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

Supplementary information for

High energy barrier hydroxyl radical dissociation mechanism of low shock sensitive dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate (TKX-50) explosive

Tuo Yang, Danyang Liu*, Kun Yang, Jianying Lu, Bin Zhang, Yiwen Xiao, Kaining Zhang, Junying Wu and Lang Chen

State Key Laboratory of Explosion Science and Safety Protection, Beijing Institute of Technology, Beijing 100081, China

*email: liudy@bit.edu.cn

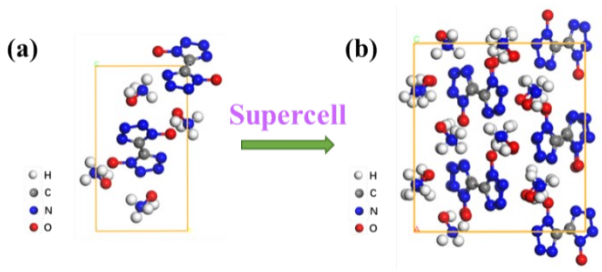


Fig. S1 (a) Unit cell of TKX-50；(b) 2×1×2 supercell of TKX-50.

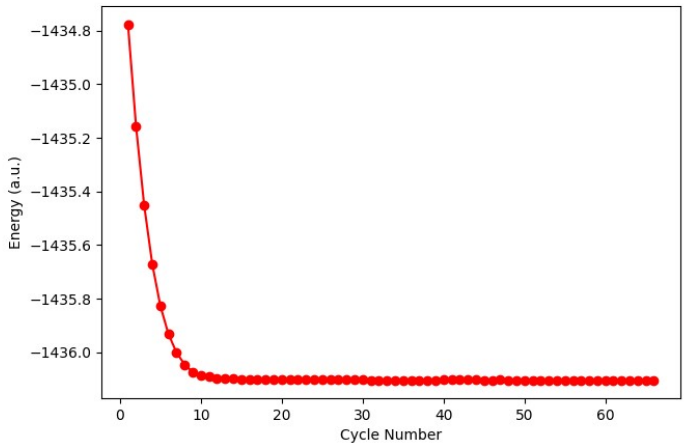


Fig. S2 Total energy vs. calculation cycle number during the optimization of the TKX-50 supercell.

Table S1 Unit cell parameters of TKX-50 before and after optimization.

	parameters	density	a/Å	b/Å	c/Å	α/°	β/°	γ/°
TKX-50	Experiment	1.915	5.426	11.660	6.501	90.000	95.256	90.000
	Calculation	1.857	5.350	11.987	6.615	90.000	95.591	90.000
	Error(%)	0.030	0.014	0.028	0.018	0.000	0.003	0.000

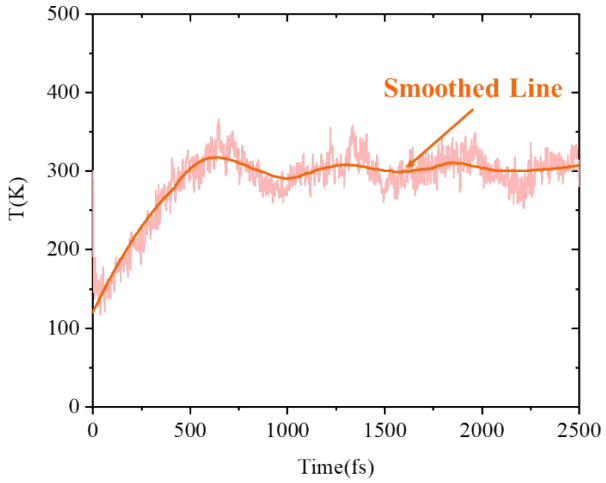


Fig. S3 Temperature vs. time during the relaxation of TKX-50 supercell by using NVT ensemble. After about 500 fs, the temperature reaches stability.

