Supporting information

Reaction Mechanism from Quantum Molecular Dynamics for the Initial Thermal Decomposition of 2,4,6-triamino-1,3,5-triazine-1,3,5-trioxide (MTO) and 2,4,6-trinitro-1,3,5-triazine-1,3,5-trioxide (MTO3N), Promising Green Energetic Materials

Cai-Chao Ye, [†,‡] Qi An, [†] Tao Cheng, [†] Sergey Zybin, [†] Saber Naserifar, [†] Xue-hai Ju [‡] and William A. Goddard III FRSC [,†]*

[†] Materials and Process Simulation Center, 139-74, California Institute of Technology, Pasadena, California 91125, United States

[‡] Key Laboratory of Soft Chemistry and Functional Materials of MOE, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China

**E-mail: wag@wag.caltech.edu*

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Coordinates for structures of MTO

```
_pd_phase_name                          'MTO'
_cell_length_a                         4.59190
_cell_length_b                         6.97240
_cell_length_c                         10.01390
_cell_angle_alpha                      90
_cell_angle_beta                       103.64060
_cell_angle_gamma                        90
_symmetry_space_group_name_H-M           'P 2(1)'
_symmetry_Int_Tables_number              4

loop_
_symmetry_equiv_pos_as_xyz
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   '-x, y+1/2, -z'

loop_
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   _atom_site_occupancy
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
   _atom_site_U_iso_or_equiv
   _atom_site_type_symbol
   C1      1.0     0.380250     0.998900     0.629760     Uiso    1.000000 C
   C3      1.0     0.079670     0.855790     0.766970     Uiso    1.000000 C
   C5      1.0     0.323140     0.151670     0.835280     Uiso    1.000000 C
   N7      1.0     0.500810     0.991020     0.523790     Uiso    1.000000 N
   N9      1.0     0.908970     0.708770     0.786500     Uiso    1.000000 N
   N11     1.0     0.389130     0.297120     0.922530     Uiso    1.000000 N
   N13     1.0     0.144230     0.004330     0.857330     Uiso    1.000000 N
   N15     1.0     0.451570     0.142250     0.725750     Uiso    1.000000 N
   N17     1.0     0.183100     0.860600     0.650180     Uiso    1.000000 N
   H19     1.0     0.645260     0.097780     0.504660     Uiso    1.000000 H
   H21     1.0     0.431900     0.888660     0.446790     Uiso    1.000000 H
   H23     1.0     0.893810     0.604650     0.713430     Uiso    1.000000 H
   H25     1.0     0.908430     0.665760     0.885290     Uiso    1.000000 H
   H27     1.0     0.552040     0.387510     0.905030     Uiso    1.000000 H
