Calculations on the unimolecular decomposition of the nerve agent VX

Supporting Information

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S1 Optimized geometries for all conformers reported in the paper.

The values in this section were calculated using M06-2X/aug-cc-pVTZ method with "tight" optimization condition. All values are in Å.

S-side TS 1			
C	-5.09551	0.18747	-0.33827
C	-3.60079	0.34830	-0.20441
O	-3.21290	-0.15982	1.08089
P	-1.66711	-0.16862	1.49252
C	-1.78066	-0.89396	3.12887
O	-0.90284	-1.09366	0.53548
S	-0.88679	1.66877	1.52141
C	0.92181	1.35148	-0.04789
C	1.32170	0.02814	-0.25998
N	2.48442	-0.42833	0.44006
C	2.54362	-1.86820	0.73727
C	1.90376	-2.15837	2.09077
C	1.94356	-2.76742	-0.34612
C	3.74315	0.16045	-0.04725
C	4.80525	0.18422	1.04564

C	4.27944	-0.48423	-1.32714
H	-5.60859	0.74050	0.44668
H	-5.42399	0.56864	-1.30458
H	-5.37491	-0.86217	-0.26465
H	-3.06964	-0.21209	-0.97589
H	-3.30441	1.39698	-0.26578
H	-2.21441	-1.88915	3.04292
H	-0.78153	-0.95371	3.55422
H	-2.40834	-0.26342	3.75471
H	0.33339	1.85570	-0.79962
H	1.49039	1.98504	0.61856
H	0.20404	-0.57831	0.17108
H	1.17619	-0.31730	-1.29272
H	3.60128	-2.12069	0.81759
H	0.83836	-1.93346	2.05348
H	2.01638	-3.21149	2.35432
H	2.36574	-1.54678	2.86495
H	2.16347	-3.81090	-0.11864
H	0.85924	-2.66091	-0.38987
H	2.35583	-2.54189	-1.32997
H	3.50117	1.19960	-0.27904
H	5.14893	-0.81891	1.30070
H	5.67530	0.74985	0.71058
H	4.40816	0.64917	1.94705
H	3.52528	-0.48023	-2.11529
H	5.15151	0.06028	-1.69081
H	4.58354	-1.51704	-1.14839

S-side TS 2 (less stable enontiomer)			
P	-1.711168	-0.087929	-1.460055
O	-0.935830	-1.080177	-0.597157
S	-0.780891	1.666312	-1.681522
C	0.867111	1.340534	0.075404
C	1.290877	0.017054	0.227969
N	2.485839	-0.370888	-0.453548
C	2.542401	-1.761457	-0.929342
C	1.924305	-1.864849	-2.319805
C	1.916170	-2.784644	0.021859
C	3.719248	0.146154	0.158188
C	4.829571	0.299450	-0.874874
C	4.200256	-0.655036	1.369914

H	0.199526	1.776238	0.804662
H	1.457560	2.033388	-0.507611
H	0.197736	-0.582642	-0.239699
H	1.111169	-0.391924	1.232978
H	3.600562	-2.008943	-1.021523
H	0.867689	-1.598056	-2.289012
H	2.002671	-2.884062	-2.702244
H	2.430806	-1.187668	-3.006524
H	2.140300	-3.793199	-0.326912
H	0.831279	-2.681885	0.053071
H	2.305690	-2.683234	1.035159
H	3.465119	1.150083	0.506009
H	5.183126	-0.666954	-1.235964
H	5.684104	0.814108	-0.434163
H	4.473216	0.873800	-1.728950
H	3.413316	-0.746667	2.119767
H	5.056089	-0.164947	1.835460
H	4.511386	-1.658781	1.075202
O	-1.943696	-0.807082	-2.873265
C	-2.374677	-0.085507	-4.033086
H	-3.338872	0.388357	-3.828923
H	-1.648143	0.697930	-4.250110
C	-2.486472	-1.068329	-5.173757
H	-3.211562	-1.846289	-4.940925
H	-2.804875	-0.551752	-6.078550
H	-1.521920	-1.537455	-5.359779
C	-3.366582	0.106003	-0.779442
H	-3.830590	-0.876168	-0.700871
H	-3.292143	0.564304	0.203990
H	-3.956931	0.750782	-1.428893

Table S1: Atomic coordinates of the S-side TSs.

