected wavelengths over the range of 200–280 nm. The majority of the experiments were conducted at 248 nm where CF₂ absorbs most strongly (CF₂ absorption coefficients from eqn (5) of ref. 13 were used for the determination of absolute CF₂ yields during (C₂F₅)₃N decomposition).

The recorded absorption-time profiles showed a number of interesting properties. Fig. 3 gives an example. The Schlieren peak at time zero indicates the arrival of the incident shock at the observation window. At the corresponding temperature of 1371 K, the concentration of CF₂ increases up to a yield of \( Y(CF_2) = [CF_2]/([C_2F_5]_N)_{t=0} = 1 \). Closer inspection of the signal near time zero indicates no absorption from the parent molecule. The nature of the absorbing species CF₂ could uniquely be identified by the wavelength dependence of the signal. At the
behind the reflected wave, on the one hand, reflects the dissociation of C$_2$F$_5$ here is about 0.025 mol cm$^{-3}$ followed by reactions (2)–(4) within less than 2 ms. These rates of $k_{ij}$ in of eqn (19), and CF$_2$ yields $Y$. (a) Experiments with $Y = 1$ and $k_{ij} \gg k$; (b) experiments with $Y < 1$ and $k_{ij} \ll k$; (c) experiments with $Y < 1$ and $k > k_{ij}$. See the text.

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Fig. 3 Decomposition of (C$_2$F$_5$)$_3$N behind the incident shock wave (absorption-time profile of formed CF$_2$ at 248 nm; incident shock: T = 1371 K, [Ar] = 7.1 × 10$^{-6}$ mol cm$^{-3}$; reflected shock: T = 2818 K, [Ar] = 1.6 × 10$^{-5}$ mol cm$^{-3}$; 212 ppm (C$_2$F$_5$)$_3$N in Ar; OD = $e$ × (C$_2$F$_5$)$_3$N with $l = 9.4$ cm and $e = 3.6 \times 10^6$ cm$^2$ mol$^{-1}$ for 1371 K and $e = 1.8 \times 10^6$ cm$^2$ mol$^{-1}$ for 2818 K; instantaneous dissociation of CF$_2$ at the time of arrival of the reflected shock, followed by the slower dissociation (4) of CF$_2$ with $k = 10^3$ s$^{-1}$ and secondary reactions, see the text).

time of arrival of the reflected shock (at $T = 2818$ K), the absorption rises abruptly to a level corresponding to $Y$ of CF$_2$. This value of $Y = 6$ corresponds to a completion of reaction (1) followed by reactions (2)–(4) within less than 2 µs (the half-life of C$_2$F$_5$ here is about 0.025 µs, see Fig. 2, and the half-life of C$_3$F$_3$ is about 1.8 µs, see ref. 12). The decrease in the absorption signal behind the reflected wave, on the one hand, reflects the dissociation of CF$_2$ (half-life of about 700 µs, see ref. 12). On the other hand, there is evidence for a superimposed absorption which seems to arise from a species which has an even larger absorption coefficient than CF$_2$. Tentatively we attribute this additional absorption to CF, being formed by the dissociation of CF$_2$ in reaction (4) and/or a reaction

$$\text{N} + \text{CF}_2 \rightarrow \text{NF} + \text{CF} \quad \Delta H_{298}^0 = 198.5 \text{ kJ mol}^{-1} \quad (14)$$

As information on further reactions like

$$\text{NF} + \text{M} \rightarrow \text{N} + \text{F} + \text{M} \quad \Delta H_{298}^0 = 319.1 \text{ kJ mol}^{-1} \quad (15)$$

(M denotes the bath gas) and reactions of (CF$_2$)$_3$N is not available, an investigation of the superimposed absorption “humps” shown in Fig. 3 did not appear warranted at the present time. Because the additional absorptions appeared only at temperatures above 2000 K, our study of (C$_2$F$_5$)$_3$N dissociation was not perturbed by this complication. The assumption of the presence of CF, however, did not appear improbable, because its absorption coefficient at 248 nm in ref. 16 was found to be about 3 times that of CF$_2$.

