Supporting Information of Size-Dependent Shock Response Mechanisms in Nanogranular RDX: A Reactive Molecular Dynamics Study

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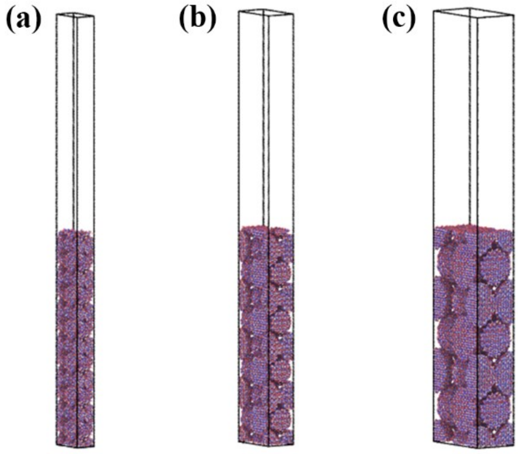

Figure S1. Configurations of (a) SR25, (b) SR35, and (c) SR50.

Hugoniot states

Wavefront position was clearly identified as a discontinuity in density profiles, which is calculated as the average densities of bins with a width of 2 Å along the shock direction. Figure S2 displays the evolution of the wavefront position of SR25, SR35, and SR50 shocked with different velocities before rarefaction occurs. The wavefront position of the systems composed of particles with different diameters shows little distinction during the shock at the same particle velocity (U_p). It indicates that particle diameter has little effect on the shock velocity (U_s) at the same system density, which is consistent with the shock responses of packed Ni and Al nanoparticles[1]. Shock velocity is the sum of wavefront position velocity (the slope of the linear fit in Figure S2) and particle velocity. The shock velocity is 5.53, 6.40, 7.20, and 7.94 km/s when the system is shocked at U_p of 2.5, 3, 3.5, and 4 km/s, respectively. The U_s-U_p relation is linear fitted as $U_s = 1.606U_p + 1.548$ (km/s). They were compared with the theoretical results of Selezenev et. al.[2] and Yadav et. al.[3], as well as the experimental results of Franken et.al.[4], as shown in Figure S3. The linear fitted slop of our results is consistent well with the theoretical results, and has some disparity compared to the experimental results. The clearly different intercept on y-axis is due to the high porosity in our systems, which agrees with the result that the lower initial density of the granularity system leads to a lower intercept on y-axis[1].

The longitudinal pressure component P_{zz} of the shocked section was calculated during the initial shockwave propagating to the upper free surface. Similar P_{zz} was found for systems with different particle sizes when shocked at the same velocity. P_{zz} is approximately 14.20, 20.29, 26.59, and 31.66 GPa, respectively, which is slightly lower than the calculated value by the Rankine-Hugoniot relation $P_s = \rho_0 U_s U_p$ (17.28, 24.00, 31.50, and 39.70 GPa, respectively). The reason is suspected that the above formula describes the ideal situation of the whole system, while P_{zz} values were calculated from atom velocities and stresses where the actual initial conditions, boundary conditions and voids between particles were considered.

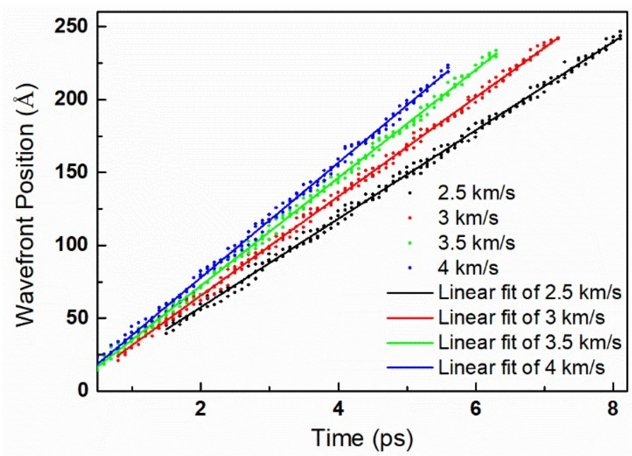

Figure S2. Evolution of wavefront position of systems shocked with different velocities before rarefaction occurs.

