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Reaction Mechanisms and Sensitivity for Silicon Nitrocarbamate and Related Systems from Quantum Mechanics Reaction Dynamics

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Table S1 The equilibrium cell parameters for PETN, Si-PETN, PETNC, and Si-PETNC crystals predicted from PBE-D3 calculations at zero temperature, compared with those from experiments and other DFT calculation

crystals	methods	*T* (K)	ρ (g/cm^3)	*a* (Å)	*b* (Å)	*c* (Å)
PETN	Exp.[a]	298	1.781	9.380	9.380	6.700
	PBE-D3	0	1.812	9.314	9.314	6.680
Si-PETN	PBD-vdW[b]	0	1.744	9.710	9.710	6.710
	PBE-D3	0	1.679	9.665	9.665	7.035
PETNC	Exp.[c]	100	1.765	9.735	9.735	9.692
	PBE-D3	0	1.750	9.798	9.798	9.650
Si-PETNC	Exp.[d]	100	1.700	10.068	10.068	9.720
	PBE-D3	0	1.712	10.082	10.082	9.630

a from Ref. 47; b from Ref. 53, DFT calculations using PBE with an empirical van der Waals correction; c from Ref. 33; d from Ref. 34.

The optimized cell parameters for PETN, Si-PETN, PETNC, and Si-PETNC at 0 K from PBE-D3 are collected in Table S1, in comparisons with those from X-ray diffraction experiments at 298 K or 100 K and from DFT calculations at 0 K. The densities predicted by PBE-D3 are 1.812, 1.75, and 1.712 g/cm^3 for PETN, PETNC, and Si-PETNC, respectively, compared to the X-ray values of 1.781, 1.765, and 1.7 g/cm^3. The relative errors are 1.741 %, -0.85 %, and 0.706 %, indicating that PBE-D3 gives accurate descriptions of these molecular crystals. We thus expect that the predicted crystal structure for Si-PETN is reasonable. The experimental measurements were carried out at 298 K for PETN and at 100 K for PETNC and Si-PETNC, whereas all the QM calculations were performed at 0 K. Thus, the discrepancy for PENT is relatively higher than those for PETNC and Si-PETNC.

Table S2 Bond order cutoff values for various atom pairs used to identify molecular fragments in PETN

	C	H	N	O
C	0.55	0.40	0.30	0.60
H		0.55	0.55	0.40
N			0.55	0.55
O				0.65

Table S3 Bond order cutoff values for various atom pairs used to identify molecular fragments in Si-PETN

	C	H	N	O	Si
C	0.55	0.40	0.30	0.60	0.40
H		0.55	0.55	0.40	0.40
N			0.55	0.55	0.40
O				0.65	0.55
Si					0.55

Table S4 Bond order cutoff values for various atom pairs used to identify molecular fragments in PETNC

	C	H	N	O
C	0.55	0.40	0.30	0.60
H		0.55	0.55	0.50
N			0.35	0.55
O				0.65

Table S5 Bond order cutoff values for various atom pairs used to identify molecular fragments in Si-PETNC