O-side TS			
C	-3.73999	-2.54719	-0.26313
C	-3.42868	-1.26330	-0.71859
O	-4.59906	0.13647	0.03282
P	-5.23214	-0.25425	1.35909
C	-6.72313	0.69598	1.67336
O	-5.55725	-1.75460	1.45014

S	-3.85025	0.24952	2.85936
C	-4.45884	-0.83611	4.20300
C	-3.82401	-2.22242	4.15441
N	-4.30729	-3.04092	5.24664
C	-4.78542	-4.37656	4.88336
C	-6.17105	-4.26902	4.25314
C	-3.85297	-5.18088	3.96818
C	-3.54399	-2.90690	6.48585
C	-4.43606	-3.09431	7.70864
C	-2.30532	-3.80260	6.57586
H	-4.71303	-2.25171	0.62807
H	-4.25503	-3.20580	-0.95185
H	-3.02005	-3.01714	0.39781
H	-2.57440	-0.73533	-0.32041
H	-3.76641	-0.92258	-1.68521
H	-7.46366	0.42693	0.92181
H	-7.10394	0.45983	2.66572
H	-6.48787	1.75610	1.60991
H	-4.22265	-0.32073	5.13274
H	-5.54189	-0.93262	4.13970
H	-4.09899	-2.66923	3.20169
H	-2.72987	-2.12247	4.15599
H	-4.88340	-4.92839	5.81977
H	-6.13159	-3.65621	3.34936
H	-6.55154	-5.25311	3.97583
H	-6.86706	-3.80393	4.95024
H	-4.20765	-6.20946	3.89287
H	-3.84255	-4.76942	2.95773
H	-2.83041	-5.20013	4.34034
H	-3.19767	-1.86982	6.49968
H	-4.79732	-4.12071	7.78529
H	-3.88108	-2.87535	8.62139
H	-5.29891	-2.43221	7.65177
H	-1.65519	-3.67060	5.71026
H	-1.72985	-3.56396	7.47084
H	-2.59116	-4.85428	6.63505

Table S2: Atomic coordinates of the O-side TS.

conf1

C	-4.096411	-1.978798	0.070074
C	-2.708086	-1.424862	0.275637
O	-2.832135	-0.144418	0.920612
P	-1.502897	0.650381	1.322593
C	-2.214396	2.022831	2.235347
O	-0.471881	-0.135732	2.038306
S	-0.784306	1.401301	-0.509639
C	0.997694	1.094901	-0.234219
C	1.630695	2.090833	0.731254
N	2.982400	1.683050	1.050197
C	3.975736	2.756837	1.120726
C	4.423532	3.138910	-0.286872
C	3.540520	4.008466	1.893637
C	3.041926	0.648943	2.090787
C	4.246931	-0.261089	1.883865
C	2.998517	1.180166	3.525149
H	-4.685899	-1.310065	-0.554909
H	-4.037332	-2.950514	-0.418845
H	-4.603718	-2.100536	1.025594
H	-2.103670	-2.074084	0.909516
H	-2.190056	-1.285512	-0.675454
H	-2.691561	1.628419	3.131035
H	-1.413843	2.705660	2.510971
H	-2.945181	2.540322	1.618002
H	1.104567	0.075747	0.124702
H	1.463148	1.172623	-1.215346
H	1.637071	3.070840	0.254757
H	1.002771	2.177295	1.629450
H	4.838841	2.335598	1.638530
H	3.577875	3.513886	-0.867802
H	5.179963	3.924334	-0.258346
H	4.830174	2.270692	-0.802953
H	4.391832	4.678081	2.021596
H	2.773566	4.562051	1.349980
H	3.149643	3.764501	2.879257
H	2.142717	0.044691	1.955453
H	5.186246	0.272607	2.038745
H	4.221452	-1.089005	2.592838
H	4.246616	-0.664228	0.871968
H	2.127635	1.816604	3.686017

H	2.932557	0.347618	4.225670
H	3.898537	1.749652	3.765535

Table S3: Atomic coordinates of the most stable conformer of VX (conf1 for both S-side and O-side reactions).