   H29     1.0     0.236680     0.344610     0.976150     Uiso    1.000000 H
   O31     1.0     0.647020     0.277330     0.711200     Uiso    1.000000 O
   O33     1.0     0.102670     0.720330     0.559400     Uiso    1.000000 O
   O35     1.0     0.038090     0.002930     0.971460     Uiso    1.000000 O
```

Coordinates for structures of MTO3N

```
_pd_phase_name                          'MTO3N'
_cell_length_a                         11.45190
_cell_length_b                         9.01690
_cell_length_c                         8.47580
_cell_angle_alpha                      90
_cell_angle_beta                       83.87740
_cell_angle_gamma                        90
_symmetry_space_group_name_H-M           'P 2(1)/c'
_symmetry_Int_Tables_number            14

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_symmetry_equiv_pos_as_xyz
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   '-x, y+1/2, -z+1/2'
   'x, -y+1/2, z+1/2'

loop_
   _atom_site_label
   _atom_site_occupancy
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
   _atom_site_U_iso_or_equiv
   _atom_site_type_symbol
   C1      1.0   0.348460   0.926770   0.342630   Uiso   1.000000 C
   C5      1.0   0.242360   0.067010   0.547910   Uiso   1.000000 C
   C9      1.0   0.174520   0.832990   0.474100   Uiso   1.000000 C
   N13     1.0   0.442150   0.915820   0.212110   Uiso   1.000000 N
   N17     1.0   0.234090   0.191210   0.658840   Uiso   1.000000 N
   N21     1.0   0.089950   0.710200   0.503770   Uiso   1.000000 N
   N25     1.0   0.155610   0.959340   0.561430   Uiso   1.000000 N
   N29     1.0   0.268440   0.813290   0.364070   Uiso   1.000000 N
   N33     1.0   0.340380   0.051410   0.437730   Uiso   1.000000 N
   O37     1.0   0.543110   0.936870   0.243960   Uiso   1.000000 O
   O41     1.0   0.409850   0.887550   0.081300   Uiso   1.000000 O
   O45     1.0   0.192520   0.162280   0.795740   Uiso   1.000000 O
   O49     1.0   0.270240   0.312820   0.607960   Uiso   1.000000 O
   O53     1.0   0.115030   0.617450   0.600770   Uiso   1.000000 O
   O57     1.0   0.004230   0.713380   1.428690   Uiso   1.000000 O
   O61     1.0   0.280170   0.693520   0.285960   Uiso   1.000000 O
   O65     1.0   0.419800   0.148060   0.422110   Uiso   1.000000 O
   O69     1.0   0.061500   0.971730   0.652560   Uiso   1.000000 O
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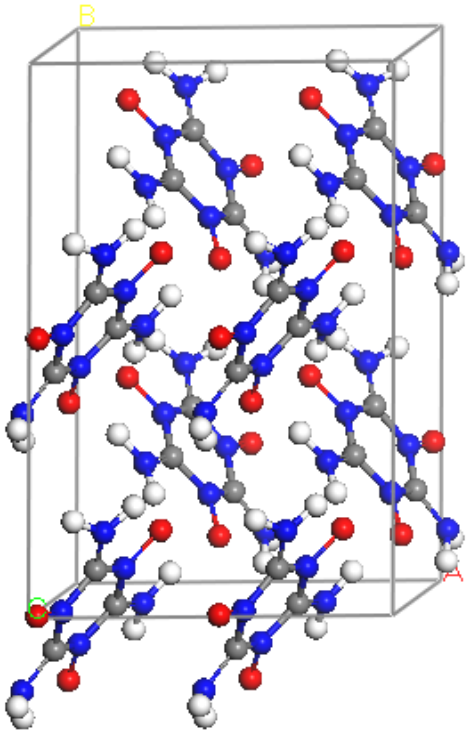
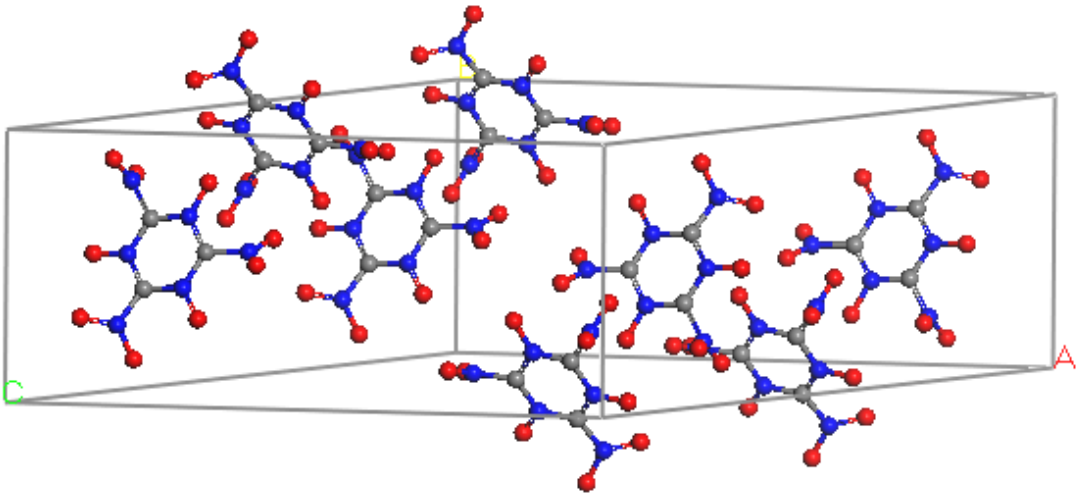


(a) P2(1)-MTO supercell



(b) P2(1)/c-MTO3N supercell

Figure S1. Structure of (a) P21-MTO supercell; (b) P21/c-MTO3N supercell.