	C	H	N	O	Si
C	0.55	0.40	0.30	0.60	0.40
H		0.55	0.55	0.50	0.40
N			0.40	0.55	0.40
O				0.65	0.55
Si					0.55

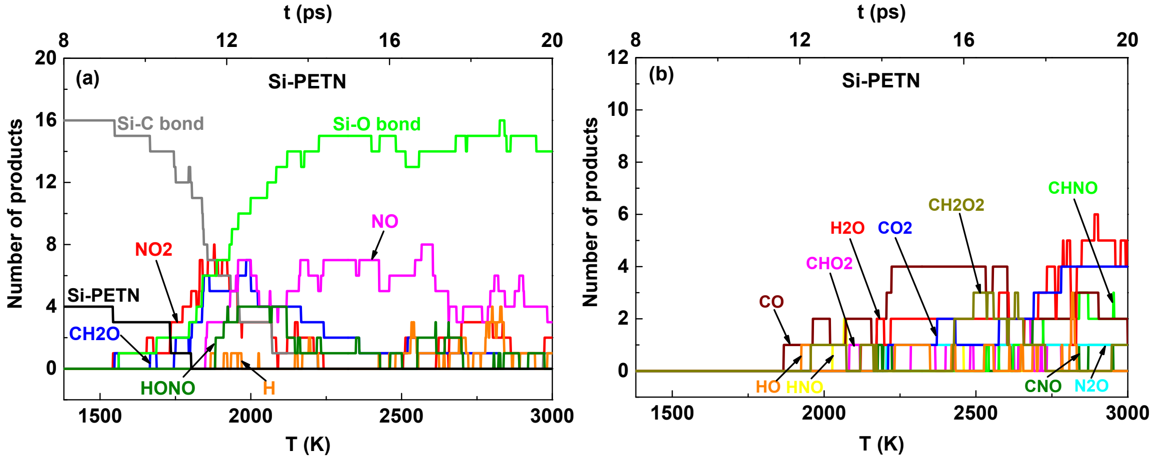

Fig. S1 Evolution with temperature/time of the reaction products formed during the thermal decomposition of Si-PETN. The products with low concentrations and short lifetimes are not included. The number of Si–O bonds increases continuously as the temperature increases and a rapid increment begins after the temperature approaches 1796 K (t = 11.08 ps).