The formation of CF$_2$ was studied behind incident and reflected shock waves, as shown in Fig. 3 and 4. The temperature of the latter experiment (1347 K) and the rate of formation of CF$_2$ (accounting for the compressed time scale, behind the incident wave) were close to that of Fig. 3, while the bath gas concentrations differed markedly ([Ar] = 7.1 × 10$^{-6}$ mol cm$^{-3}$ behind the incident shock as shown in Fig. 3 and [Ar] = 4.2 × 10$^{-5}$ mol cm$^{-3}$ behind the reflected shock as shown in Fig. 4). A pressure effect thus was not observed. The CF$_2$ yields in both cases reached $Y \approx 1$. This changed at lower temperatures. The CF$_2$ concentration at 1246 K, as shown in Fig. 5, rose up to a yield of $Y \approx 0.6$ only. As Fig. 4 and 5 were obtained with the same reaction mixture (209 ppm of (C$_2$F$_5$)$_3$N in Ar), this observation could not have been produced by concentration uncertainties (with reaction mixtures above 1000 ppm, the small (C$_2$F$_5$)$_3$N vapour pressure caused problems with accurate concentration determinations). Because of the limitation of the observation time behind the reflected shock to about 1 ms, the drop of $Y$ with decreasing temperature could only be followed down to about $T \approx 1130$ K.

Fig. 4 Decomposition of (C$_2$F$_5$)$_3$N behind the reflected shock wave (absorption-time profile of formed CF$_2$ at 248 nm; T = 1347 K, [Ar] = 4.2 × 10$^{-5}$ mol cm$^{-3}$; 209 ppm (C$_2$F$_5$)$_3$N in Ar).
The recorded absorption-time profiles of CF$_2$ were evaluated in two different ways. For the temperature range of 1130–1540 K, where a practically time-independent final CF$_2$ yield $Y(T)$ was reached within the observation time, an effective rate law

$$[\text{CF}_2]/[(\text{C}_2\text{F}_5)_3\text{N}]_{t=0} \approx Y(T)[1 - \exp(-k(T)t)]$$  

(16) appeared suitable. The resulting rate constants $k(T)$ and yields $Y(T)$ are summarized in Table 2 and plotted in Fig. 6 and 7, respectively. The Arrhenius representation of $k(T)$ as shown in Fig. 6 led to

$$k(T) \approx 2.5 \times 10^{13}\exp(-213\text{ kJ mol}^{-1}/RT)s^{-1}$$  

(17)

while $Y(T)$ in the form of ref. 27 was approximated by

$$Y(T) \approx [1 - (T - T_0)/(T_e - T_m)][(T - T_0)/(T_e - T_0)]^{(T_e - T_0)/(T_e - T_m)}$$  

(18)

Values of $k_{in}(T)$ could also be derived for lower temperatures where a final stationary CF$_2$ level could not be attained within the observation time. Fig. 6 and Table 2 include values of $k_{in}(T)$. In Arrhenius form they are represented by

$$k_{in}(T) \approx 1.4 \times 10^{17}\exp(-339\text{ kJ mol}^{-1}/RT)s^{-1}$$  

(20)

with the parameters $T_e = 1351\text{ K}$, $T_0 = 1020\text{ K}$, and fitted $T_m = 1295\text{ K}$. Alternatively, the formation of CF$_2$ was characterized by its initial rate

$$\frac{d[\text{CF}_2]}{dr} \bigg|_{t=0} \approx k_{in}(T) [(\text{C}_2\text{F}_5)_3\text{N}]_{t=0}$$  

(19)

when high-temperature limiting values of $k(T)$ near 1500 K are combined with the measured points of $k_{in}$ over the range of 1130–1250 K (one should note that the scatter of the values of $k_{in}$ is due to some uncertainties of the (C$_2$F$_5$)$_3$N concentration in the reaction mixtures, see eqn (19); this problem does not exist for the measurements of $k(T)$; thus eqn (20) is of qualitative importance only). The relation of the apparent $k(T)$, $k_{in}(T)$, and $Y(T)$ to the dissociation pathways illustrated in Fig. 1 will be considered in Section 4.

