

## Supporting information for

# A Reaction of Formaldehyde with Acetonitrile: Understanding the Preparation of RDX (I)

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## Computational Details

The geometries of reactants, intermediates, products, and transition states were optimized by using the recently-developed M06-2X functional<sup>1</sup> with the 6-311+G\*\* basis set<sup>2</sup> in an excellent solvent CCl<sub>4</sub> used in experiments, where the SMD solvation model<sup>3</sup> was selected. For Mannich reactions, M06-2X functionals predict energies with mean errors of ~ 2 kcal/mol.<sup>4</sup> All stationary points were located without imposing any symmetry constraints. Harmonic frequencies were performed with analytical force constants at all the optimized geometries for the zero-point energy corrections and thermal corrections at 298.15 K and 1 atm. In all cases, transition states were further identified to connect a specific pair of stationary points (reactants, products or minima associated to intermediate species) by performing the necessary intrinsic reaction coordinates (IRC) calculations. The Gibbs free energies in the CCl<sub>4</sub> solvent are used in the discussion, unless otherwise specified, while enthalpies in the CCl<sub>4</sub> solvent are only used as the reference. All calculations were carried out by using Gaussian 09<sup>5</sup> suit of package

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**Below are the XYZ coordinates of all stationary points calculated at the M06-2X (SMD, CCl<sub>4</sub>)/6-311+G\*\* level.**

```
# CH3CN
C 1.17593400 0.00002100 0.00000100
H 1.54246900 -0.61316300 -0.82328200
H 1.54460600 -0.40675500 0.94170100
H 1.54349500 1.01914500 -0.11947700
C -0.28067600 0.00026000 0.00018000
N -1.42887400 -0.00013000 -0.00000400
# H2SO4
S -0.00001357 0.00014938 -0.16023910
O 0.56999300 -1.1227785 -0.83610843
O -0.57006537 1.12430436 -0.83402589
O 1.07919246 0.60933999 0.84547652
H 1.65230558 -0.08803382 1.20255186
O -1.07910600 -0.61088812 0.84445895
H -1.65220110 0.08581671 1.20286443
# HCHO
C 0.00000000 0.00000000 -0.52701900
O 0.00000000 0.00000000 0.67216700
H 0.00000000 0.93944400 -1.10760900
H 0.00000000 -0.93944400 -1.10760900
# IM1
C 3.24707500 -0.83722400 -0.01659300
H 2.56527500 -1.66115600 -0.23348100
H 4.00195600 -0.76898100 -0.80008100
H 3.73004200 -1.00283000 0.94638400
C 2.47202100 0.38885600 0.02651600
N 1.83074400 1.34051900 0.05177800
S -1.18463600 -0.17068300 -0.11489600
O -2.55619500 -0.36169700 -0.47870500
O -0.13884500 -1.02676900 -0.59601500
O -1.05335200 -0.23061000 1.48160700
H -1.81231100 0.20412000 1.90155700
O -0.84860100 1.33709600 -0.42286400
H 0.11537400 1.52218200 -0.27020800
# IM2
C 2.71367900 -0.84801700 0.08184600
H 2.49180500 -1.49758200 0.93078100
H 2.80030700 -1.47669800 -0.80674500
H 3.64301800 -0.30931800 0.24982300
C 1.60780800 0.12860600 -0.10634200
N 1.70257700 1.37243700 -0.04317200
O -1.05565500 -0.06942900 -0.09938900
O -1.92648600 -1.14014300 -0.43939500
O 0.42168600 -0.61253100 -0.39347700
O -1.03897300 0.03526600 1.49186900
H -0.79355900 0.92683100 1.78753300
O -1.19923200 1.25455300 -0.64149800
H 0.84599300 1.87987200 -0.26198000
# IM3
C 0.72046600 1.39863800 0.29337700
N 1.32361900 1.07956600 1.34309100
S -1.30300000 -0.24679100 0.05295700 2
O -0.68459700 1.24363000 -0.14185000
O -2.70106700 -0.06058200 -0.14234000
H 0.68781500 0.69974600 2.04647900
O 1.79095100 -1.47234600 -0.78937700
C 2.23814700 -1.63490300 0.32419800
H 1.57960600 -1.72354500 1.19858300
H 3.32333100 -1.70645300 0.47933800
C 1.32891100 1.99060900 -0.92648900
H 2.39792200 2.12393800 -0.77676400
H 1.14413700 1.33923300 -1.78491200
H 0.85685600 2.95242800 -1.13881200
O -0.77832700 -1.01295600 1.15756600
O -0.67473400 -0.78296500 -1.28024100
H 0.25003900 -1.14383500 -1.11904000
```