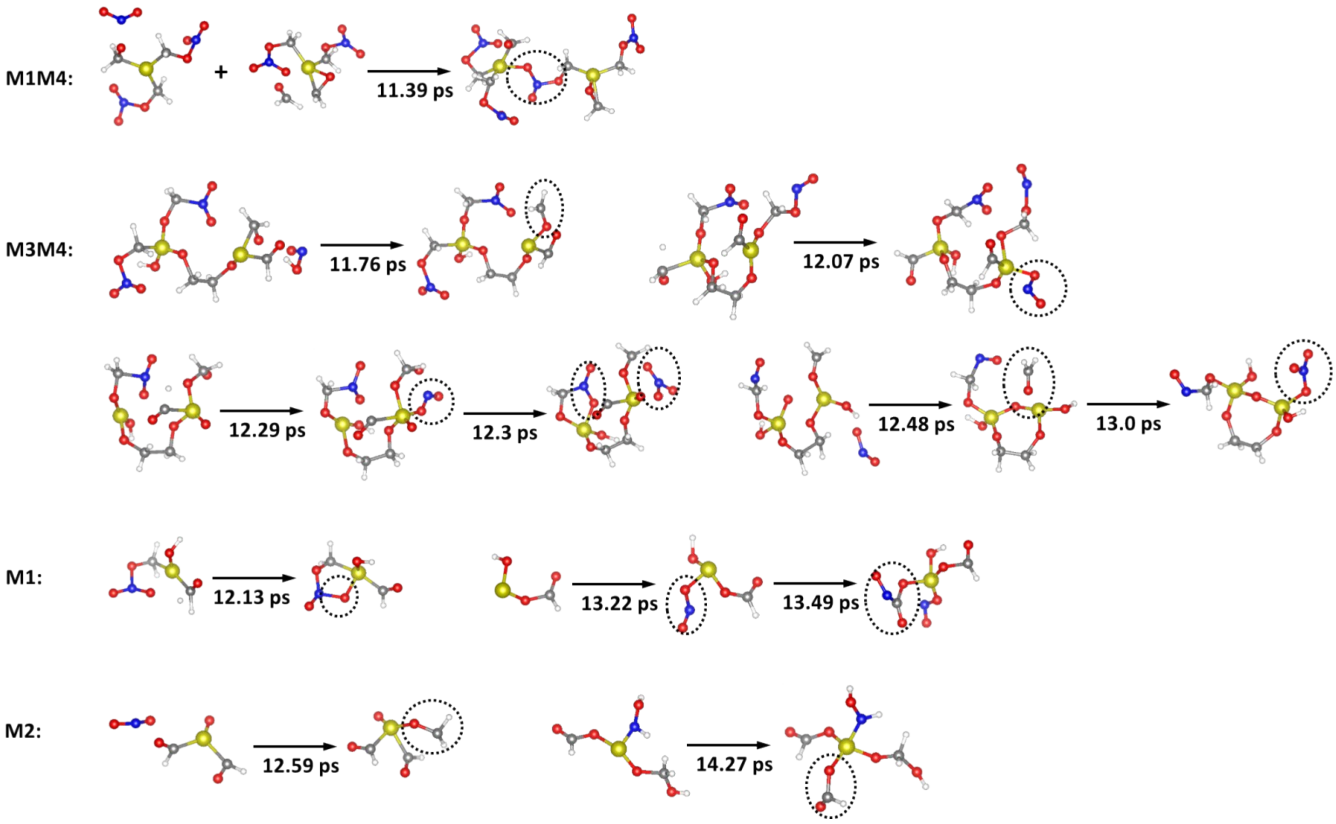

Fig. S2 The molecular structures before and after Si–O bond formation during the thermal decomposition of Si-PETN. The C, H, N, O, and Si atoms are represented by gray, white, blue, red, and yellow balls, respectively. M1M4 means that the Si-O bond is formed due to intermolecular reaction between the partially decomposed M1 and M4; M3M4 means that the Si-O bond formation is occurred in the fragment with two Si formed via the combination of two partially decomposed Si-PETN molecules, M3 and M4; M1 means that these Si-O bonds are formed in the partially decomposed M1; M2 means that these Si-O bonds are formed in the partially decomposed M2. The other five Si-O bonds are shown in Fig. 2.

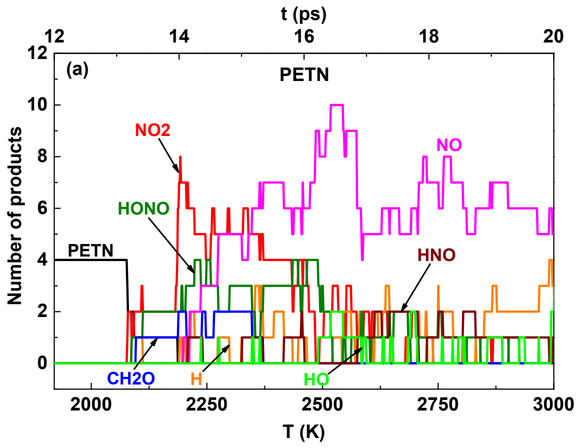

Fig. S3 Evolution with temperature/time of the reaction products formed during the thermal decomposition of PETN. The products with low concentrations and short lifetimes are not included.

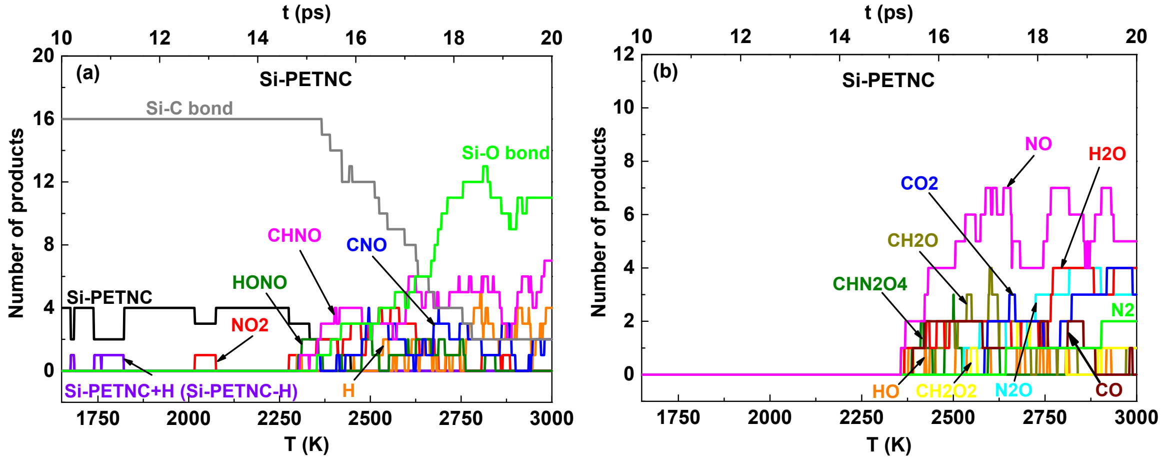

Fig. S4 Evolution with temperature/time of the reaction products formed during the thermal decomposition of Si-PETNC. The products with low concentrations and short lifetimes are not included.