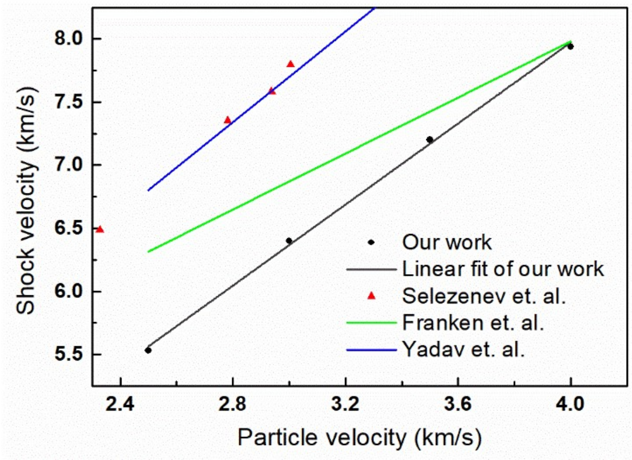

Figure S3. U_s-U_p relation of systems shocked with different velocities and compared with other researchers.

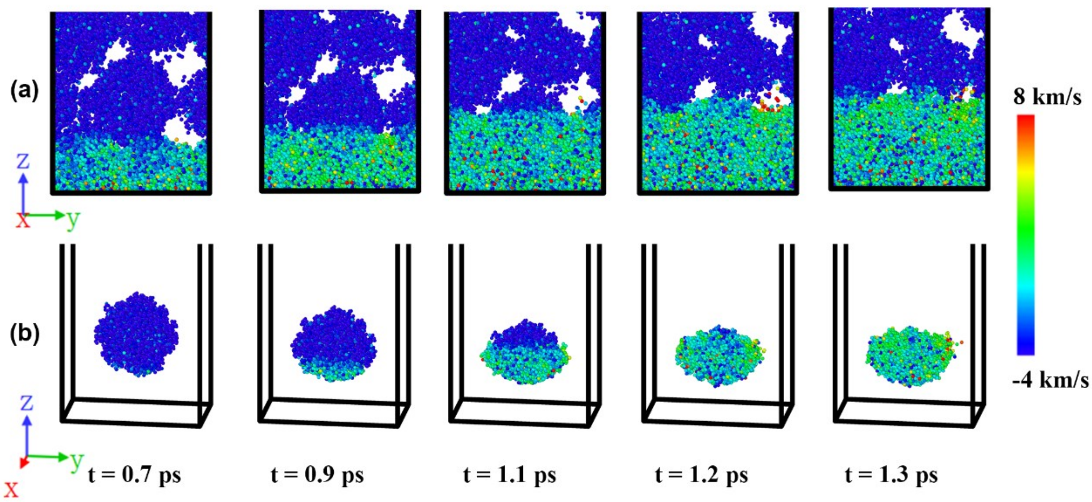

Figure S4. The snapshots of (a) 2 nm thickness slice of the model and (b) one nanoparticle during the shock wave propagate through the nanoparticle in SR25 shocked with the U_p of 4 km/s. Atoms are color-coded by its velocity magnitude along *z*-direction.

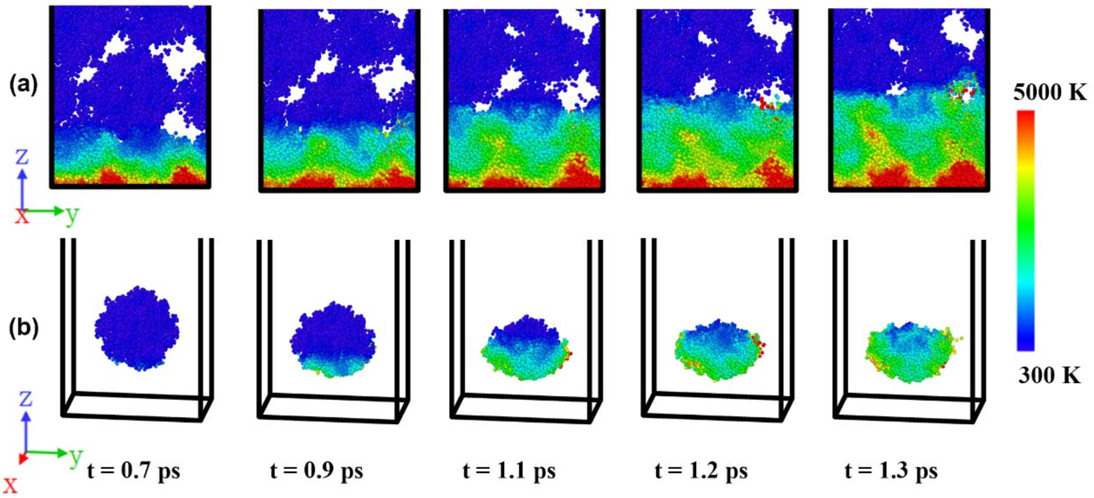

Figure S5. The snapshots of (a) 2 nm thickness slice of the model and (b) one nanoparticle during the shock wave propagate through the nanoparticle in SR25 shocked with the U_p of 4 km/s. Atoms are color-coded by atom temperature.

