Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Shock Wave and Modelling Study of the Dissociation Pathways of $(C_2F_5)_3N$

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Supplementary Information

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SI-1. Comparison of quantum-chemical results for selected reaction enthalpies

Energetics of the reactions $(C_2F_5)N \rightarrow C_2F_5 + N$ and $(C_2F_5)N \rightarrow (CF_2)N + CF_3$ (DFT calculations with B3LYP, [1,2] M06-2X,[3] BMK,[4] and ωB97X-D[5] models, combined with a 6-311+G(3df) basis set; *ab initio* calculations employing CBS-QB3[6,7] and G4 models;[8] all calculations performed using the Gaussian set of codes[9]).

model	$(C_2F_5)N \rightarrow C_2F_5 + N$	$(C_2F_5)N \rightarrow (CF_2)N + CF_3$	TS12
CBS-QB3	288.7	115.9	134.7
G4	293.3	117.2	143.1
B3LYP	290.4	79.9	107.5
M06-2X	297.9	125.1	138.9
BMK	299.6	107.1	135.1
ωB97X-D	291.2	103.8	123.4

(enthalpies at 0 K in kJ mol^{-1}; ground state multiplicities: $(C_2F_5)N$: triplet, $(CF_2)N$: doublet, N: quartet, CF_3: doublet, C_2F_5: doublet, TS12: triplet; $(C_2F_5)N \rightarrow C_2F_5 + N$ is a simple bond fission without barrier for the reverse reaction; the reaction $(C_2F_5)N \rightarrow (CF_2)N + CF_3$ has a rigid activated complex TS12).

SI-2. Reaction enthalpies for the decomposition of $(C_2F_5)_2N$.

(Reaction enthalpies at 0 K in kJ mol^{-1})

model	$(C_2F_5)_2N \rightarrow (C_2F_5)N + C_2F_5$	$(C_2F_5)_2N \rightarrow (C_2F_5)NCF_2 + CF_3$	$(C_2F_5)NCF_2 \rightarrow (C_2F_5)N + CF_2$
B3LYP	297.5	25.5	495.0
M06-2X	328.0	53.1	518.0
BMK	321.3	45.2	513.0
ωB97X-D	320.9	46.0	512.5

(ground state multiplicities: $(C_2F_5)_2N$: doublet, $(C_2F_5)NCF_2$: singlet, CF_2: singlet, other species: table SI-1; all reactions are simple bond fissions without barrier for the reverse reactions).

SI-3. Reaction enthalpies for the decomposition of $(C_2F_5)_3N$.

(at 0 K in kJ mol^{-1})

model	$(C_2F_5)_3N \rightarrow (C_2F_5)_2N + C_2F_5$	$(C_2F_5)_3N \rightarrow (C_2F_5)_2NCF_2 + CF_3$	$(C_2F_5)_2NCF_2 \rightarrow (C_2F_5)_2N + CF_2$
B3LYP	272.8	307.1	187.9
M06-2X	354.8	363.2	234.3
BMK	322.6	347.3	207.1
ωB97X-D	327.2	345.6	218.0

(ground state multiplicities: $(C_2F_5)_3N$: triplet, $(C_2F_5)_2NCF_2$: doublet, other species: tables SI-1 and SI-2; all reactions are simple bond fissions without barrier for the reverse reactions).

SI-4. Reaction enthalpies for the decomposition of C_2F_5

(at 0 K in kJ mol^{-1}; literature value 240.2 kJ mol^{-1}).

model	$C_2F_5 \rightarrow CF_3 + CF_2$
B3LYP	222.6
M06-2X	242.3
BMK	234.7
ωB97X-D	237.2

SI-5. Parameters in the calculation of C_2F_5 dissociation rate constants.

Vibrational frequencies (in cm^{-1}, from B3LYP/6-311+G(3df) calculations):

C_2F_5 : 61, 208, 220, 363, 416, 509, 581, 606, 697, 813, 1103, 1166, 1207, 1274;

CF_3 : 504, 504, 698, 1076, 1235, 1235;

CF_2 : 671, 1104, 1226.

Rotational constants (in cm^{-1}, from B3LYP/6-311+G(3df) calculations):

C_2F_5 : 0.125, 0.0796, 0.0655 ($\sigma = 3$);

CF_3 : 0.362, 0.362, 0.187 ($\sigma = 3$);

CF_2 : 2.935, 0.418, 0.366 ($\sigma = 2$).

Morse-potential for the CF_3 - CF_2 bond, with Morse-parameter β = 3.24 $Å^{-1}$ (from G4//B3LYP/6-311+G(3df) calculations; for details of the fitting of the potential, see e.g. refs 3,15, and 16 of the main text).

Average looseness parameter of the transitional modes α = 1.68 $Å^{-1}$ (from G4//B3LYP/6-311+G(3df) calculations; for details of the fitting of the potential, see e.g. refs 13, 15, and 16 of the main text).

SI-6. Modelled rate constants for the dissociation of C_2F_5.

Limiting high-pressure rate constants (between 1000 and 2000 K):

$k_{2,\infty} = 7.88 \times 10^{14} \exp(-226 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$

(the corresponding recombination rate constants are

$k_{-2,\infty} = 1.51 \times 10^{12} (T/1500)^{0.24} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).

SACM/CT calculations following ref. 10.

Limiting low-pressure rate constants (between 1000 and 2000 K):

$k_{2,0} = [Ar] 5.45 \times 10^{21} (T/1500)^{-14.89} \exp(-292 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Calculations following ref. 11 with rotational factor F_{rot} for the Morse potential of SI-5, leading to centrifugal constants $B_{cent}(r) = 0.0726/[1 + 0.4094(r - 1.520) + 0.1659(r - 1.520)^2]$ cm^{-1} ($C_\nu = 6.66 \times 10^{-3}$ cm^{-1}, $\nu = 1.14$) (from B3LYP/6-311+G(3df) calculations); $F_{rotint} \approx F_{rotint}^{free}$ (the rotational barrier at the G4//B3LYP/6-311+G(3df) level is 10.5 kJ mol^{-1}); collision efficiencies β_c were calculated using a temperature independent value of $-\langle\Delta E\rangle/hc$ = 100 cm^{-1} for M = Ar.

Falloff curves

Falloff curves were represented in the form proposed in refs. 12 and 13 with strong collision broadening factors F_{cent} = 0.084 (1000 K), 0.078 (1250 K), 0.080 (1500 K), 0.086 (1750 K), 0.095 (2000 K) from ref. 14.

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