		conf2	
C	-5.004461	-0.297533	-1.375486
C	-3.579366	-0.406020	-0.881978
O	-3.568126	-0.097516	0.534421
P	-2.206480	-0.195853	1.390299
C	-2.867679	0.035312	3.058926
O	-1.387513	-1.422443	1.204142
S	-1.175406	1.584306	0.851791
C	0.584177	1.046931	1.053699
C	1.127992	0.271552	-0.150509
N	2.538093	-0.030821	0.021310
C	2.943897	-1.437696	-0.116235
C	2.517435	-2.243401	1.116490
C	2.471415	-2.141809	-1.402732
C	3.459705	1.015265	-0.437905
C	4.722923	1.084770	0.426185
C	3.821935	0.961286	-1.933143
H	-5.392637	0.709512	-1.225028
H	-5.041273	-0.524560	-2.441875
H	-5.651773	-1.000722	-0.852151
H	-3.181671	-1.411528	-1.020022
H	-2.926528	0.300247	-1.397439
H	-3.478158	-0.831389	3.309792
H	-2.035717	0.106484	3.756531
H	-3.467289	0.941152	3.109989
H	1.126096	1.979116	1.208309
H	0.674029	0.450914	1.957652
H	0.555760	-0.648516	-0.230902
H	0.932785	0.846197	-1.065606
H	4.034506	-1.430216	-0.136832
H	1.430988	-2.264428	1.218143
H	2.862393	-3.276493	1.040638
H	2.936070	-1.804683	2.022027
H	2.916449	-3.136489	-1.465682

H	1.388677	-2.273292	-1.413271
H	2.755694	-1.590828	-2.297580
H	2.922899	1.953951	-0.277715
H	5.345683	0.196795	0.307966
H	5.330761	1.945510	0.142114
H	4.461980	1.176760	1.480053
H	2.929586	0.916761	-2.558518
H	4.385388	1.851238	-2.219775
H	4.441861	0.093078	-2.161593

conf3

C	-4.467670	0.260913	-0.730596
C	-3.081320	-0.100396	-0.258328
O	-3.062146	-0.012803	1.180776
P	-1.634428	-0.091906	1.911082
C	-2.115457	-0.302900	3.630579
O	-0.704862	-1.123915	1.414290
S	-0.793507	1.820513	1.643531
C	-2.260497	2.891252	1.432547
C	-3.170538	2.992757	2.650029
N	-4.204156	3.985220	2.436254
C	-5.539246	3.610229	2.913623
C	-6.194269	2.660467	1.915673
C	-5.587526	3.004226	4.322151
C	-3.773740	5.362951	2.686425
C	-4.522279	6.340612	1.787154
C	-3.844824	5.806746	4.149872
H	-4.715508	1.285258	-0.453171
H	-4.523377	0.171873	-1.814900
H	-5.206625	-0.405604	-0.288178
H	-2.803070	-1.114784	-0.541538
H	-2.330398	0.581490	-0.665951
H	-2.583131	-1.282109	3.724204
H	-1.207911	-0.275080	4.229891
H	-2.798208	0.473727	3.962848
H	-1.833997	3.861418	1.180720
H	-2.837701	2.549909	0.575151
H	-3.647090	2.023702	2.781358
H	-2.567704	3.183647	3.550323
H	-6.125080	4.530456	2.930356
H	-5.614343	1.738197	1.828364

H	-7.201047	2.389970	2.236407
H	-6.247336	3.123604	0.931181
H	-6.624352	2.902145	4.644085
H	-5.147428	2.005597	4.337177
H	-5.064600	3.617460	5.052819
H	-2.722463	5.397592	2.390933
H	-5.582208	6.384775	2.041331
H	-4.118144	7.346889	1.900197
H	-4.433600	6.039037	0.744513
H	-3.303907	5.121410	4.803128
H	-3.402710	6.796950	4.262247
H	-4.879897	5.865235	4.490708

conf4

C	-2.870632	1.071399	-1.900329
C	-2.042819	0.607980	-0.727891
O	-2.918796	0.492226	0.409564
P	-2.277045	0.009933	1.801124
C	-3.759185	-0.405251	2.730199
O	-1.265955	-1.059365	1.698727
S	-1.429643	1.723345	2.659481
C	-2.746201	2.957502	2.349388
C	-2.395531	3.902946	1.203471
N	-3.477749	4.838014	0.980394
C	-3.126323	6.257498	0.928852
C	-2.863413	6.775451	2.339879
C	-1.951803	6.614831	0.009657
C	-4.499258	4.355861	0.051194
C	-5.887601	4.838927	0.456606
C	-4.221937	4.676743	-1.419941
H	-3.339438	2.030423	-1.681856
H	-2.238827	1.185720	-2.780459
H	-3.652459	0.347442	-2.124315
H	-1.583231	-0.362950	-0.909763
H	-1.249164	1.320631	-0.489875
H	-4.231027	-1.254376	2.238196
H	-3.455073	-0.684673	3.736087
H	-4.455916	0.428241	2.770392
H	-3.684049	2.445924	2.141188
H	-2.874073	3.528651	3.267027
H	-1.481763	4.434842	1.467105