Table S1. The bond type and bond cut-off table in the fragment analysis.

Bond type	$\mathbf{r_{cut\text{-}off}}$ **(Å)**
C-C	2.31
C-H	1.63
C-O	2.15
C-N	2.20
H-H	1.11
H-O	1.50
H-N	1.61
O-O	2.22
O-N	2.10
N-N	2.17

Atomic coordinates of all TS shown in this study

TS1

&zmat

C12	1.9262279030	7.5567911070	5.1737244419
C13	0.3508144119	6.5630992194	6.6385779905
C14	1.7788289158	8.2136046787	7.4570521942
C15	2.5268735475	11.0963132029	3.3615584810
C16	3.2568216362	10.4060532633	1.2035082774
C17	1.8171635519	12.2278064821	1.4039494161
N24	2.4475218087	7.6284547917	3.9925049385
N25	-0.6225102174	5.7011120906	6.8482491574
N26	2.2011293798	8.9491542644	8.4688140290
N27	0.7849146272	7.3325078696	7.6708892508
N28	2.3269431107	8.3334747906	6.2279282127
N29	0.9029775658	6.6683456499	5.4170014028
N30	2.5051528228	10.9939968140	4.6504025775
N31	3.9668875750	9.5988889723	0.4362661163
N32	1.1211765806	13.1898941883	0.8342848943
N33	2.5480249312	11.3906519656	0.6225635891
N34	1.8011832063	12.0885067392	2.7410404925
N35	3.2353113426	10.2548354333	2.5457497606
H24	3.2603581001	8.4259196555	3.5933279884
H25	1.9872298614	6.9529998867	3.3805220689
H26	-0.9199776921	5.1456928797	6.0560376010
H27	-1.0063998893	5.6594818395	7.7837645090
H28	3.0043964484	9.5440149402	8.3278873896
H29	1.7595336263	8.7623449142	9.3621307234
H30	1.9132183936	11.7321683513	5.0346178344
H31	2.9887645903	10.1154931963	5.3323898697
H32	4.5862846089	8.9382619163	0.8824801261
H33	3.9703862425	9.8261175693	-0.5519383873
H34	1.1646077840	13.2529760697	-0.1749912857
H35	0.5897016977	13.7946302245	1.4475807612
O12	3.3636701459	9.1746442567	6.0950253434
O13	0.4667251354	5.9120223441	4.4447671030
O14	0.2480033918	7.2096993950	8.8597667516
O15	1.0917226022	12.9120207628	3.4665348806
O16	4.0231512984	9.3048673074	3.0711927664

O17	2.5663114707	11.5464212133	-0.6783236365

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TS2

&zmat

C12	1.7838465935	7.6782716337	5.1490258457
C13	0.3643887203	6.4643475926	6.6858228943
C14	1.6175748648	8.3966372158	7.3072123119
N24	2.1808718458	7.7411287992	3.8967095472
N25	-0.4493517993	5.4706935643	6.9532894350
N26	2.0970120432	9.0600868800	8.3035421082
N27	0.6257593589	7.4138066893	7.6146105768
N28	2.0205122976	8.5746311292	6.0543639624
N29	0.9884749431	6.5363719085	5.4621155918
H24	2.7672756948	8.5098570503	3.6024463416
H25	1.9019144888	7.0190713058	3.2421326089
H26	-0.6481788606	4.7826559107	6.2367629263
H27	-0.8494286659	5.4063354616	7.8827084224
H28	2.9887011415	9.5617341444	8.0477313115
H29	1.7422322213	8.8807732534	9.2401438313
H31	4.5738958618	10.0350064839	6.3381605023
O12	4.1039862034	9.3516600923	6.8371470758
O13	0.6697051636	5.7216552306	4.5707690183
O14	0.1947480653	7.2809408241	8.7906157289

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TS3

&zmat

C12	2.2586555015	7.1966422416	5.0260278616