The reaction details about the initial products during the thermal decomposition of Si-PETNC:

By looking into the reaction pathways, we find that the NO_2 formed at an early stage is due to NH–NO_2 bond cleavage, and the ones formed at a later time arise from the decomposition of other products such as CN_2O_3, HONO, and the fragment with two Si. The H atom is initially dissociated from the Si-PETNC after losing one NO_2 and then formed due to the decompositions of other products such as CHNO and HONO. The attraction between the O in dissociated NO_2 and the H in –NH results in the elimination of HONO at an early stage, which is lately formed via the secondary reactions between NO_2 and isolated H or the H in other products. The further decomposition of Si-PETNC after losing H and NO_2 leads to the generation of CNO, which is also generated from the decompositions of other products like CHNO and CN_2O_3. CHNO is dissociated partially from Si-PETNC after losing NO_2, H, HONO, and CNO and partially from the further decompositions of the fragment with two Si.

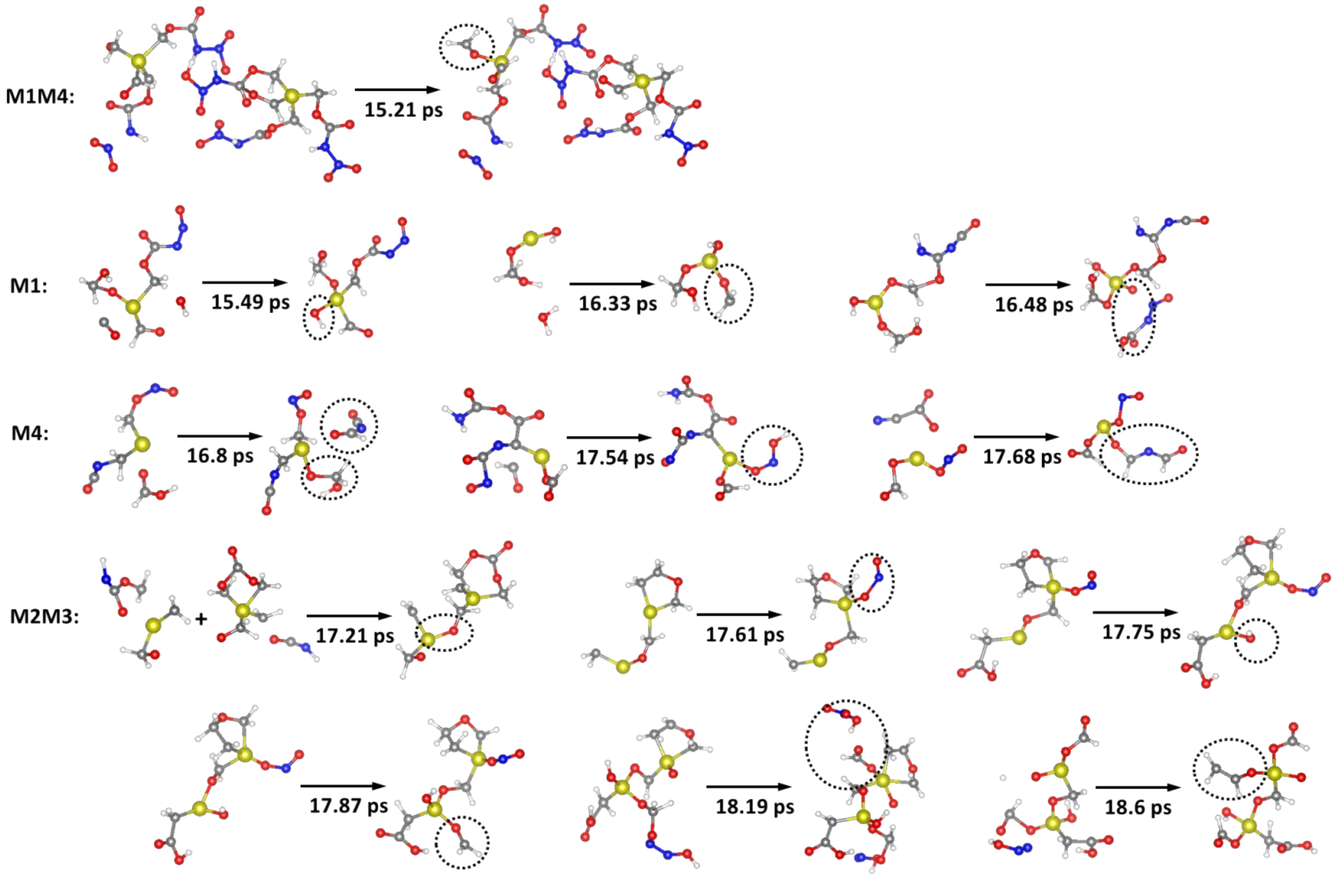

Fig. S5 Molecular structures before and after Si-O bond formation during the thermal decomposition of Si-PETNC. The C, H, N, O, and Si atoms are represented by gray, white, blue, red, and yellow balls, respectively. M1M4 means that the Si-O bond formation is occurred in the fragment with two Si formed via the combination of two partially decomposed Si-PETNC molecules, M1 and M4; M2M3 means that the Si-O bond formation is occurred between M2 and M3 or in the fragment with two Si formed via the combination of two partially decomposed Si-PETNC molecules, M2 and M3; M1 means that these Si-O bonds are formed in the partially decomposed M1; M4 means that these Si-O bonds are formed in the partially decomposed M4.