H	-2.163415	3.315108	0.304530
H	-4.010401	6.771843	0.547945
H	-2.013118	6.254118	2.785449
H	-2.628310	7.840263	2.328682
H	-3.733474	6.609339	2.973284
H	-1.855422	7.698828	-0.060859
H	-1.009235	6.233231	0.404263
H	-2.084066	6.220550	-0.995478
H	-4.492927	3.266213	0.156110
H	-5.972481	5.922976	0.368121
H	-6.648579	4.397929	-0.187868
H	-6.096514	4.564457	1.489639
H	-3.223770	4.353003	-1.717758
H	-4.946999	4.173270	-2.060737
H	-4.302315	5.749349	-1.605341

conf5

C	-3.453486	-2.310500	0.230296
C	-2.323270	-1.335465	0.453539
O	-2.892477	-0.060407	0.784372
P	-1.904968	1.141309	1.177685
C	-3.105440	2.434737	1.501942
O	-0.946945	0.815478	2.259799
S	-0.934787	1.721277	-0.590997
C	0.756854	1.114304	-0.237346
C	1.562396	2.015765	0.692492
N	1.664788	3.377734	0.224069
C	1.581988	4.406602	1.261953
C	0.132227	4.575623	1.709010
C	2.479458	4.174822	2.484145
C	2.625684	3.589648	-0.855613
C	2.157787	4.697722	-1.794117
C	4.067861	3.834434	-0.401843
H	-4.095640	-1.969663	-0.580106
H	-3.052996	-3.289583	-0.030155
H	-4.053939	-2.408971	1.133011
H	-1.675295	-1.652886	1.271919
H	-1.718521	-1.219451	-0.449899
H	-3.735855	2.114094	2.329593
H	-2.574597	3.346119	1.765540
H	-3.715491	2.601419	0.616305

H	0.689953	0.113707	0.184876
H	1.211679	1.037045	-1.224160
H	1.070220	1.994787	1.661528
H	2.547904	1.540747	0.829466
H	1.894873	5.340139	0.791034
H	-0.223915	3.658710	2.186095
H	0.042130	5.385219	2.434707
H	-0.504835	4.786295	0.850476
H	2.433682	5.039792	3.147045
H	2.143355	3.308913	3.056072
H	3.519150	4.016291	2.205395
H	2.623783	2.662773	-1.434504
H	2.166159	5.669024	-1.297542
H	2.816574	4.768530	-2.660295
H	1.142694	4.497463	-2.134658
H	4.415756	3.044851	0.265073
H	4.734142	3.866552	-1.264573
H	4.154263	4.789070	0.119971

conf6

C	-3.731873	-0.112671	-2.022647
C	-2.600409	-0.071202	-1.025092
O	-3.147546	-0.336127	0.279256
P	-2.132743	-0.507890	1.511608
C	-3.287978	-1.019242	2.791733
O	-0.985089	-1.404165	1.273198
S	-1.432972	1.413435	1.962927
C	-3.004966	2.344181	2.105924
C	-3.440982	2.589520	3.549610
N	-2.448821	3.306009	4.322230
C	-2.777277	4.678517	4.702537
C	-2.718317	5.593562	3.482239
C	-4.118539	4.870307	5.425300
C	-1.684146	2.501598	5.278852
C	-0.244610	2.992071	5.383089
C	-2.322502	2.376606	6.664131
H	-4.485547	0.635038	-1.779720
H	-3.350496	0.090917	-3.022577
H	-4.203146	-1.094038	-2.023551
H	-1.841407	-0.822877	-1.242474
H	-2.119960	0.909592	-1.006455