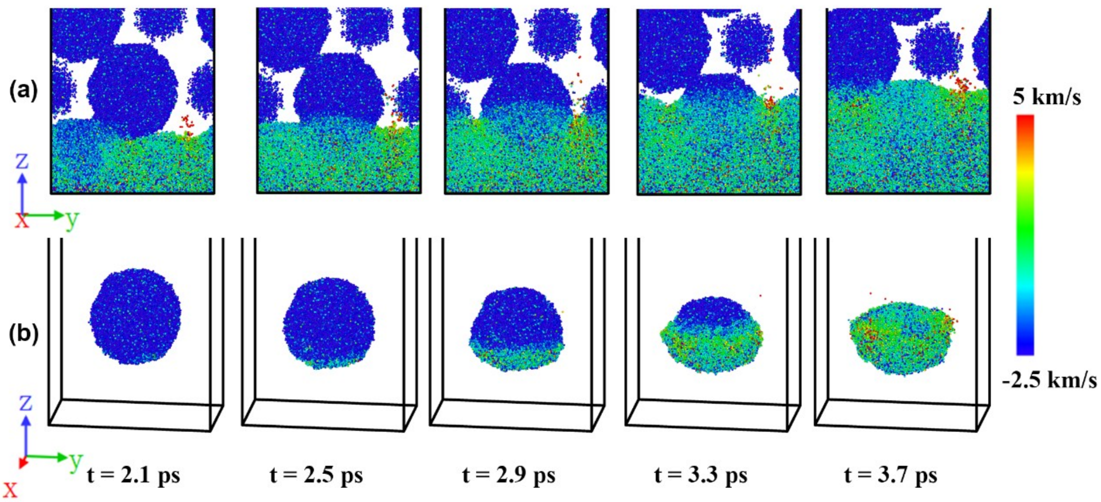

Figure S6. The snapshots of (a) 2 nm thickness slice of the model and (b) one nanoparticle during the shock wave propagate through the nanoparticle in SR50 shocked with the U_p of 2.5 km/s. Atoms are color-coded by its velocity magnitude along *z*-direction.

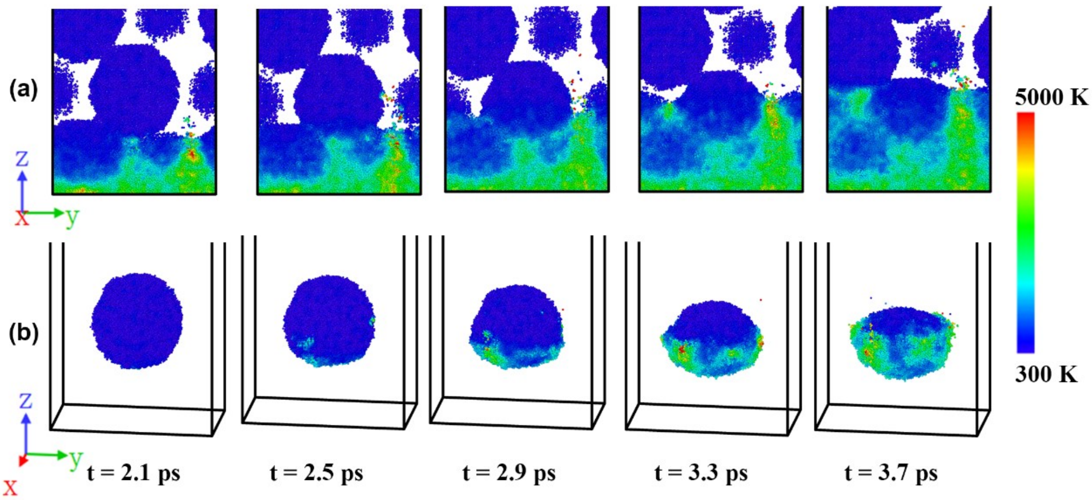

Figure S7. The snapshots of (a) 2 nm thickness slice of the model and (b) one nanoparticle during the shock wave propagate through the nanoparticle in SR50 shocked with the U_p of 2.5 km/s. Atoms are color-coded by atom temperature.

