

Explanation of the Colossal Detonation Sensitivity of Silicon Pentaerythritol Tetranitrate (Si-PETN) Explosive

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A new extremely sensitive silicon-based explosive was recently synthesized by the nitration of tetrakis(hydroxymethyl)silane, $\text{Si}(\text{CH}_2\text{OH})_4$, with nitric acid.¹ This sila-pentaerythritol tetranitrate (Si-PETN), $\text{Si}(\text{CH}_2\text{ONO}_2)_4$ (tetrakis(nitratomethyl)silane) has a molecular structure nearly identical to its carbon analogue, Pentaerythritol Tetranitrate (PETN), $\text{C}(\text{CH}_2\text{ONO}_2)_4$, with the central carbon atom replaced by silicon. Unexpectedly, Si-PETN shows a dramatically increased sensitivity, exploding with just a touch of a spatula (no impact), making it extremely dangerous and difficult to study. Thus it is more sensitive than mercury fulminate and far more sensitive than PETN. Although detonation sensitivity is an extremely important issue in explosives, there is no clear understanding about the molecular and structural determinants controlling their sensitivity to external stimuli. Since the molecular structures of PETN and Si-PETN are very similar with very similar contacts between various molecules in the crystal, we considered that elucidating how replacing the central C with Si dramatically increases sensitivity might provide clues useful for understanding sensitivity in other systems. Indeed DFT calculations on pathways for unimolecular decomposition show a dramatic difference that suggests an explanation of the colossal sensitivity.

The various unimolecular decomposition pathways considered for PETN and Si-PETN are shown in Figure 1. All calculations were carried out with the Jaguar 7.0 package,² using the unrestricted hybrid functional UB3LYP³ and UM06⁴ to locate all the stationary points and to calculate the Hessian matrix for zero-point energy and reaction enthalpy at the 6-311G** level. Data in the Supporting Information (SI) for small nitrate esters show that B3LYP tends to underestimate the O–N Bond Dissociation Energy (BDE) by ~5 kcal/mol, in agreement with previous calculations,⁵ while the M06 functional generally reproduces the experimental BDEs.⁶ Thus M06 leads to a BDE for reaction 1 in PETN of 39.0 kcal/mol, within the range of experimental values of 35.0,⁷ 39.5,⁸ and 45.9⁹ kcal/mol. Consequently we will quote only the M06 values below.

NO_2 dissociation (reaction 1) generally provides the lowest barrier for unimolecular decomposition of energetic materials with a nitro group, such as RDX,¹⁰ PETN,^{7–9} and HMX,¹¹ although HONO elimination (reaction 3) is often close. The calculated O– NO_2 BDEs are 39.0 kcal/mol for PETN and 35.6 kcal/mol for Si-PETN. This lower O–N bond energy of Si-PETN may facilitate the propagation of chain reactions to contribute partially to its sensitivity. However, this reaction is not exothermic and it is *not* the decomposition pathway with the lowest barrier, as discussed below.

The C–O bond-breaking reaction 2 leads to BDE = 82.2 (C) and 77.6 (Si) kcal/mol. With such high barriers, they would only

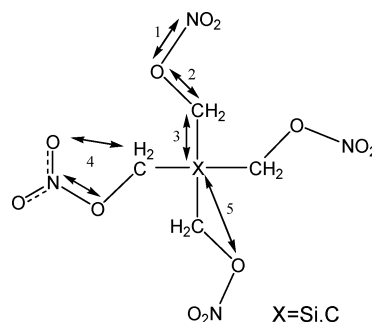


Figure 1. Structure of PETN (X = C) and SiPETN (X = Si) and the five reactions studied in this work.

be observed in high energy laser experiments¹² and would not explain the difference in sensitivity.

The potential energy surface near the transition state to break the X–C bond (reaction 3) is very flat, (see SI) making it difficult to locate the precise transition state. Consequently, we carried out a 2-D scan of the X–C and O– NO_2 bond lengths, which shows that the central Si–C bond of Si-PETN and C–C bond of PETN are strongly dependent on the O– NO_2 bond. Stretching the O– NO_2 bond weakens the X–C bond because the oxygen forms a C=O double bond by withdrawing electron density from the X–C bond. The products of this reaction are CH_2O , NO_2 , and a tertiary C/Si free radical. The lower electronegativity of Si (1.8) compared to C (2.5) explains the drastically different charges on the central atoms: –0.19 in PETN, +0.25 in Si-PETN (B3LYP, with similar trends from M06). However the similar transition state (TS) barriers of 51.3 (C) and 49.7 (Si) kcal/mol would not explain the difference in sensitivity.

Next we examined HONO dissociation (reaction 4) involving simultaneous formation of a new OH bond with breaking of the O– NO_2 bond. This is a well-known mechanism for energetic molecules with the nitro group, discovered first in DFT calculations,¹⁰ which leads to an activation energy of 39.2 kcal/mol for RDX¹⁰ and 44.6 kcal/mol for HMX.¹¹ For PETN this leads to TS energies of 39.2 (C) and 39.4 (Si) kcal/mol, very similar to reaction 1. Such a tiny difference would not explain the huge difference in sensitivity.