H	-3.639862	-2.018568	2.539251
H	-2.761968	-1.043924	3.743467
H	-4.134077	-0.337588	2.845442
H	-2.810073	3.299516	1.621762
H	-3.773215	1.824227	1.532021
H	-4.378247	3.150989	3.506532
H	-3.682591	1.634720	4.027752
H	-1.989568	4.993043	5.388492
H	-3.491152	5.316862	2.760832
H	-2.893587	6.631957	3.765682
H	-1.748273	5.516406	2.992923
H	-4.177812	5.883384	5.824932
H	-4.961389	4.747953	4.743524
H	-4.242898	4.171816	6.249614
H	-1.641291	1.503778	4.839704
H	-0.187968	3.987185	5.826776
H	0.337872	2.320567	6.014384
H	0.210098	3.026372	4.394091
H	-3.350223	2.016117	6.596584
H	-1.756072	1.674654	7.276812
H	-2.328314	3.337510	7.181816

conf7

C	-2.825285	1.148337	-1.807038
C	-2.105252	0.490046	-0.655824
O	-3.009610	0.432028	0.461242
P	-2.424397	-0.057592	1.877375
C	-3.950565	-0.360101	2.779650
O	-1.483625	-1.192710	1.817360
S	-1.479872	1.618648	2.705103
C	-2.707546	2.918358	2.303833
C	-2.240854	3.794836	1.148158
N	-1.083054	4.590653	1.495970
C	-0.078435	4.754570	0.438026
C	0.856384	3.551486	0.414308
C	-0.643819	5.020133	-0.962445
C	-1.403027	5.789386	2.275046
C	-0.255655	6.151822	3.211309
C	-1.835590	6.999534	1.442154
H	-3.135832	2.158860	-1.540963
H	-2.166826	1.203706	-2.673293

H	-3.711210	0.576865	-2.079024
H	-1.790259	-0.524521	-0.897768
H	-1.216588	1.056467	-0.365004
H	-4.468272	-1.184539	2.291882
H	-3.685858	-0.641136	3.796210
H	-4.590852	0.518439	2.792272
H	-3.659600	2.451769	2.058455
H	-2.842922	3.501044	3.212698
H	-1.991681	3.137200	0.316251
H	-3.090081	4.413670	0.815516
H	0.515363	5.625524	0.718233
H	0.299502	2.637467	0.200662
H	1.623163	3.668847	-0.352774
H	1.333851	3.422260	1.384147
H	0.163367	5.307043	-1.636976
H	-1.107994	4.124630	-1.379944
H	-1.384318	5.818387	-0.960462
H	-2.251937	5.513465	2.905111
H	0.627933	6.468791	2.655686
H	-0.543238	6.975657	3.865109
H	0.016938	5.292390	3.822260
H	-2.669428	6.755231	0.782985
H	-2.152425	7.811940	2.096607
H	-1.010951	7.369028	0.830385

Table S4: Atomic coordinates of the S-side conformers of VX .

		conf2	
C	-1.971019	-1.689287	-0.882105
C	-2.726498	-1.426952	0.402249
O	-2.826891	-0.023190	0.711293
P	-1.529162	0.790644	1.173834
C	-2.287346	2.114278	2.121712
O	-0.506174	-0.016314	1.880313
S	-0.766380	1.680956	-0.579418
C	1.003099	1.306750	-0.307387
C	1.652162	2.213843	0.732454
N	2.991174	1.750578	1.029237
C	4.012299	2.790136	1.174429

C	4.477409	3.252755	-0.203109
C	3.606413	3.999088	2.027182
C	3.018424	0.647798	1.997962
C	4.199773	-0.278299	1.733545
C	2.982805	1.082877	3.464513
H	-0.919217	-1.425165	-0.778067
H	-2.034699	-2.750080	-1.124595
H	-2.393401	-1.113819	-1.704344
H	-3.758025	-1.763310	0.327361
H	-2.249735	-1.929385	1.243655
H	-2.765350	1.681165	2.998762
H	-1.509961	2.812565	2.423746
H	-3.025348	2.628775	1.509681
H	1.082221	0.261687	-0.020946
H	1.481767	1.440869	-1.276045
H	1.686176	3.224811	0.327218
H	1.018462	2.250375	1.629649
H	4.861282	2.312393	1.665890
H	3.644589	3.686785	-0.761011
H	5.253357	4.014935	-0.119915
H	4.864723	2.410453	-0.774119
H	4.474725	4.635101	2.203315
H	2.858162	4.608266	1.518096
H	3.202663	3.700818	2.992432
H	2.103922	0.078617	1.819509
H	5.152206	0.218256	1.927002
H	4.149183	-1.151324	2.384756
H	4.193675	-0.611758	0.696596
H	2.128087	1.729762	3.665042
H	2.892767	0.207611	4.108006
H	3.896325	1.611556	3.744123

