Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Assessing the effective factors on the conformational preferences and the early and late transition states of the unimolecular retro-ene decomposition reactions of ethyl cyanate, ethyl thiocyanate and ethyl selenocyanate

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Table SI-1. MP2/6-311++G**[(a)] and G3MP2[(b)] calculated zero-point energies (ZPE, in hartree), relative *ZPE* (ΔZPE in kcal mol^{-1}), corrected electronic energies (E_o, in hartree), ΔE_o, thermodynamic parameters [ΔH, ΔG (in kcal mol^{-1})] and ΔS (in cal mol^{-1}K^{-1}) at 25 ºC and 1 atm pressure for the *gauche*- and *anti*-conformations of compounds **1-3**.

Geometry	*ZPE*	E_o	*H*	*S*	*G*	ΔZPE	ΔE_o	ΔH	ΔS	ΔG
					-246.644394					
1-*gauche*	0.079617[a]	-246.574604[a]	-246.568090[a]	74.170[a]	-246.603330[a]	0.00[a]	0.00[a]	0.00[a]	0.000[a]	0.00[a]
	0.076203[b]	-246.89629 [b]	-246.889679[b]	74.779[b]	-246.925209[b]	0.00[b]	0.00[b]	0.00[b]	0.000[b]	0.00[b]
1-*anti*	0.079400[a]	-246.574457[a]	-246.567767[a]	75.362 [a]	-246.603574[a]	-0.14[a]	0.09[a]	0.20[a]	1.192[a]	-0.15[a]
	0.076065[b]	-246.896211[b]	-246.889493[b]	75.150[b]	-246.925199 [b]	0.09[b]	0.05[b]	0.12[b]	0.371[b]	0.01[b]
1-*TS*	0.073215[a]	-246.524863[a]	-246.519017[a]	70.797[a]	-246.552655[a]	-4.017	31.21	30.79	-3.373	31.80[a]
	0.068660[b]	-246.846455[b]	-246.840118	72.828	-246.874721[b]	-4.733	31.27	31.10	-1.951	31.68[b]
2-*gauche*	0.076094[a]	-569.188551[a]	-569.181485[a]	77.923[a]	-569.218509[a]	0.08[a]	0.00[a]	0.00[a]	0.000[a]	0.00[a]
	0.072760[b]	-569.52857 [b]	-569.521394[b]	78.578[b]	-569.558729[b]	0.02[b]	0.00[b]	0.00[b]	0.000[b]	0.00[b]
2-*anti*	0.075960[a]	-569.186766[a]	-569.179492[a]	79.794[a]	-569.217404[a]	0.00	1.12[a]	1.25[a]	1.871[a]	0.69[a]
	0.072733[b]	-569.527201[b]	-569.519914[b]	79.250[b]	-569.557568[b]	0.00[b]	0.86[b]	0.93[b]	0.672[b]	0.73[b]
								1.00±0.07[c]		
								1.68±0.07[d]		
2-*TS*	0.069488[a]	-569.125025[a]	-569.118716[a]	74.094[a]	-569.153920[a]	-4.145	39.86	39.39	-3.829	40.53[a]
	0.065461[b]	-569.463968[b]	-569.457013[b]	77.271[b]	-569.493727[b]	-4.580	40.538	40.40	-1.307	40.79[b]
3-*gauche*	0.074752[a]	-2571.439534[a]	-2571.432128[a]	81.532[a]	-2571.470867[a]	0.07[a]	0.00[a]	0.00[a]	0.000[a]	0.00[a]
	0.071571[b]	-2572.014730[b]	-2572.007183[b]	82.306[b]	-2572.046289[b]	0.02[b]	0.00[b]	0.00[b]	0.000[b]	0.00[b]
3-*anti*	0.074635[a]	-2571.437632[a]	-2571.430061[a]	83.012[a]	-2571.469502[a]	0.00	1.19[a]	1.30[a]	1.480[a]	0.86[a]
	0.071537[b]	-2572.013301[b]	-2572.005656[b]	83.093[b]	-2572.045136[b]	0.00[b]	0.90[b]	0.96[b]	0.787[b]	0.72[b]
3-*TS*	0.068305[a]	-2571.376455[a]	-2571.369847[a]	77.468[a]	-2571.406655[a]	-4.046	39.58	39.09	-4.064	40.29[a]
	0.064442[b]	-2571.949412[b]	-2571.942138[b]	80.996[b]	-2571.980623[b]	-4.474	40.99	40.82	-1.310	41.21[b]