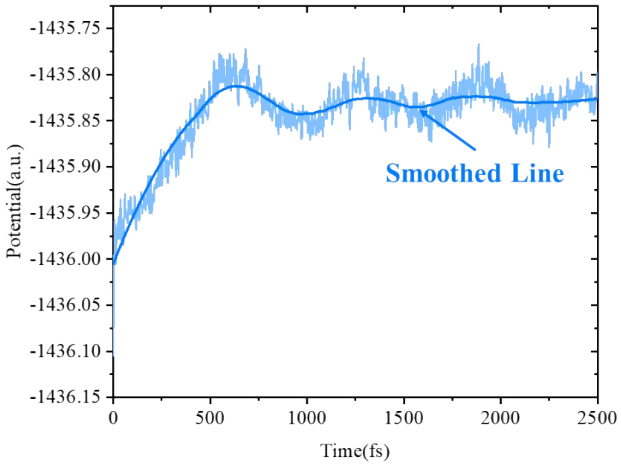


Fig. S4 Potential energy vs. time during the relaxation of TKX-50 supercell by using NVT ensemble. After about 500 fs, the potential reaches stability.

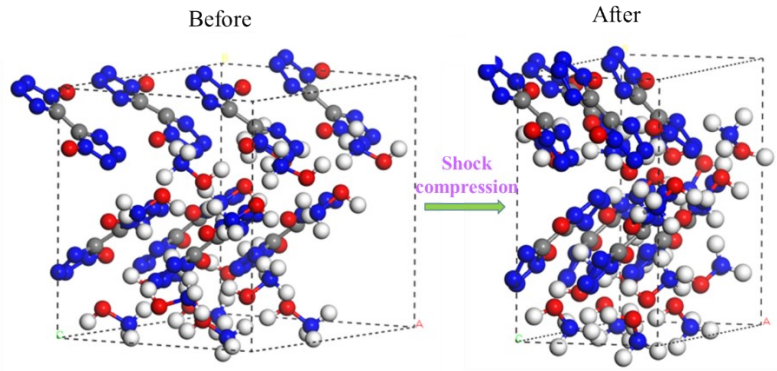


Fig. S5 TKX-50 supercell before and after shock loading at 10km/s shock velocity. The supercell is compressed in the A direction.

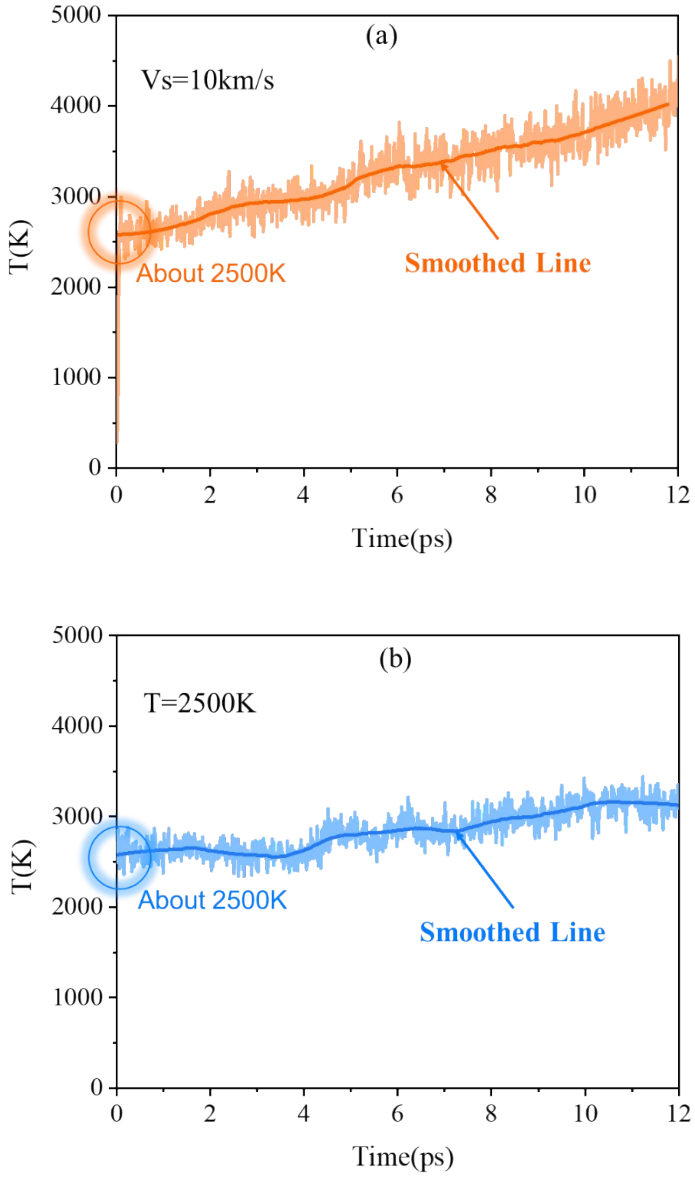


Fig. S6 Time evolution of the temperature of the TKX-50 supercell at 10km/s shock velocity by MSST(a) and 2500K thermal stimuli by NVE ensemble (b). The initial temperatures are both around 2500 K. The subsequent temperature changes are different indicating different reactions under different stimuli.