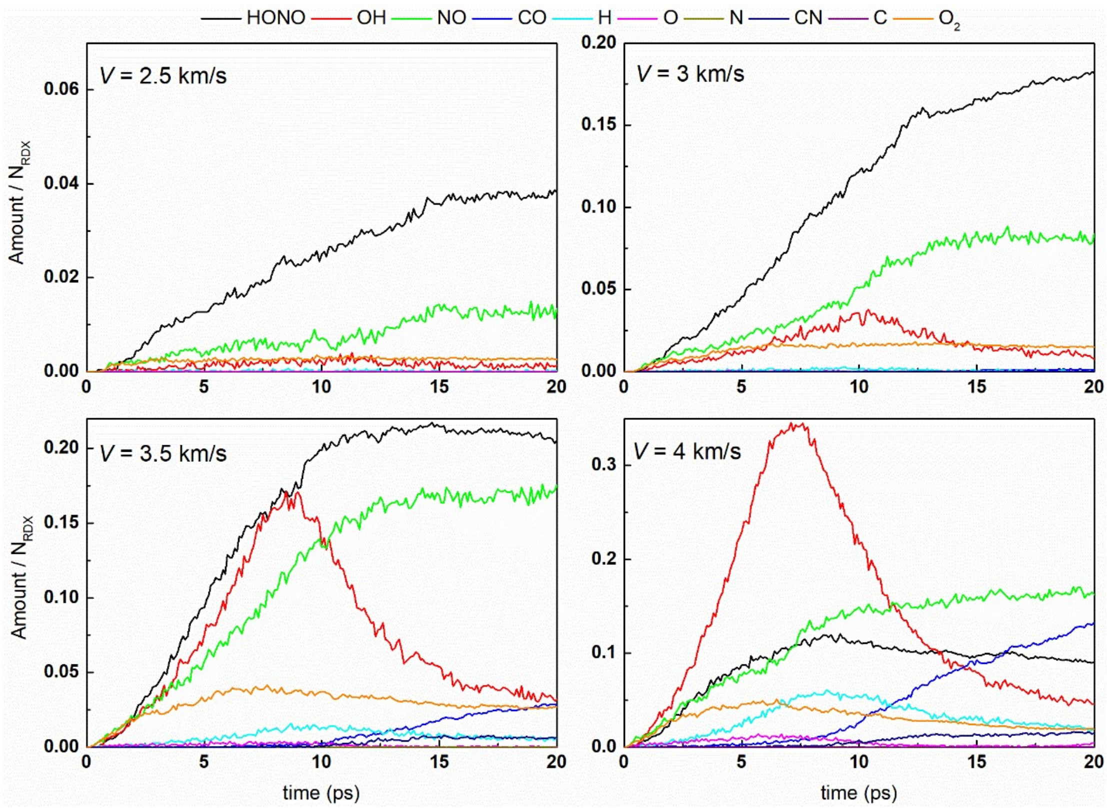

Figure S8. Evolution of key products in SR25 when shocked at different velocities.