It should be noted that experiments at higher temperatures (see Fig. 8), correspond to the dissociation of CF$_3$ through reaction (3). The increase of the CF$_2$ absorption behind the absorption step at the time of arrival of the reflected shock wave as shown in Fig. 8 ($T = 1854\text{ K}$) leads to a value of the rate constant for reaction (3) of $k_7 \approx 3.5 \times 10^3\text{ s}^{-1}$. This is in perfect agreement with the result obtained from the CF$_3$ dissociation study of ref. 12. While this confirms the overall mechanism, it limits the study of the later stages of (C$_2$F$_5$)$_3$N dissociation. One observes that the absorption step at the time of arrival of the reflected wave as shown in Fig. 8 corresponds to $Y \approx 2$ while finally $Y \approx 3$ is reached (as most clearly seen in the inset of Fig. 8). Apparently, CF$_3$ dissociation and the slower steps of the (C$_2$F$_5$)$_3$N dissociation here are superimposed and could not be separated in the present experiments. Monitoring CF$_3$ near 200 nm did not help, as the strong CF$_2$ absorption at high temperatures extends from 248 nm down to 200 nm and is

![Fig. 5](image-url)  

**Fig. 5** The same as Fig. 4, but at lower temperature ($T = 1246\text{ K}$, [Ar] = 4.8 \times 10^{-5}\text{ mol cm}^{-3}$, 209 ppm (C$_2$F$_5$)$_3$N in Ar; $\tau(1246\text{ K})/\tau(1347\text{ K}) \approx 1.15$).

![Fig. 6](image-url)  

**Fig. 6** Apparent rate constants $k$ of eqn (17) and $k_{in}$ of eqn (20) (×: see Table 2a); (●: see Table 2b); (○: see Table 2c); $k$ represented by eqn (17) with the points × and ●, $k_{in}$ represented by eqn (20) with the high-temperature limit of $k$ and points (○: see the text).

![Fig. 7](image-url)  

**Fig. 7** Apparent final CF$_2$ yields $Y = [\text{CF}_2]/[(\text{C}_2\text{F}_5)_3\text{N}]_{t=0}$ over the range of 1130–1450 K (representation by eqn (18)).
then superimposed on the CF₃ absorption. In any case, in the intermediate temperature range between 1500 and 2000 K a CF₃ yield of $Y = 6$ was not reached. On the other hand, $Y$ approached unity in the range of 1300–1500 K.

4. Discussion

Although only limited experimental and theoretical information about the reaction network of Fig. 1 became available, a number of important conclusions could be drawn. The following pathways appear possible: (i) (C₂F₅)₃N dissociates in a sequence of C–N bond ruptures (5)–(7) followed by fast dissociation (2) of the product C₂F₅; (ii) (C₂F₅)₃N dissociates in a sequence of C–C bond ruptures (8), (10), and (12), followed by C–N bond ruptures (9), (11), and (13); (iii) two pathways (i) and (ii) occur in parallel and the possibility of cross-over at the stages of formation of (C₂F₅)₂N and (C₂F₅)N. At temperatures where the reactions of pathways (i)–(iii) are complete, and where CF₃ dissociates for a slow completion of the reaction after reaching the bottle-neck.

An exclusive mechanism (i) can be excluded for a number of reasons: although the enthalpies of the reaction steps slightly decrease from (5) to (7), rate constants $k₅$, $k₆$, and $k₇$ should be of similar magnitude. With a fast dissociation of C₂F₅ this would then result in $Y = 3$. A modelling of the kinetics indicates that the effective rate constant $k(T)$ in eqn (16) would correspond to about $k(T) \approx 2 k₅$. Furthermore, the derived value of $k(T)$ should correspond to a simple bond fission process with a preexponential factor of the order of $10^{15}$–$10^{17}$ s⁻¹ while the activation energy should be of the order of the reaction enthalpy of reaction (5). These expectations are in disagreement with the experimental observations from Section 3.