# IM4  
C 1.70329700 1.92593800 0.02492700  
H 2.63823900 1.68737200 -0.48096600  
H 1.21550300 2.77255900 -0.45186600  
H 1.91616900 2.18486600 1.06657400  
C 0.76911500 0.76249300 0.00641900  
N 1.20702600 -0.45401500 0.26490100  
S -1.84950700 -0.22941100 -0.01089200  
O -2.85947300 0.46343900 -0.75451800  
O -0.45278600 1.01462000 -0.24774400  
O -1.24253700 -1.40207800 -0.62159800  
O -1.90934400 -0.22495000 1.42966600  
H 0.54324200 -1.22061900 0.15768800  
C 2.60783000 -0.77417900 0.53501200  
H 3.00887700 -0.05759400 1.24921900  
O 3.40492800 -0.70074100 -0.60738300  
H 3.20064700 -1.43843400 -1.19257500  
H 2.61249700 -1.76729300 0.98640600  
# IM5  
C -0.98680400 1.37456800 0.14827900  
H -1.92891400 1.77672600 -0.21676500  
H -0.86546700 1.64873400 1.19930000  
H -0.15773700 1.80090800 -0.41947400  
C -1.02528500 -0.12731800 -0.00232900  
O -2.01924700 -0.72512300 -0.36159900  
C 1.40010500 -0.20294900 0.53317400  
N 0.12393500 -0.80678000 0.32290000  
H 0.10510100 -1.79023200 0.08559400  
H 2.04187000 -0.93509300 1.02973000  
H 1.29087000 0.66742600 1.18582500  
O 1.95509400 0.18294900 -0.71763700  
H 2.83186300 0.55058200 -0.56536800  
# IM6  
C -2.73853700 0.57317900 -1.05592800  
H -1.89061900 0.86831900 -1.67755300  
H -3.46909500 -0.04381300 -1.66252800  
H -3.20083700 1.47510100 -0.64653400  
C -2.29411400 -0.34470000 0.05428800  
N -1.31011900 0.14174100 0.90067300  
S 1.74529200 -0.34951100 -0.09607200  
O 1.03128900 -1.30701300 -0.88485100  
O -2.76036600 -1.44420700 0.23670100  
O 2.83836700 0.37649100 -0.67957600  
O 1.64807600 -0.42037200 1.33845800  
H -0.95076600 -0.52623300 1.57202800  
C -0.61807800 1.35579200 0.74478400  
H -1.27331100 2.16977400 0.43563900  
O 0.38722300 1.22125600 -0.32071600  
H 0.87901300 2.04939800 -0.43751400  
H -0.10056900 1.60495500 1.66991400  
# IM7  
C 2.69263200 -1.66483100 -0.23083800  
H 2.29271800 -1.80461100 -1.23851000  
H 3.67512000 -2.12188700 -0.14144800  
H 1.99241100 -2.14101000 0.46166600  
C 2.77058400 -0.20682000 0.08267800  
N 1.49009600 0.46662800 -0.08894100  
S -1.92395500 -0.03967300 -0.09699000  
O -0.64496400 -0.91533100 -0.09542300  
O 3.73906800 0.38602300 0.45908900  
O -2.99449100 -0.78078200 -0.70338400  
O -1.59498700 1.29447000 -0.53113400  
H 0.24968700 -0.31947700 -0.07820700  
C 1.51004200 1.72016300 -0.29284900  
H 2.45294200 2.26635100 -0.34326400  
O -2.25783800 0.12033600 1.46842000  
H -2.68907900 -0.68171900 1.79984800  
H 0.56497000 2.24193200 -0.42014100  
# IM8  
C -1.56329700 -0.74374900 0.15148000  
H -2.43149800 -0.18459300 0.49369700  
H -1.79354000 -1.25764400 -0.78491600  
H -1.28680300 -1.50932900 0.87986000  
C -0.40806000 0.18570800 -0.08049400  
O -0.47648200 1.38796500 -0.05024100  
C 1.83355100 -0.20209300 0.22704800  
H 1.83286300 0.50936900 1.05856900  
H 2.77636100 -0.67595300 -0.04008800  
N 0.79161600 -0.48925200 -0.42762800  
# SO3  
O -1.42983900 -0.00480500 0.00001100  
S 0.00006600 0.00000000 -0.00001700  
O 0.71901500 -1.23583000 0.00001100  