Finally we considered the attack of the γ O on the α central C/Si atom, reaction 5, in which the β CH_2 group stays bonded to the γ O as the X–O bond forms simultaneously to a terminal O of the NO_2 . Thus the transition state in Si-PETN is formed by bending the C– ONO_2 angle, breaking the partial Si–C bond, and making the Si–O bond concurrently, as shown in Figure 2. This was studied by first locating the transition structure through 2-D scans followed by intrinsic reaction coordinate (IRC) scans. We

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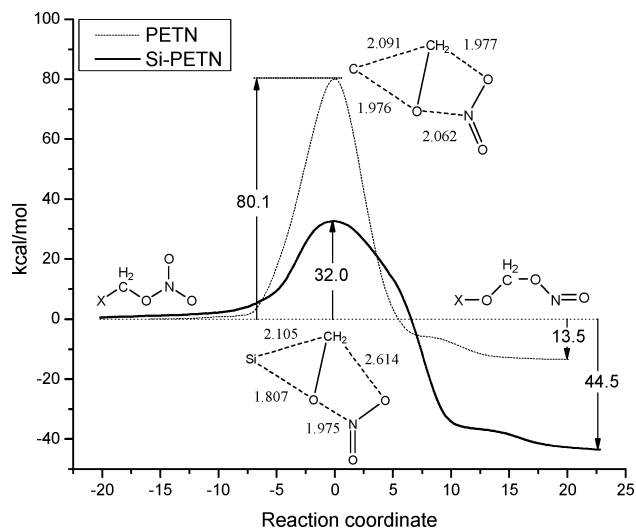


Figure 2. Energy vs reaction coordinate and the geometry of the transition state (from DFT at the M06/6311G** level). The IRC step is 0.1 au with mass-weighted coordinate.

find that Si-PETN has a 32.0 kcal/mol barrier for this rearrangement, which is dramatically lower than the value 80.1 kcal/mol for PETN. This is partly due to the larger size of silicon (Si covalent radius of 1.17 Å compared to 0.771 Å for C¹³) resulting in a more stable five-coordinate transition state in Si-PETN, allowing the Si–C and Si–O bonds to be shorter with the O–N bond is broken later thereby decreasing the energy barrier significantly.

An additional important factor in detonation sensitivity and a second dramatic difference between PETN and Si-PETN is the heat release which is 44.5 kcal/mol exothermic for reaction 5 with Si-PETN, whereas the favorable decomposition for PETN (reaction 1) is 39.0 kcal/mol endothermic. To estimate the difference between the two exothermic reactions in Si-PETN, the corresponding unimolecular decomposition rates of reactions 4 and 5 were calculated using the transition state theory.¹⁴ Assuming no tunneling, the rate of reaction 5 is 1.6×10^4 times faster than that of reaction 4 at 298 K (see SI), making it plausible that reaction 5 may contribute significantly to sensitivity.

This mechanism also explains the Si NMR spectroscopy of the decomposition product from Si-PETN, which contains the signal for siloxane –OSi–(CH₂OR)₂O–. Reaction 5 is similar to the Brook rearrangement¹⁵ of the silyl group in silyl alcohols from carbon to oxygen, but this analogue reaction cannot reach the transition state without breaking the O–H bond leading to a calculated barrier of 83.3 kcal/mol.¹⁶ In Si-PETN the α -silyl alcohol is replaced by the α -silyl nitro-ester and a flexible bond angle with a weak O–N bond, all of which favors the reaction 5 rearrangement product by dramatically decreasing the TS energy.

Summarizing, the DFT calculations have identified a novel carbon–oxygen rearrangement of the newly synthesized Si derivative of the PETN energetic molecule that provides a plausible explanation of the dramatic increase in sensitivity observed experimentally. The primary factors leading to this are the much stronger Si–O bond over C–O, the ability of the much larger Si

Table 1. BDE of Each Bond and Energies of Transition State (All Energies in kcal/mol)

Reaction	PETN		SiPETN	
	B3LYP ^a	M06 ^a	B3LYP ^a	M06 ^a
1: O–NO ₂ (BDE)	35.8	39.0	28.7	35.6
2: C–ONO ₂ (BDE)	73.3	82.2	69.4	77.6
3: C–X (TS)	41.7	49.1	40.6	48.2
4: HONO (TS)	36.2	39.2	36.5	39.4
5: O–X (TS)	73.1	80.1	30.5	32.0

^a Numbers listed here are DFT using the 6-311G** basis set. ^b The most recent experimental BDE is 39.5 kcal/mol after correcting for the zero-point energy correction and thermal correction to 298.15 K indicating that the M06 results are more accurate than the B3LYP results.

to adopt the five-coordinate transition state required for reaction 5, and the ability of the terminal O of NO₂ to stabilize this five-coordinate transition state. In addition to the significantly lower barrier (32 vs 80 kcal/mol), reaction 5 is also far more exothermic (45 vs 13 kcal/mol) because a new SiO bond is formed. This provides a large net energy release at the very early stages of Si-PETN decomposition facilitating a fast temperature increase and expansion of the reaction zone. This combination of kinetic and thermodynamic enhancement factors for the Si analogue illustrates a path to controlled sensitivity of other Si analogues of energetic molecules.

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Supporting Information Available: Comparison of B3LYP and M06 for various bond energies, all single-bond scans, IRC scans along with the change of important bond length, and unimolecular reaction rates for reactions 4 and 5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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