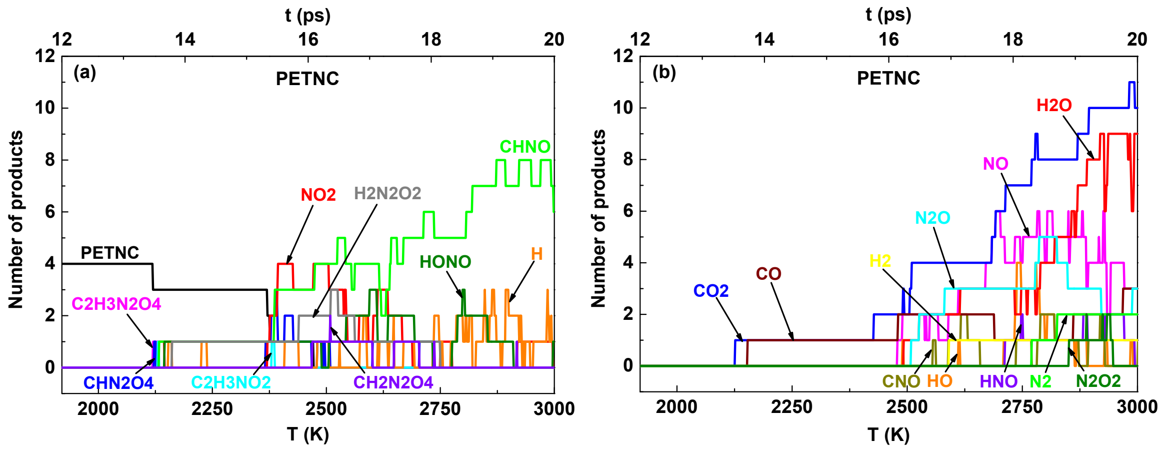

Fig. S6 Evolution with temperature/time of the reaction products formed during the thermal decomposition of PETNC. The products with low concentrations and short lifetimes are not included.

The reaction details about the initial products during the decomposition of PETNC: The first H is formed due to the further decomposition of initial product $C_2H_3N_2O_4$ and the second H is dissociated directly from the PETNC after losing $C_2H_3N_2O_4$ and CHN_2O_4. The further decompositions of PETNC moieties and other products like CHO, HONO, and CHNO lead to the generation of H at a later time. The first NO_2 and $C_2H_3NO_2$ are formed due to the decomposition of initial product $C_2H_3N_2O_4$, and the second and third NO_2 are dissociated directly from PETNC. The decomposition of initial product CHN_2O_4 results in the formation of NO_2 at a later time. The formation of CHNO at an early stage is attributed partially to the decomposition of initial product $C_2H_3NO_2$ and partly to the further decomposition of PETNC after losing NO_2 and CHN_2O_4 or after losing NO_2. The secondary reactions between other products and the further decompositions of PETN moieties contribute to the formation of CHNO later on. Because of the various reaction routes, the population of CHNO continuously increases with temperature/time increasing.