O 0.71069300 1.24063500 0.00001100  
# TS1  
C 2.82947800 -0.91776500 0.00034100  
H 2.69240100 -1.46149400 -0.93381000  
H 3.85835500 -0.56672800 0.09580200  
H 2.56139100 -1.56236900 0.83673100  
C 1.96354000 0.24755300 0.00078700  
N 1.74245500 1.40139700 0.05932100  
S -1.02493200 -0.06564400 -0.12841400  
O -2.09054300 -0.59475100 -0.93810600  
O 0.27965900 -0.78178300 -0.26034600  
O -1.38121700 -0.37363700 1.42027800  
H -2.28183000 -0.07265300 1.61115100  
O -0.82487900 1.39433700 -0.21700900  
H 0.74913300 1.77171600 -0.01580200  
# TS2  
C 1.57234200 2.22918800 -0.45670800  
H 1.18213800 3.21521600 -0.19351800  
H 2.63970400 2.19056700 -0.25021200  
H 1.37211100 2.07802300 -1.52104800  
C 0.85199600 1.19443200 0.33119500  
N 1.44532500 0.30421300 1.02325100  
S -1.37613800 -0.14557000 -0.00824800  
O -2.62456400 0.32150800 -0.52165500  
O -0.49569000 1.28578100 0.17286800  
O -0.54572500 -0.86105300 -1.05572300  
H 0.41928300 -1.54350600 -0.70982900  
O -1.31064300 -0.81138200 1.27258600  
H 0.79744100 -0.29391400 1.54207600  
H 3.19257200 -1.44091500 0.40030800  
C 2.33836400 -1.22469200 -0.23992200  
O 1.38502700 -2.02552600 -0.25338100  
H 2.45422400 -0.47402500 -1.02352500  
# TS3  
C -2.54112300 -0.20358500 -1.28725400  
H -1.66178200 0.00457300 -1.89846400  
H -3.02344800 -1.11837500 -1.62377400  
H -3.25402600 0.62155500 -1.36830000  
C -2.12800200 -0.39486900 0.13091500  
N -1.26376400 0.67557900 0.69596900  
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H -0.55877800 0.33980800 1.39127100  
C -1.18090500 1.87325700 0.28602100  
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O 1.46330000 1.24089100 -0.69793600  
H 2.32307000 1.66369600 -0.56779000  
H -0.47210600 2.54143800 0.76226500  
# TS4  
C 0.35364400 -1.50967000 1.66284600  
N -1.88350700 -0.25996600 0.99356200  
C -1.79130600 0.91518700 1.46729600  
N 0.84294900 1.65703700 0.93130500  
C 1.77583300 0.80132200 1.31164200  
N 1.21351500 -0.98882600 0.89026400  
O -2.26857200 0.55902100 -1.14414000  
O 1.43238500 1.21777800 -1.24583000  
O 0.49893100 -2.14181200 -0.96544600  
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H -2.10034300 1.80160400 0.90846300  
H 1.85046300 0.59657700 2.37779300  
H 2.70980400 0.72417300 0.75173800  
C 0.84128100 1.91302000 -0.42553400  
C -0.00173100 3.08238600 -0.86340200  
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H -2.10488300 -2.40863700 -0.71258100  
H -3.42785700 -1.67297800 -1.65421700  
C 2.82752900 -1.54921500 -0.89434700  
H 3.52550100 -1.78739000 -0.08907500  
H 3.01032300 -0.52402300 -1.22643600  
H 2.95611500 -2.23407200 -1.72981900  
C 1.41997800 -1.62030100 -0.40161100  
C -2.36342100 -0.34907800 -0.35948200  
# TRAT  
C 2.16125400 -2.13061300 -0.82507000  
H 2.20411200 -2.87565600 -1.61586600  
H 2.46431400 -1.15780100 -1.21933600  
H 2.85635700 -2.40656100 -0.02908700  
C 0.74313200 -2.08310100 -0.31297700  
O -0.14658200 -2.74511500 -0.81590000  
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C -2.18755100 0.39731700 -0.30591200