Mechanism (ii) would have properties which are in closer agreement with the experiments. Particularly in its later stages, this mechanism would be governed by the alternation of low and high reaction barriers such that the reaction flux may “get stuck” at the level of (C₂F₅)N + 2CF₃ + CF₂. This would explain CF₂ yields $Y(T)$ near unity for experiments in the range of 1100–1500 K. However, the apparent rate constant $k$ should again correspond to a simple bond fission and $Y(T)$ should be close to unity even at the lowest temperatures of the present experiments. The latter two expectations are again in disagreement with the experimental observation.

It remains to inspect mechanism (iii) with the possibility of at least a partial cross-over between the two pathways (i) and (ii). The observation of a CF₂ yield near unity over a wide temperature range suggests that the reaction gets stuck at the level of (C₂F₅)₂NCF₂ + CF₂ + 2 CF₃, regardless of whether pathway (ii) or (i) with a cross-over at the level of (C₂F₅)₂N precedes the approach of the bottle-neck of reaction (10). Unfortunately, CF₂ formation beyond the bottle-neck at higher temperatures in our experiments could not be distinguished from CF₂ formation by decomposition of CF₃ (see Section 3). However all evidence is for a slow completion of the reaction after reaching the bottle-neck. Finally, the properties of the apparent rate constant $k₅(T)$, $k₆(T)$, and the decrease of $Y(T)$ to values below unity at low temperatures need to be rationalized. While the Arrhenius representation of $k(T)$ by eqn (17) corresponds more to a rigid-activated complex process, $k₃(T)$ in eqn (19) would appear consistent with a loose-activated complex of bond-fission type, like that expected for $k₅$ and/or $k₆$ (from reactions (5) and (8)).

It appears more difficult to explain the decrease of $Y(T)$ with decreasing temperature, while $k₅(T)$ corresponds to $k₅$ and/or $k₆$. An answer may come from speculations about the formation of the low-temperature final product (C₂F₅)NCF₃. If there is a branching of the reaction flux at the level of (C₂F₅)NCF₂, i.e. beyond the low-temperature rate-determining step (8) of pathway (ii), then the rate constant $k₆(T)$ for CF₂ formation would not be influenced while the CF₂ yield would be. This branching by yet unidentified rearrangement processes should involve rigid activated complexes with lower preexponential factors and activation energies than the competing bond fission (9). It would then win at lower temperatures and reduce here the CF₂ yield of $Y(T)$, and this was observed in our experiments. Obviously, more work would be necessary to validate the given interpretation which would be able to reconcile the present high-temperature observations with the earlier low-temperature measurements of final products from ref. 6.

5. Conclusions

The combination of quantum-chemical calculations and experiments monitoring the formation of product CF₂ in (C₂F₅)₃N decomposition provided evidence for a sequence of C–N and C–C bond ruptures taking place simultaneously. Apparently, dissociation steps in the inner CF₂-shell and in the outer CF₃-shell occur in parallel and proceed as simple bond fission processes. The alternation of bond energies for the C–C and C–N bond rupture sequence of reactions (8)–(13) deserves particular attention. At temperatures that are sufficiently high for reactions (5)–(13) to occur,
but low enough to keep CF$_2$ undissociated, the observed overall yield of 6 CF$_2$ per consumed (C$_2$F$_5$)$_3$N confirms the kinetic analysis.

Details of the mechanism would not have been understood without the quantum-chemical calculations. As the decomposition of C$_2$F$_5$ through reaction (2) forms an essential part of the mechanism and its rate was not well known before, the falloff curves of this important reaction also had to be modelled. Finally, the present experiments at temperatures above about 2000 K generate mixtures of N, F, and CF$_2$ in a concentration ratio 1 : 3 : 6. Recording absorption-time profiles for this mixture suggests contributions from CF$_2$ and CF, the latter not only arising from CF$_2$ dissociation (4) but also from other, so far unidentified processes.

Finally, a branching of the mechanism at the level of (C$_2$F$_5$)$_2$NCF$_2$, on the one hand, may provide an explanation for the low-temperature production of an end product like perfluoro-N-methylpyrrolidene, (C$_2$F$_4$)$_3$NCF$_3$, such as was observed earlier in ref. 6; on the other hand, this detail may also be responsible for the properties of the CF$_2$ yields observed at the low-temperature end of the present experiments.

Conflicts of interest

There are no conflicts to declare.

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