conf3

C	-2.565710	-2.610679	1.259074
C	-2.614790	-1.488352	0.247199
O	-2.730201	-0.213245	0.908103
P	-1.402508	0.581928	1.309776
C	-2.114191	1.933858	2.252864
O	-0.352641	-0.202664	2.000843
S	-0.708201	1.359135	-0.520093
C	1.082785	1.109774	-0.247433

C	1.684621	2.116445	0.726666
N	3.049105	1.749938	1.041299
C	4.007074	2.854897	1.121238
C	4.442413	3.263066	-0.282924
C	3.531382	4.085141	1.904481
C	3.142690	0.709338	2.072841
C	4.377170	-0.158495	1.858674
C	3.081485	1.226450	3.511777
H	-3.456339	-2.594721	1.885680
H	-2.521885	-3.569962	0.743268
H	-1.685725	-2.507290	1.891212
H	-1.725978	-1.484569	-0.387224
H	-3.489960	-1.561711	-0.394971
H	-2.577704	1.520594	3.147277
H	-1.316376	2.618749	2.531258
H	-2.856376	2.455331	1.652877
H	1.223011	0.091309	0.101972
H	1.544926	1.211702	-1.227941
H	1.658546	3.100581	0.259545
H	1.055554	2.174378	1.626389
H	4.883319	2.457561	1.635845
H	3.585209	3.615719	-0.860900
H	5.173299	4.072037	-0.247518
H	4.876677	2.412741	-0.806237
H	4.360889	4.780218	2.039618
H	2.748022	4.619140	1.364639
H	3.147289	3.820242	2.887361
H	2.264089	0.076684	1.931512
H	5.298235	0.404711	2.018430
H	4.379162	-0.992818	2.560571
H	4.390280	-0.552781	0.843395
H	2.190194	1.832658	3.677741
H	3.043052	0.386294	4.205239
H	3.962159	1.823338	3.757224

conf4

C	-4.677849	-1.450942	1.198254
C	-3.627498	-0.646459	1.924104
O	-2.927180	0.148161	0.950081
P	-1.596402	0.920572	1.402873
C	-2.197612	2.363246	2.304887

O	-0.622684	0.111255	2.172159
S	-0.886073	1.591907	-0.447742
C	0.876686	1.175115	-0.181072
C	1.587733	2.149613	0.751113
N	2.918676	1.667166	1.052906
C	3.972575	2.683763	1.093464
C	4.420814	3.019275	-0.325781
C	3.619607	3.968768	1.853222
C	2.936496	0.646664	2.108683
C	4.084795	-0.332928	1.897189
C	2.946318	1.200262	3.535178
H	-4.210306	-2.105883	0.465475
H	-5.234329	-2.060996	1.908980
H	-5.374356	-0.792595	0.681887
H	-4.085275	0.017299	2.662252
H	-2.909167	-1.289604	2.433144
H	-2.687257	2.030808	3.219970
H	-1.346830	2.990148	2.562944
H	-2.895712	2.925826	1.688431
H	0.921541	0.158395	0.197497
H	1.329562	1.199862	-1.170735
H	1.644159	3.117118	0.252869
H	0.984402	2.293064	1.658746
H	4.817833	2.221565	1.605694
H	3.589275	3.432473	-0.901104
H	5.220448	3.761203	-0.319663
H	4.770678	2.122017	-0.833709
H	4.509400	4.590084	1.961414
H	2.878709	4.557803	1.310719
H	3.227832	3.760767	2.846691
H	2.002687	0.092300	1.996942
H	5.055006	0.148497	2.031546
H	4.022938	-1.148715	2.617875
H	4.046484	-0.748529	0.891116
H	2.114915	1.886537	3.699922
H	2.845392	0.382748	4.249133
H	3.880657	1.721555	3.752913
		conf5	
C	-3.689328	-1.201864	-0.426010
C	-3.522850	0.173592	0.174604