C13	0.7716021269	7.2714357808	6.9069772243
C14	2.3267902526	7.9658137272	7.1283380013
N24	2.5692054682	6.9238593076	3.8373551582
N25	-0.3734766292	7.7566711419	7.4841512588
N26	2.5469108557	8.7022250728	8.1257063380
N27	1.2306142560	5.8122046270	7.4965769385
N28	3.0264644618	7.5394724695	6.0954845627
N29	0.8207051611	7.2104683390	5.5109655247

H25	1.7470497272	6.6983715465	3.2794130409
H26	-1.1174553914	7.9915668008	6.8376119691
H27	-0.6985807523	7.2255728453	8.2857153643
H29	1.8233008772	8.6968438121	8.8394664192
O13	-0.1662925756	7.1840846208	4.7694534157
O14	0.5999937585	5.5000101632	8.4338465867

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INT4

&zmat

C12	1.9761449035	7.5856877224	5.2038265716
C13	0.4378161488	6.5707231648	6.6646910064
C14	1.8261078688	8.2774944323	7.4955333033
N24	2.5155056586	7.6392025398	4.0057789237
N25	-0.4881953289	5.6806881929	6.8728305975
N26	2.2203831841	9.0013333592	8.5200129477
N27	0.8539084873	7.3665706055	7.6941175387
N28	2.3028526012	8.4360454731	6.2237018879
N29	1.0030486170	6.6810422533	5.4258979312
H24	3.3607933326	8.1577666419	3.8165224024
H25	2.1603110688	6.9351144894	3.3576090206
H26	-0.7611262020	5.0887039722	6.0930236935
H27	-0.8737498627	5.6076257343	7.8104202378
H28	3.0532617974	9.5711984858	8.4907458156
H29	1.7643215967	8.7601114839	9.4008575491
H31	2.9928914522	10.1339303996	5.7555508183
O12	3.3613369568	9.2787221179	6.0382553979
O13	0.6298489589	5.8917462850	4.4751698410
O14	0.3412881473	7.2193596140	8.8695514292

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TS4

&zmat

C12	1.7838465935	7.6782716337	5.1490258457
C13	0.3643887203	6.4643475926	6.6858228943
C14	1.6175748648	8.3966372158	7.3072123119
N24	2.1808718458	7.7411287992	3.8967095472

N25	-0.4493517993	5.4706935643	6.9532894350
N26	2.0970120432	9.0600868800	8.3035421082
N27	0.6257593589	7.4138066893	7.6146105768
N28	2.0205122976	8.5746311292	6.0543639624
N29	0.9884749431	6.5363719085	5.4621155918
H24	2.7672756948	8.5098570503	3.6024463416
H25	1.9019144888	7.0190713058	3.2421326089
H26	-0.6481788606	4.7826559107	6.2367629263
H27	-0.8494286659	5.4063354616	7.8827084224
H28	2.9887011415	9.5617341444	8.0477313115
H29	1.7422322213	8.8807732534	9.2401438313
H31	4.5738958618	10.0350064839	6.3381605023
O12	4.1039862034	9.3516600923	6.8371470758
O13	0.6697051636	5.7216552306	4.5707690183
O14	0.1947480653	7.2809408241	8.7906157289

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TS5

&zmat

C12	2.1891476098	7.2359392813	5.1412400535
C13	0.6242754348	7.2811774990	6.8680405986
C14	2.4763772891	8.0187514035	7.1866246210
N24	2.4743579232	6.9331370847	3.8967639409
N25	-0.5738104405	7.6151298085	7.3253431984
N26	2.7162763806	8.7257341311	8.1448826102
N27	1.2785005725	5.7346663549	7.5465248193
N28	3.0364018631	7.5294940401	6.0961878206
N29	0.8051194900	7.2555405666	5.5069090159