[c]From infrared spectroscopy, [Ref. 26]. [d] From Raman spectroscopy, [Ref. 25].

Table SI-2. MP2/6-311++G** calculated thermodynamic parameters [ΔH, ΔG (in kcal mol^{-1}) and ΔS (in cal mol^{-1} K^{-1})] at 300, 400, 500 and 600 K for the retro-ene decomposition reactions of compounds **1-3**.

	300 K			400 K			500 K			600		
	ΔH^a	ΔS^a	ΔG^a	ΔH^a	ΔS^a	ΔG^a	ΔH^a	ΔS^a	ΔG^a	ΔH^a	ΔS^a	ΔG^a
Geometries												
1-*gauche*	0.00	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00	0.00	0.00
(**1**-*gauche*→[*TS*]$^{\neq}$→**1**-*P*)	30.79	-3.373	31.80	30.74	-3.536	32.15	30.73	-3.561	32.51	30.73	-3.551	32.86
1-*P*	-6.29	36.859	-17.28	-6.18	37.160	-21.05	-6.18	37.206	-24.78	-6.23	37.112	-28.50
2-*gauche*	0.00	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00
(**2**-*gauche*→[*TS*]$^{\neq}$→**2**-*P*)	39.39	-3.829	40.53	39.34	-3.980	40.93	39.34	-3.976	41.33	39.36	-3.933	41.72
2-*P*	21.50	35.959	10.78	21.54	36.068	7.11	21.49	35.987	3.50	21.39	35.809	-0.09
3-*gauche*	0.00	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00
(**3**-*gauche*→[*TS*]$^{\neq}$→**3**-*P*)	39.08	-4.064	40.29	39.02	-4.239	40.72	39.02	-4.254	41.14	39.03	-4.228	41.57
3-*P*	23.34	35.321	12.80	23.34	35.348	9.20	23.27	35.219	5.66	23.16	35.013	2.15

Table SI-3. MP2/6-311++G** calculated structural parameters for the ground and transition structures of compounds **1-3**.