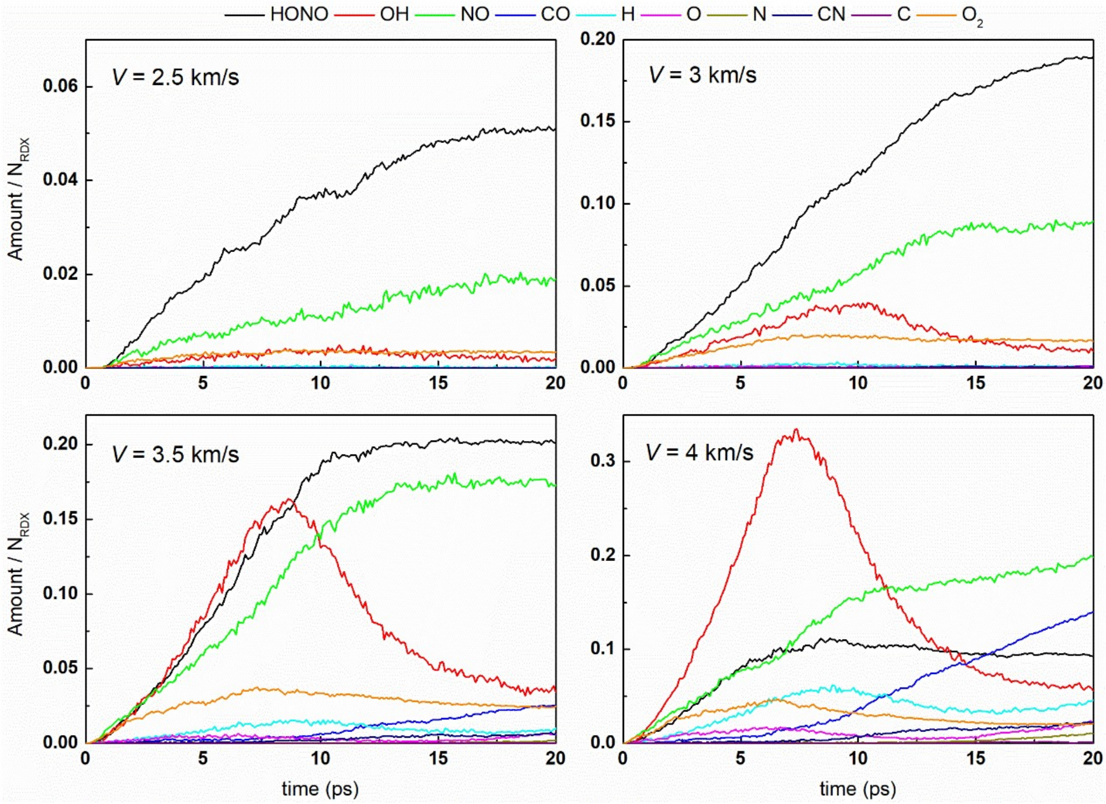

Figure S9. Evolution of key products in SR35 when shocked at different velocities.

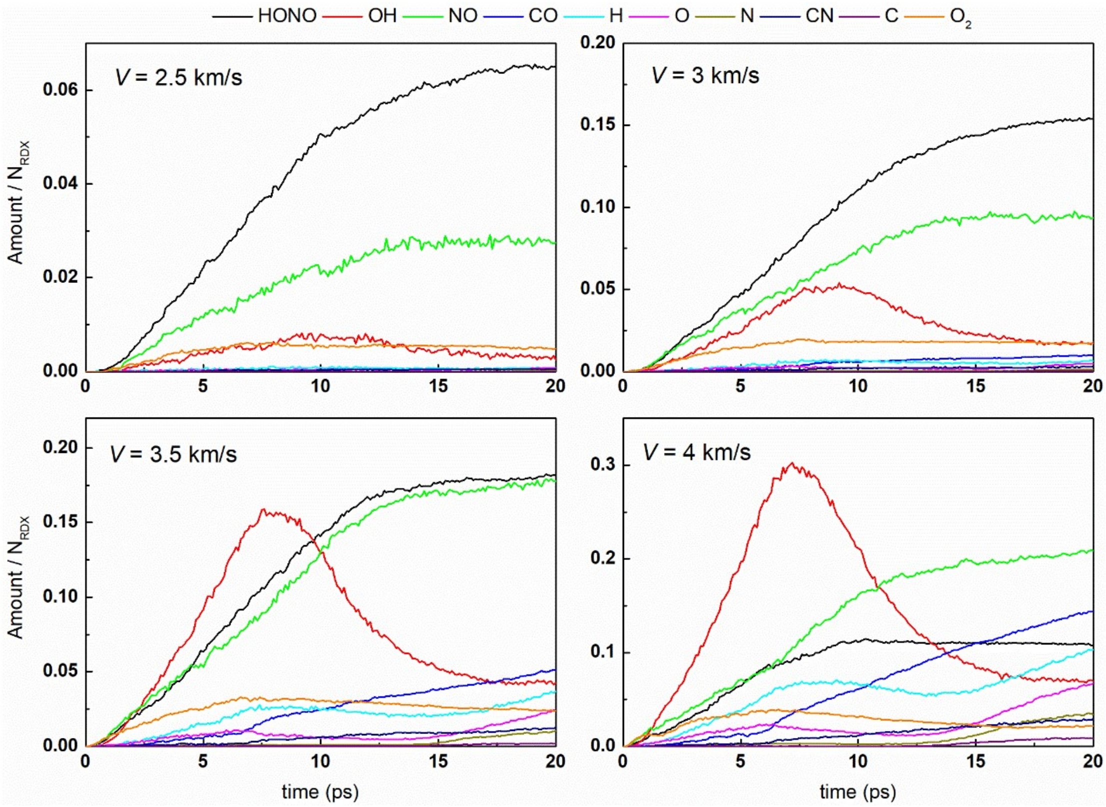

Figure S10. Evolution of key products in SR50 when shocked at different velocities.