H24	3.4310211648	6.9697637735	3.5709944915
H25	1.7231131450	6.7259138545	3.2488691076
H26	-1.3280236488	7.8298313962	6.6784012278
H27	-0.8160210547	7.4706014431	8.2963853945
H29	2.1278195073	8.8783194644	8.9532990021
O13	-0.1189155793	7.2804797261	4.6443268944
O14	0.6846608449	5.3915275970	8.4594308594

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TS6

&zmat

C9	6.9001942148	3.4406328533	1.7857359644
C10	8.0716581204	2.5669645705	-0.0467723783
C11	7.5178465944	4.8601076182	-0.0544010413
N18	6.2805768337	3.5491044246	2.9163849258
N20	7.5520379619	6.0391005546	-0.6669600025
N21	8.0936896891	3.7885225679	-0.6570380952
N22	6.9422430056	4.6643357244	1.1343233400
N23	7.4832976397	2.3793893823	1.1666402693
H18	6.0563876802	4.8300620789	2.7457942251
H19	6.1801030727	2.7254273675	3.4926364234
H20	8.6026241201	0.6475313518	-0.1682838950
H21	9.0685096682	1.7006805424	-1.5509143772
H22	7.1307984568	6.8454918231	-0.2363676877
H23	8.0177301648	6.0541927302	-1.5659677934
O9	6.3248048436	5.6413365720	1.8556786599
O10	7.4841807989	1.1809530924	1.7210414421
N19	8.6377058688	1.5350567539	-0.6520688326
O11	8.6783849047	3.9323147949	-1.8422322341

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TS7

&zmat

C22	8.3475814188	0.8370040831	0.6021780725
N34	7.9485799128	2.1703582317	0.1058000514
N38	9.6177580644	0.4511814429	0.4466069130
N42	7.3963790506	0.0514374108	1.1750972968
O54	8.0329218326	3.0729424037	0.9091448849
O58	7.5864871667	2.2095925029	-1.0499155031
O62	6.1961382190	0.4489467923	1.3113561966
O70	10.5104690660	1.1807499404	-0.0988096060
C14	7.7889295235	-1.1844029144	1.6022651132
C18	10.0665652338	-0.7884424753	0.9847140565
N26	6.7663155836	-2.0676187211	2.1999253737
N30	10.8097066193	-1.5592195914	-0.2051486215
N46	9.0376079030	-1.6466865016	1.4844659741
O38	6.6595360569	-1.9978020831	3.4051286674

O42	6.1539432737	-2.7635352642	1.4203594556
O50	10.0394933112	-2.0166914271	-1.0077348968
O66	9.3946000991	-2.8028862877	1.8542705682
O46	12.0128326285	-1.5569771217	-0.2184411993
O17	10.9686324123	-0.4647806115	2.1480506339
N9	12.3429700585	-0.7562788683	2.1872194546
N17	14.4077156192	-0.1559141791	1.1206355821
O21	12.7094076004	-1.8436750524	2.5677985133
O25	14.7418002617	-1.3521449131	0.9934737857
C1	15.2390646521	0.8231691565	0.6908721975
C5	13.7167112445	2.4836233387	1.2585786881
C9	13.1704021992	0.2186984928	1.6703689874
N1	16.5221880337	0.4289612559	0.0750512095
N5	13.3842386926	3.9175870948	1.3847910619
N13	12.8581973120	1.5777614538	1.7872846206
N21	14.9161301624	2.1472835566	0.7148807760
O1	16.5000480834	0.2727987022	-1.1257989672
O5	17.4525922217	0.3089373436	0.8423431512
O9	13.7344885291	4.4397341357	2.4216571202
O13	12.8078739821	4.4084814835	0.4408956634
O29	15.7048580516	3.0197183581	0.2719089043
O33	11.8159180694	1.9774288904	2.3497242037

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