O	-2.441770	0.123393	1.110107
P	-1.744069	1.445130	1.693109
C	-3.089927	2.468661	2.313377
O	-0.696439	1.082686	2.667384
S	-1.023706	2.525673	0.042847
C	0.644281	1.762929	0.004299
C	1.624969	2.487988	0.921554
N	2.856822	1.730112	1.018146
C	4.093492	2.513514	0.977527
C	4.433344	2.865149	-0.467790
C	4.102661	3.779649	1.843835
C	2.786160	0.648971	2.009499
C	3.684093	-0.515530	1.608275
C	3.059792	1.080789	3.451268
H	-3.887399	-1.934897	0.353870
H	-4.521887	-1.202961	-1.128621
H	-2.784063	-1.493901	-0.955103
H	-3.298530	0.912215	-0.598762
H	-4.429853	0.481900	0.700224
H	-3.644264	1.893589	3.054194
H	-2.659505	3.351122	2.780440
H	-3.754286	2.772087	1.505257
H	0.548440	0.715195	0.279827
H	0.976847	1.812842	-1.030662
H	1.823274	3.470226	0.492982
H	1.151602	2.647493	1.896991
H	4.879859	1.855654	1.350826
H	3.640657	3.475032	-0.907277
H	5.361183	3.435951	-0.525778
H	4.533712	1.959515	-1.063941
H	5.109947	4.196710	1.877270
H	3.448777	4.547728	1.428509
H	3.783426	3.578163	2.864070
H	1.753212	0.296203	1.983688
H	4.740289	-0.244315	1.652910
H	3.535354	-1.357437	2.284930
H	3.457111	-0.836022	0.592149
H	2.400208	1.895584	3.750514
H	2.878704	0.245161	4.127506
H	4.096797	1.397569	3.580328

Table S5: Atomic coordinates of the O-side conformers of VX .

S2 Calculated reaction rate constants.

	S-side		O-side	
T(K)	TST	1D SCTST	TST	1D SCTST
200	9.00(−35)	1.74(−29)	2.58(−38)	1.87(−33)
220	1.42(−30)	7.29(−27)	8.64(−34)	2.37(−30)
240	4.52(−27)	2.07(−24)	5.10(−30)	1.57(−27)
260	4.17(−24)	3.99(−22)	7.93(−27)	5.85(−25)
280	1.46(−21)	5.04(−20)	4.32(−24)	1.24(−22)
300	2.35(−19)	4.09(−18)	1.02(−21)	1.54(−20)
320	2.01(−17)	2.16(−16)	1.22(−19)	1.17(−18)
340	1.02(−15)	7.71(−15)	8.30(−18)	5.67(−17)
360	3.39(−14)	1.94(−13)	3.55(−16)	1.87(−15)
380	7.87(−13)	3.60(−12)	1.02(−14)	4.39(−14)
400	1.31(−11)	5.09(−11)	2.12(−13)	7.68(−13)
450	5.16(−9)	1.46(−8)	1.27(−10)	3.42(−10)
500	6.24(−7)	1.43(−6)	2.16(−8)	4.74(−8)
550	3.19(−5)	6.31(−5)	1.45(−6)	2.77(−6)
600	8.52(−4)	1.51(−3)	4.88(−5)	8.37(−5)
650	1.38(−2)	2.26(−2)	9.62(−4)	1.52(−3)
700	1.52(−1)	2.31(−1)	1.25(−2)	1.85(−2)
750	1.21(0)	1.75(0)	1.15(−1)	1.62(−1)
800	7.47(0)	1.37(1)	8.12(−1)	1.10(0)
850	3.73(1)	5.01(1)	4.57(0)	6.00(0)
900	1.56(2)	2.03(2)	2.13(1)	2.71(1)
950	5.63(2)	7.15(2)	8.44(2)	1.05(2)
1000	1.79(3)	2.22(3)	2.93(2)	3.58(2)
1100	1.32(4)	1.58(4)	2.52(3)	2.99(3)
1200	1.45(5)	1.68(5)	3.39(4)	3.88(4)
1300	2.87(5)	3.28(5)	7.07(4)	8.02(4)
1400	1.66(6)	1.86(6)	2.64(5)	2.94(5)
1500	2.76(6)	3.07(6)	8.28(5)	9.13(5)
1600	6.96(6)	7.65(6)	2.26(6)	2.47(6)
1700	1.57(7)	1.71(7)	5.50(6)	5.94(6)
1800	3.26(7)	3.52(7)	1.21(7)	1.30(7)
1900	6.25(7)	6.71(7)	2.47(7)	2.64(7)
2000	1.13(8)	1.20(8)	4.69(7)	4.98(7)

Table S6: Calculated rate constants for the reactions.