Table S1. Key gas products (top 5) at 20 ps and their scaled amounts (divided by the original amount of RDX in the system) located at the upper 100 Å part along the *z* axis when shocked at 4 km/s.

	1st	2nd	3rd	4th	5th
SR25	NO_2 (3.74%)	NO (0.81%)	$C_3H_6O_6N_6$ (0.65%)	CH_2N (0.63%)	H_2O (0.55%)
SR35	H (4.65%)c	NO (3.11%)	N_2 (2.89%)	CO (2.20%)	O (2.16%)
SR50	H (10.10%)	O (6.51%)	N_2 (4.76%)	CO (4.33%)	N (3.45%)

Table S2. Reaction frequencies (Top10) in 0.5 ps intervals during 0–20 ps in SR25 when shocked at different velocities.

Particle velocity	Scale normalized freq. (%)	Primary reactions
2.5 km/s	18.3	$C_3H_6N_6O_6 \rightarrow C_3H_6N_5O_4 + NO_2$
	3.54	$C_3H_6N_5O_4 \rightarrow C_3H_6N_4O_2 + NO_2$
	3.21	$C_3H_6N_6O_6 + NO_2 \rightarrow C_3H_6N_6O_5 + NO_3$
	2.57	$C_3H_6N_7O_8 \rightarrow C_3H_6N_6O_5 + NO_3$
	2.27	$C_3H_6N_6O_6 + NO_2 \rightarrow C_3H_6N_7O_8$
	1.57	$C_3H_5N_5O_4 \rightarrow C_3H_5N_4O_2 + NO_2$
	1.34	$C_3H_6N_6O_6 \rightarrow C_3H_6N_4O_2 + NO_2 + NO_2$
	1.22	$C_3H_6N_6O_5 \rightarrow C_3H_6N_5O_3 + NO_2$
	0.90	$NO_2 + NO_2 \rightarrow N_2O_4$
	0.60	$C_3H_6N_4O_2 + NO_2 \rightarrow C_3H_5N_4O_2 + HONO$
3 km/s	34.61	$C_3H_6N_6O_6 \rightarrow C_3H_6N_5O_4 + NO_2$
	7.69	$C_3H_6N_5O_4 \rightarrow C_3H_6N_4O_2 + NO_2$
	4.85	$C_3H_6N_6O_6 + NO_2 \rightarrow C_3H_6N_6O_5 + NO_3$
	4.23	$C_3H_6N_6O_5 \rightarrow C_3H_6N_5O_3 + NO_2$
	3.44	$C_3H_6N_6O_6 \rightarrow C_3H_6N_4O_2 + NO_2 + NO_2$
	2.93	$C_3H_5N_5O_4 \rightarrow C_3H_5N_4O_2 + NO_2$
	2.57	$NO_2 + NO_2 \rightarrow N_2O_4$
	2.40	$C_3H_6N_7O_8 \rightarrow C_3H_6N_6O_5 + NO_3$
	1.89	$C_3H_6N_6O_6 + NO_2 \rightarrow C_3H_6N_7O_8$
	1.89	$C_3H_6N_4O_2 \rightarrow C_3H_6N_3 + NO_2$
3.5 km/s	27.58	$C_3H_6N_6O_6 \rightarrow C_3H_6N_5O_4 + NO_2$
	4.67	$C_3H_6N_5O_4 \rightarrow C_3H_6N_4O_2 + NO_2$
	3.39	$C_3H_6N_6O_6 \rightarrow C_3H_6N_4O_2 + NO_2 + NO_2$

	3.00	$C_3H_6N_6O_5$ → $C_3H_6N_5O_3$ + NO_2
	2.13	NO_2 + NO_2 → N_2O_4
	1.82	NO + NO → N_2O_2
	1.69	$C_3H_6N_4O_2$ → $C_3H_6N_3$ + NO_2
	1.66	HO + HNO → H2O + NO
	1.38	HONO + NO_3 → HNO_3 + NO_2
	1.34	$C_3H_6N_6O_6$ + NO_2 → $C_3H_6N_6O_5$ + NO_3
4 km/s	20.63	$C_3H_6N_6O_6$ → $C_3H_6N_5O_4$ + NO_2
	2.61	$C_3H_6N_5O_4$ → $C_3H_6N_4O_2$ + NO_2
	2.49	C_2O_3 → CO + CO_2
	2.47	$C_3H_6N_6O_6$ → $C_3H_6N_4O_2$ + NO_2 + NO_2
	2.05	N_2H + HO → H_2O + N_2
	1.89	H + HO → H_2O
	1.57	CN_2O → CO + N_2
	1.52	HO + HNO → H_2O + NO
	1.52	$C_3H_6N_6O_5$ → $C_3H_6N_5O_3$ + NO_2
	1.43	N_2H_2 → H_2 + N_2

Table S3. Reaction frequencies (Top10) in 0.5 ps intervals during 0–20 ps in SR35 when shocked at different velocities.