Table S2 Initial elementary reaction, frequencies, and reaction time of TKX-50 under shock velocity of 10km/s.

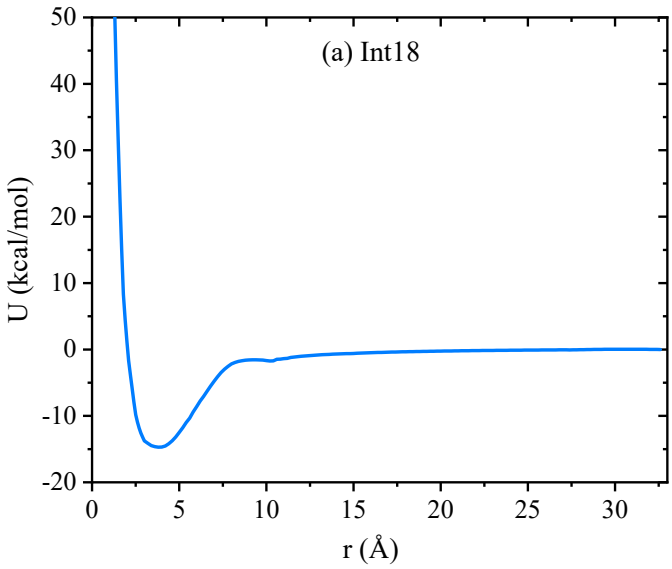
total frequencies	frequencies	time(ps)	elementary reactions	illustration
3	3	0-0.25	$H_4NO + C_2N_8O_2 = C_2H_4N_9O_3$	polymerization
13	13	0.05-3.3	$H_4NO = H + H_3NO$	generate H^+
10	10	0.18-2.55	$H + H_3NO = H_4NO$	H_3NO capture H^+
22	2	0.05-0.05	$H_4NO + C_2N_8O_2 = H_3NO + C_2HN_8O_2$	$C_2N_8O_2$ capture H^+
	1	0.05-0.05	$C_2N_8O_2 + C_2H_4N_9O_3 = H_3NO + C_4HN_{16}O_4$	
	3	0.3-0.8	$C_2H_4N_9O_3 = H_3NO + C_2HN_8O_2$	
	3	0.65-4.35	$C_2N_8O_2 + C_2H_2N_8O_2 = C_2HN_8O_2 + C_2HN_8O_2$	
	2	0.85-4.75	$H + C_2N_8 = C_2HN_8$	
	3	1.9-2.8	$H_3NO + C_2N_8O_2 = H_2NO + C_2HN_8O_2$	
	3	1.95-4.45	$H_3O + C_2N_8O_2 = H_2O + C_2HN_8O_2$	
	3	2.6-7.25	$H+C_2HN_8 = C_2H_2N_8$	
	2	3.15-6	$H + C_2N_8O_2 = C_2HN_8O_2$	
22	5	0.6-2.45	$H_3NO + C_2H_2N_8O_2 = H_4NO + C_2HN_8O_2$	generate H^+
	5	0.65-3.25	$C_2HN_8O_2 = H + C_2N_8O_2$	
	2	1.6-5	$H_2O + C_2H_2N_8O_2 = H_3O + C_2HN_8O_2$	
	3	2.8-6.05	$H_2O+C_2HN_8O_2 = H_3O+C_2N_8O_2$	
	3	3.55-7.2	$C_2H_2N_8 = H+C_2HN_8$	
	2	4-4.35	$H_3N+C_2HN_8O_2 = H_4N+C_2N_8O_2$	
	2	4.15-5.45	$C_2H_2N_8O_2 = H+C_2HN_8O_2$	
84	1	0.35-0.35	$H_4NO+H_4NO= H_2O+ H_3N+ H_3NO$	generate H_2O
	6	0.9-4.95	$H_3O+H_3NO =H_2O+H_4NO$	
	2	1.15-3.2	$HO+C_2H_2N_8O = H_2O+C_2HN_8O$	
	12	2.8-12.05	$H_3O= H+H_2O$	
	14	3.15-12.25	$H_4O_2 = H_2O+H_2O$	
	35	3.45-12.3	$H+HO = H_2O$	
	6	5.7-8	$H_5NO = H_2O+H_3N$	
	6	5.85-10.5	$HO+H_3O =H_2O+ H_2O$	
	2	6.55-12.1	$N_2+H_3O = HN_2+H_2O$	
35	1	0.35-0.35	$H_4NO+H_4NO= H_2O+ H_3N+ H_3NO$	generate NH_3
	7	3.35-11.15	$H_4N = H+H_3N$	
	21	4.55-11.8	$H+H_2N=H_3N$	
	6	5.7-8	$H_5NO = H_2O+H_3N$	
12	2	0.95-2.85	$H_2N_2O_2 = NO+H+HNO$	generate NO
	4	1.75-4.4	$H_2N_2O_2 = NO+H_2NO$	
	4	3.05-10.1	$HNO = NO + H$	
	2	8.85-10.3	$HNO_2 =NO+HO$	
33	1	3.55-3.55	$C_4H_7N_{19}O_4=N_2+H_2N+H_2O+ C_4H_3N_{16}O_3$	generate N_2
	1	4.55-4.55	$C_2HN_8O = N_2+C_2HN_6O$	