	1				**2**				**3**			
	gauche	*anti*	*TS*	*P*	*gauche*	*anti*	*TS*	*P*	*gauche*	*anti*	*TS*	*P*
Bond lengths (Å)												
r_{N1-C2}	1.180	1.179	1.214	1.225	1.181	1.181	1.220	1.217	1.182	1.182	1.218	1.213
r_{C2-X3}	1.293	1.294	1.220	1.173	1.693	1.692	1.594	1.568	1.842	1.842	1.738	1.716
r_{X3-C4}	1.466	1.464	2.013	-	1.827	1.829	2.479	-	1.972	1.974	2.667	-
r_{C4-C5}	1.513	1.510	1.410	1.339	1.521	1.525	1.400	1.339	1.521	1.525	1.396	1.339
r_{C5-H9}	1.093	1.092	1.275	-	1.093	1.093	1.390	-	1.093	1.093	1.403	-
d_{H9-N1}	3.114	5.000	1.443	1.009	3.063	5.456	1.252	1.007	3.092	5.619	1.240	1.007
Bond angles (°)												
$\theta_{N1-C2-X3}$	178.7	178.7	159.6	171.5	179.4	179.2	155.8	172.5	179.6	179.6	155.7	173.3
$\theta_{C2-X3-C4}$	113.3	113.2	100.7	-	98.1	98.4	84.9	-	95.1	95.8	80.4	-
$\theta_{X3-C4-C5}$	111.3	106.8	107.9	-	113.2	108.2	110.8	-	113.4	108.7	111.1	-
$\theta_{C4-C5-H9}$	111.0	110.6	104.8	121.4	110.9	111.3	108.1	121.4	110.9	111.3	109.0	121.4
$\theta_{C5-H9-N1}$	112.5	68.3	162.0	-	123.4	65.0	163.2	-	126.7	64.7	164.7	-
$\theta_{H9-N1-C2}$	57.0	12.1	85.1	122.9	61.3	19.5	97.1	131.9	61.9	21.7	99.1	135.1
Torsion angles (°)												
$\phi_{N1-C2-X3-C4}$	-	-	0.0	-	-	-	0.0	-	0.0	-	0.1	-
$\phi_{C2-X3-C4-C5}$	-64.8	179.8	0.0	-	-61.1	180.0	0.0	-	-59.3	180.0	-0.1	-
$\phi_{X3-C4-C5-H9}$	62.9	-60.6	0.0	-	62.5	-60.7	0.0	-	62.4	-60.7	0.1	-
$\phi_{C4-C5-H9-N1}$	-29.8	18.6	0.0	-	-27.0	12.9	0.0	-	-28.1	11.9	-0.3	-
$\phi_{C5-H9-N1-C2}$	0.5	67.4	0.0	-	-5.4	96.1	-0.3	-	-5.4	99.8	0.2	-
$\phi_{H9-N1-C2-X3}$	-	-	0.0	178.8	-	-	0.1	180.0	-	-	-0.1	180.0

Table SI-4. MP2/6-311++G** calculated rate constants (in s^{-1}), Arrhenius A factors (in s^{-1}) and activation energies (in kcal mol^{-1}) of the thermal decomposition reactions of compounds **1-3** at 300, 400, 500 and 600 K.

	300 K			400 K			500 K			600 K		
	E_a	A	k	E_a	A	k	E_a	A	k	E_a	A	k
1-*GS*→[*TS*]$^{\neq}$→**1**-*P*	31.38	3.07×10^{12}	2.50×10^{-11}	31.33	3.79×10^{12}	1.95×10^{-5}	31.32	4.69×10^{12}	5.70×10^{-2}	31.92	5.65×10^{12}	$1.21\times10^{+1}$
2-*GS*→[*TS*]$^{\neq}$→**2**-*P*	39.98	2.44×10^{12}	0.95×10^{-17}	39.93	3.03×10^{12}	2.99×10^{-10}	39.93	3.79×10^{12}	7.70×10^{-6}	39.95	4.66×10^{12}	2.99×10^{-3}
3-*GS*→[*TS*]$^{\neq}$→**3**-*P*	39.67	2.17×10^{12}	1.42×10^{-17}	39.61	2.66×10^{12}	3.90×10^{-10}	39.61	3.30×10^{12}	9.36×10^{-6}	39.62	4.01×10^{12}	7.94×10^{-3}

Table SI-5. The Cartesian coordinates of the optimized structures of the *gauche*- and *anti*-conformations of compounds **1-3** and their corresponding decomposition and isomerization transition state structures at the MP2/6-311++G** level of theory.