Particle velocity	Scale normalized freq. (%)	Primary reactions
2.5 km/s	18.78	$C_3H_6N_6O_6$ → $C_3H_6N_5O_4$ + NO_2
	3.89	$C_3H_6N_5O_4$ → $C_3H_6N_4O_2$ + NO_2
	3.45	$C_3H_6N_6O_6$ + NO_2 → $C_3H_6N_6O_5$ + NO_3
	2.17	$C_3H_6N_7O_8$ → $C_3H_6N_6O_5$ + NO_3
	1.88	$C_3H_6N_6O_6$ + NO_2 → $C_3H_6N_7O_8$
	1.77	$C_3H_5N_5O_4$ → $C_3H_5N_4O_2$ + NO_2
	1.40	$C_3H_6N_6O_5$ → $C_3H_5N_5O_3$ + NO_2
	1.36	NO_2 + NO_2 → N_2O_4
	1.35	$C_3H_6N_6O_6$ → $C_3H_6N_4O_2$ + NO_2 + NO_2
	0.71	$C_3H_6N_4O_2$ + NO_2 → $C_3H_5N_4O_2$ + HONO
3 km/s	33.69	$C_3H_6N_6O_6$ → $C_3H_6N_5O_4$ + NO_2
	7.28	$C_3H_6N_5O_4$ → $C_3H_6N_4O_2$ + NO_2
	4.61	$C_3H_6N_6O_5$ → $C_3H_6N_5O_3$ + NO_2
	4.10	$C_3H_6N_6O_6$ + NO_2 → $C_3H_6N_6O_5$ + NO_3
	3.26	$C_3H_6N_6O_6$ → $C_3H_6N_4O_2$ + NO_2 + NO_2
	2.54	NO_2 + NO_2 → N_2O_4
	2.21	$C_3H_5N_5O_4$ → $C_3H_5N_4O_2$ + NO_2
	2.07	$C_3H_6N_7O_8$ → $C_3H_6N_6O_5$ + NO_3
	2.02	$C_3H_6N_5O_3$ → $C_3H_6N_4O$ + NO_2
	1.74	$C_3H_6N_6O_6$ + NO_2 → $C_3H_6N_7O_8$

3.5 km/s	29.31	$C_3H_6N_6O_6 \rightarrow C_3H_6N_5O_4 + NO_2$
	5.04	$C_3H_6N_5O_4 \rightarrow C_3H_6N_4O_2 + NO_2$
	3.13	$C_3H_6N_6O_5 \rightarrow C_3H_6N_5O_3 + NO_2$
	2.88	$C_3H_6N_6O_6 \rightarrow C_3H_6N_4O_2 + NO_2 + NO_2$
	2.39	$NO_2 + NO_2 \rightarrow N_2O_4$
	2.24	$NO + NO \rightarrow N_2O_2$
	1.93	$C_3H_6N_6O_6 + NO_2 \rightarrow C_3H_6N_6O_5 + NO_3$
	1.77	$C_3H_6N_4O_2 \rightarrow C_3H_6N_3 + NO_2$
	1.64	$HO + HNO \rightarrow H_2O + NO$
	1.60	$C_3H_6N_5O_3 \rightarrow C_3H_6N_4O + NO_2$
4 km/s	23.36	$C_3H_6N_6O_6 \rightarrow C_3H_6N_5O_4 + NO_2$
	3.07	$C_3H_6N_5O_4 \rightarrow C_3H_6N_4O_2 + NO_2$
	2.47	$C_3H_6N_6O_6 \rightarrow C_3H_6N_4O_2 + NO_2 + NO_2$
	2.46	$N_2H + HO \rightarrow H_2O + N_2$
	2.23	$C_2O_3 \rightarrow CO + CO_2$
	1.88	$HO + HNO \rightarrow H_2O + NO$
	1.86	$CN_2O \rightarrow CO + N_2$
	1.69	$HONO \rightarrow HO + NO$
	1.65	$C_3H_6N_6O_5 \rightarrow C_3H_6N_5O_3 + NO_2$
	1.50	$CHNO + HO \rightarrow CNO + H_2O$

Table S4. Reaction frequencies (Top10) in 0.5 ps intervals during 0–20 ps in SR50 when shocked at different velocities.