total frequencies	frequencies	time(ps)	elementary reactions	illustration
	1	4.6-4.6	$C_2H_3N_7O= N_2+ CHNO+CHN_4O$	
	1	4.8-4.8	$C_2N_7O_2 =N_2+C_2N_5O_2$	
	1	5.4-5.4	$N_3O=NO+N_2$	
	1	6.6-6.6	$HN_2+H_2O = N_2+H_3O$	
	1	7.2-7.2	$C_4H_3N_{12}O_2= N_2+N_2+ C_4H_3N_8O_2$	
	1	7.4-7.4	$C_4H_2N_{10}O_2 = N_2+C_4H_2N_8O_2$	
	2	7.55-8.7	$H_2N_2O = N_2+H_2O$	
	2	7.75-10.3	$HO+HN_2 = N_2+H_2O$	
	1	8.85-8.85	$C_2H_2N_6O =2N_2 + H_2O + C_2N_2$	
	2	8.95-10.05	$HN_2 = N_2+H$	
	1	9.0-9.0	$HN_2+ CHN_2O_2= N_2+ CH_2N_2O2$	
	1	9.4-9.4	$HN_5O = N_2+HN_3O$	
	1	9.5-9.5	$CHN_2O_2 = N_2+CHO_2$	
	2	9.6-9.95	$CHN_4O = N_2+CHN_2O$	
	1	9.7-9.7	$H_2O+CN_4O = N_2+HO+CHN_2O$	
	1	9.9-9.9	$C_2H_2N_7O=N_2+ C_2H_2N_5O$	
	1	9.9-9.9	$CH_4N_4O_2 = N_2+H+H_2O+CHN_2O$	
	1	9.95-9.95	$H_2O+CHN_4O= N_2+HO+CH_2N_2O$	
	2	10.1-10.1	$CH_2N4O = N_2+CH_2N_2O$	
	1	10.25-10.25	$CH_2N_4 = N_2+H+CHN_2$	
	2	11.2-11.9	$HN_2+CHN = N_2+CH_2N$	
	2	11.25-11.75	$CN_2O= N_2+CO$	
	1	12.1-12.1	$CHN_3 = N_2+CHN$	
	1	12.2-12.2	$NO_2+C_2H_4N_5O = N_2+C_2H_4N_4O_3$	
10	10	7.37-12.2	$HN_3 = N_3+H$	generate N_3
9	9	8.3-12.25	$N_3+H= HN_3$	generate HN_3
	1	9.75-9.75	$CH_2O_2 = H_2O+CO$	
	2	10.45-12.2	$C_2HNO= CO+CHN$	
7	2	11.25-11.75	$CN_2O= N_2+CO$	generate CO
	1	11.5-11.5	$CH_4NO= H_4N+CO$	
	1	11.9-11.9	$CN+CH_2O_2 = CO+CH_2NO$	

Table S3 Mulliken fragment charge of the structure before and after H transfer

	Before H transfer		After H transfer	
Structure	NH_3OH	$C_2N_8O_2$	NH_2OH	$C_2N_8O_2H$
Mulliken charge	0.6833	-1.5830	0.0456	-0.7814

First, we extracted the TKX-50 supercell during the AIMD calculation and used Gaussian 16 software to perform single-point calculations to obtain the .fch file. Next, we used Multiwfn software to calculate the Mulliken fragment charge of the structure before and after the H transfer. The calculation results are shown in the table below. It can be seen that after H transfer, the charge of the cation decreases from 0.6833 to 0.0456, and the charge of the anion changes from -1.5830 to -0.7814. This indicates that the H transfer is a proton transfer.