Ethyl cyanate (**1**), *gauche*-conformation	Ethyl cyanate (**1**), *anti*-conformation	Ethyl cyanate (**1**), *TS-decomposition*	Ethyl cyanate (**1**), *TS-isomerization*
C,0,-2.1144133675,-0.3280127618,0.0136295773	C,0,-2.0874727644,-0.1072577269,0.0157337226	C,0,-0.9061458453,-0.0697128138,-1.23168727	C,0,-0.3069327838,-0.5281831375,-0.296009388
C,0,-0.6540242092,0.0631893881,-0.0456258597	C,0,-0.5782182147,-0.08630136,-0.0086943179	C,0,0.4957790458,0.0508373966,-1.3265686787	C,0,-1.7533500319,-0.5476965825,0.0247361398
O,0,-0.3083443573,0.9913445253,1.0348527363	O,0,-0.1529753944,0.9497999229,0.9347980749	H,0,-1.4823507919,0.835066152,-1.4132506152	H,0,0.3440741345,-1.2212736443,0.2272171272
C,0,-0.9137036532,2.1302851934,0.9447375528	C,0,1.1325340918,1.070241801,1.0134137537	H,0,-1.3400367702,-0.9865990318,-1.62495601	H,0,-0.0636422466,-0.3901586279,-1.341540798
N,0,-1.4520107741,3.1782688825,0.8846089387	N,0,2.3012441037,1.2021218047,1.1012522235	H,0,0.9548615107,1.0275007707,-1.4284047646	H,0,-2.1719333252,-1.347695345,-0.6077164455
H,0,-2.7592365019,0.5418863212,-0.1332737448	H,0,-2.4901184849,0.8604100481,-0.290067729	H,0,1.0972176979,-0.7946894775,-1.64018363	H,0,-2.2334604559,0.38538956,-0.2785426847
H,0,-2.348242517,-0.7877164094,0.9764263345	H,0,-2.4523011634,-0.3467845412,1.0164979552	H,0,-1.1345580463,-0.2320520522,0.011683672	H,0,-1.9403161238,-0.7456546776,1.07713553
H,0,-2.3247264642,-1.0503602687,-0.7804898983	H,0,-2.4466813865,-0.871048359,-0.6796095132	O,0,1.258927304,-0.1053092055,0.5298873459	N,0,0.0851564087,0.6615179154,1.8613331695
H,0,0.0083802124,-0.7829310472,0.1332183508	H,0,-0.1463481989,-1.0358221865,0.3183971973	C,0,0.2389666537,-0.2607297818,1.1815667663	C,0,0.3469618432,0.9793084883,0.7127554484
H,0,-0.390036368,0.5403841767,-0.9934529877	H,0,-0.1843945883,0.1754845968,-0.9943293671	N,0,-0.9419397037,-0.3823406539,1.434169106	O,0,0.6447935808,1.388639051,-0.4315510974

Ethyl thicyanate (**2**), *gauche*-conformation	Ethyl thiocyanate (**2**), *anti*-conformation	Ethyl thiocyanate (**2**), *TS-decomposition*	Ethyl thiocyanate (**2**), *TS-isomerization*
C,0,-2.1169568315,-0.3398785633,-0.015411074	C,0,-2.3399269843,-0.2231522168,-0.08634002	C,0,-0.7776827485,-0.1063053463,-1.060473518	C,0,-0.2887184565,-0.5374758687,-0.40295944
C,0,-0.6256058405,-0.046438454,-0.0758225837	C,0,-0.8164622908,-0.1634087483,-0.0768501391	C,0,0.6107057812,0.0335270316,-1.1703937881	C,0,-1.674510632,-0.4401686742,0.1114000869
S,0,-0.0367427869,0.9843378193,1.3134223748	S,0,-0.3027628353,1.1355330482,1.104284797	S,0,1.6874576433,-0.0720177575,1.0605853991	N,0,0.0494601123,1.8127610345,-0.157927214
C,0,-0.9813111388,2.3557472384,1.0096032149	C,0,1.373259612,0.9904340708,0.9199626026	C,0,0.2037786195,-0.260471916,1.6115698129	C,0,0.6653632795,0.9774331084,0.4747401658
N,0,-1.6425196024,3.3140661177,0.808782365	N,0,2.5451114543,0.9013163915,0.8012043205	N,0,-1.0089727589,-0.3651844183,1.530148542	S,0,1.5745736364,0.0034824908,1.4392028267
H,0,-2.6991930338,0.5821568279,-0.08588694	H,0,-2.7726060881,0.7292030387,-0.4035335581	H,0,-1.3882267043,0.7827700088,-1.203036448	H,0,0.2530900193,-1.4315526338,-0.133825914
H,0,-2.3767245019,-0.8422727869,0.9194002887	H,0,-2.7335651328,-0.473805617,0.9021047767	H,0,-1.2168656625,-1.0514027898,-1.37265735	H,0,-0.0881269582,-0.1825140423,-1.40737804
H,0,-2.3991502815,-0.9880212644,-0.8506851217	H,0,-2.6673281838,-0.9949602698,-0.7877041597	H,0,1.0349041405,1.0194831124,-1.3264062035	H,0,-2.1833103516,-1.3347929256,-0.28380136
H,0,-0.0365254277,-0.9631637091,0.0227723575	H,0,-0.3889874735,-1.1142950832,0.2461679219	H,0,1.2058536141,-0.8123327257,-1.497096151	H,0,-2.1792755492,0.4610403561,-0.227940160
H,0,-0.3416065549,0.4398567746,-1.0116048809	H,0,-0.4281410777,0.0927863858,-1.0641865417	H,0,-1.0907009245,-0.2596851991,0.285122712	H,0,-1.6998381002,-0.5076898453,1.200272060