S3 Coordinates and atomic numbers of the transition states of the simulant molecule reported in Fig. 2

O-side TS			
C	-3.244007	-1.738655	-1.370542
C	-4.366580	-1.040697	-0.915693
O	-3.977353	0.186310	0.533213
P	-2.563190	0.270526	1.101159
C	-2.577371	-0.101647	2.859122
O	-1.598101	-0.653058	0.339778
S	-1.791622	2.219488	1.058387
C	-1.139425	2.217242	-0.652495
C	-2.214839	2.151738	-1.721660
H	-3.186709	-2.793298	-1.129992
H	-2.840892	-1.451608	-2.334634
H	-2.313240	-1.232115	-0.522488
H	-4.755070	-0.201574	-1.473561
H	-5.088064	-1.523249	-0.273678
H	-3.042388	-1.077082	2.993452
H	-1.558172	-0.116000	3.237821
H	-3.161199	0.653034	3.383700
H	-0.572788	3.144270	-0.716418
H	-0.446023	1.383551	-0.730675
H	-2.744284	1.200726	-1.678833
H	-2.943506	2.950382	-1.593182
H	-1.761855	2.244673	-2.709520
S-side TS			
P	0.764582	0.725228	-0.813706
O	0.494914	1.607611	0.409876
C	-2.056744	-0.247700	0.773670
C	-1.614874	0.742064	1.657373
H	-1.841424	-1.287742	0.968195
H	-2.219503	1.638284	1.734169
H	-1.151445	0.405146	2.577749
H	-0.529278	1.230488	1.039069
H	-2.919017	-0.073495	0.147748
S	-0.805269	-0.434312	-1.255663
O	1.172409	1.642191	-2.056512

C	2.280740	-0.206443	-0.592204
H	3.096194	0.489291	-0.401983
H	2.154508	-0.875212	0.256073
H	2.481344	-0.786199	-1.490158
C	0.236436	2.605954	-2.567852
H	-0.652719	2.075769	-2.911782
H	-0.047924	3.277698	-1.756569
C	0.907034	3.353010	-3.694613
H	1.197405	2.664822	-4.486591
H	0.221086	4.091064	-4.108736
H	1.797015	3.867212	-3.336022

Table S7: Atomic coordinates of the O-side and S-side TS's of the simulant molecule shown in Fig. 2

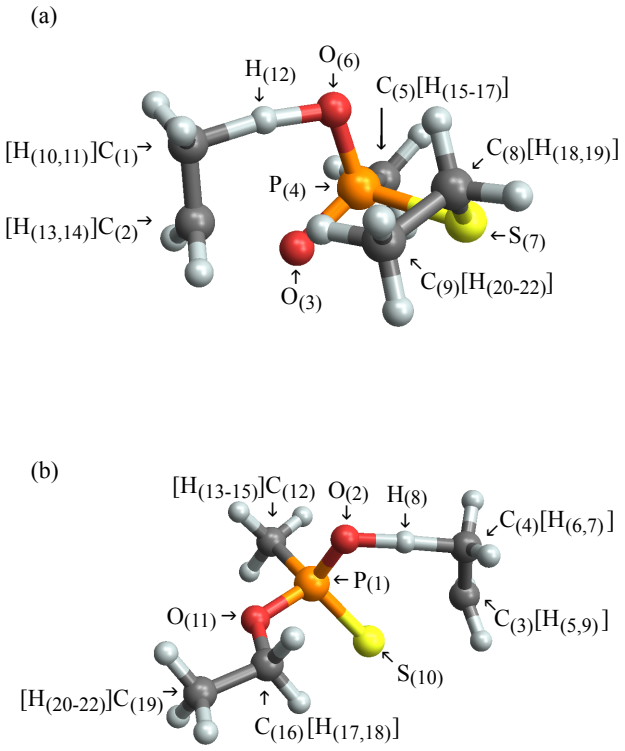

Figure S1: The optimized geometries of the (a) O-side and (b) TS's for pericyclic H transfer reaction of the simulant. Atomic numbers are shown in the parentheses, the atomic numbers of the H atoms attached to C atoms are in the square brackets.