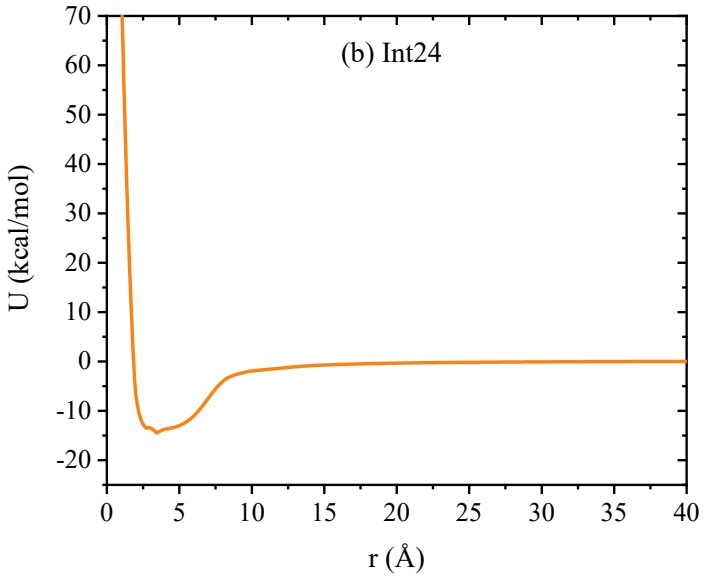


Fig. S7 Distance-potential energy relationship between $(C_2N_8O_2H)^-$ and H_2O by scan calculation through Gaussian16 software at the B3LYP-D3/TZVP level. Then, the Lennard-Jones (L-J) potential is used to simulate the intermolecular interaction between the target species and the bath gas. For Int18 used in this study, the L-J parameters are σ=2.10Å, ε/k_B=1.322×10⁴K. For Int24 the L-J parameters are σ=1.85Å, ε/k_B=1.478×10⁴K. The L-J parameters of H_2O are σ=2.71Å, ε/k_B=506K, from the KiSThelP program.

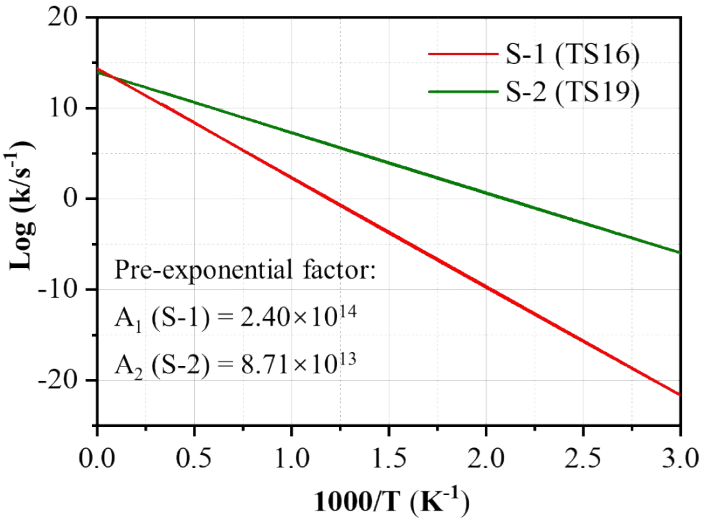


Fig. S8 Reaction rate constants of paths S-1 and S-2 in Arrhenius coordinate as a function of temperature, calculated using transition state theory (TST). The radical reaction path S-1 (A_1=2.40×10¹⁴) has a higher pre-exponential factor than path S-2 (A_2=8.71×10¹³). With increasing temperature, the reaction rate constant differences between the two reactions decrease. High temperature has a stronger promotion of radical reaction which aligns with what we have found in

Fig. 14.

Table S4 Bond cutoffs

Bond type	Cutoff(Å)
C-C	1.7457
C-H	1.2903
C-O	1.70775
C-N	1.7181
H-H	0.8349
H-O	1.25235
H-N	1.2627
O-O	1.6698
O-N	1.68015
N-N	1.6905