Table SI-5 continud….

Ethyl selenocyanate (**3**), *gauche*-conformation	Ethyl selenocyanate (**3**), *anti*-conformation	Ethyl selenocyanate (**3**), *TS-decomposition*	Ethyl selenocyanate (**3**), *TS-isomerization*
C,0,-2.1242018422,-0.3493055266,-0.0182811242 C,0,-0.6253491611,-0.102078761,-0.1023341277 Se,0,0.0715518677,0.9922158303,1.3830297374 C,0,-0.9964431718,2.4506380327,1.0277372319 N,0,-1.6872951908,3.3832247766,0.8037305819 H,0,-2.6788333335,0.5903887695,-0.0795144465 H,0,-2.3878236118,-0.8470180431,0.9179480938 H,0,-2.4370786383,-0.9850909158,-0.8531013158 H,0,-0.0518135523,-1.029881465,-0.0126715068 H,0,-0.3390483659,0.3932993024,-1.0319741241	C,0,-2.2323546536,-0.9883079823,-0.8607960119 C,0,-0.7082528486,-0.9378162842,-0.8482967772 Se,0,-0.1328059811,0.4587925663,0.4225582521 C,0,1.6740567194,0.2156680607,0.1583373006 N,0,2.8345690476,0.0653861079,-0.006362705 H,0,-2.6598344937,-0.0339948756,-1.1806163315 H,0,-2.630477734,-1.2360156387,0.1270101805 H,0,-2.5642748292,-1.7590168661,-1.5621006256 H,0,-0.2744296018,-1.8810746278,-0.5135898053 H,0,-0.3037947403,-0.6751249962,-1.8267635708	C,0,-0.7872732487,-0.1055091581,-1.07651276 C,0,0.5945627994,0.0366925505,-1.2181432974 Se,0,1.8166567685,-0.0689692176,1.150481584 C,0,0.1683220021,-0.2691153749,1.6652115868 N,0,-1.0366942146,-0.3677249079,1.517158543 H,0,-1.4011177772,0.7830762742,-1.20973195 H,0,-1.2295663996,-1.0527438747,-1.37855471 H,0,1.028584867,1.0217147487,-1.3533241588 H,0,1.1997986489,-0.8104661652,-1.522970935 H,0,-1.0930224461,-0.258574875,0.2837491138	C,0,-0.3052367012,-0.5389365853,-0.421389058 C,0,-1.6844395921,-0.4457728435,0.1113345336 N,0,0.0583894783,1.8248189867,-0.2049841088 C,0,0.6547277757,1.0013316363,0.4512436614 Se,0,1.6498916493,-0.0217818869,1.5591381703 H,0,0.2623664113,-1.4155267742,-0.148483348 H,0,-0.1180931853,-0.1805399831,-1.427147004 H,0,-2.1975561898,-1.3341244086,-0.293408377 H,0,-2.1940368138,0.4583497673,-0.213662105 H,0,-1.6973058326,-0.5272949087,1.19914063