Particle velocity	Scale normalized freq. (%)	Primary reactions
2.5 km/s	17.84	$C_3H_6N_6O_6 \rightarrow C_3H_6N_5O_4 + NO_2$
	3.91	$C_3H_6N_5O_4 \rightarrow C_3H_6N_4O_2 + NO_2$
	2.87	$C_3H_6N_6O_6 + NO_2 \rightarrow C_3H_6N_6O_5 + NO_3$
	1.55	$C_3H_6N_6O_6 \rightarrow C_3H_6N_4O_2 + NO_2 + NO_2$
	1.52	$C_3H_6N_7O_8 \rightarrow C_3H_6N_6O_5 + NO_3$
	1.43	$NO_2 + NO_2 \rightarrow N_2O_4$
	1.42	$C_3H_6N_6O_5 \rightarrow C_3H_6N_5O_3 + NO_2$
	1.40	$C_3H_5N_5O_4 \rightarrow C_3H_5N_4O_2 + NO_2$
	1.30	$C_3H_6N_6O_6 + NO_2 \rightarrow C_3H_6N_7O_8$
	0.66	$N_2O_4 \rightarrow NO + NO_3$
3 km/s	30.25	$C_3H_6N_6O_6 \rightarrow C_3H_6N_5O_4 + NO_2$
	6.39	$C_3H_6N_5O_4 \rightarrow C_3H_6N_4O_2 + NO_2$
	3.86	$C_3H_6N_6O_5 \rightarrow C_3H_6N_5O_3 + NO_2$
	3.40	$C_3H_6N_6O_6 + NO_2 \rightarrow C_3H_6N_6O_5 + NO_3$
	2.80	$C_3H_6N_6O_6 \rightarrow C_3H_6N_4O_2 + NO_2 + NO_2$
	2.02	$C_3H_6N_7O_8 \rightarrow C_3H_6N_6O_5 + NO_3$
	1.89	$C_3H_5N_5O_4 \rightarrow C_3H_5N_4O_2 + NO_2$

	1.85	$NO_2 + NO_2 \rightarrow N_2O_4$
	1.78	$C_3H_6N_6O_6 + NO_2 \rightarrow C_3H_6N_7O_8$
	1.60	$C_3H_6N_4O_2 \rightarrow C_3H_6N_3 + NO_2$
3.5 km/s	29.61	$C_3H_6N_6O_6 \rightarrow C_3H_6N_5O_4 + NO_2$
	5.40	$C_3H_6N_5O_4 \rightarrow C_3H_6N_4O_2 + NO_2$
	3.53	$C_3H_6N_6O_5 \rightarrow C_3H_6N_5O_3 + NO_2$
	2.87	$C_3H_6N_6O_6 \rightarrow C_3H_6N_4O_2 + NO_2 + NO_2$
	2.46	$C_3H_6N_6O_6 + NO_2 \rightarrow C_3H_6N_6O_5 + NO_3$
	1.88	$NO + NO \rightarrow N_2O_2$
	1.69	$C_3H_6N_4O_2 \rightarrow C_3H_6N_3 + NO_2$
	1.47	$C_3H_5N_4O_2 \rightarrow C_3H_5N_3 + NO_2$
	1.46	$C_3H_6N_5O_3 \rightarrow C_3H_6N_4O + NO_2$
	1.39	$NO_2 + NO_2 \rightarrow N_2O_4$
4 km/s	26.01	$C_3H_6N_6O_6 \rightarrow C_3H_6N_5O_4 + NO_2$
	4.06	$C_3H_6N_5O_4 \rightarrow C_3H_6N_4O_2 + NO_2$
	2.56	$C_3H_6N_6O_6 \rightarrow C_3H_6N_4O_2 + NO_2 + NO_2$
	2.11	$C_3H_6N_6O_5 \rightarrow C_3H_6N_5O_3 + NO_2$
	2.01	$C_2O_3 \rightarrow CO + CO_2$
	1.97	$N_2H + HO \rightarrow H_2O + N_2$
	1.70	$HO + HNO \rightarrow H_2O + NO$
	1.68	$C_3H_6N_4O_2 \rightarrow C_3H_6N_3 + NO_2$
	1.37	$HONO \rightarrow HO + NO$
	1.34	$HO \rightarrow H + O$

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