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Quantum chemical comparison of ethynylation and C-vinylation routes in superbase catalyzed reaction of acetylenes with imines

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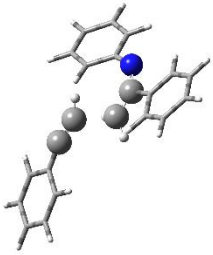
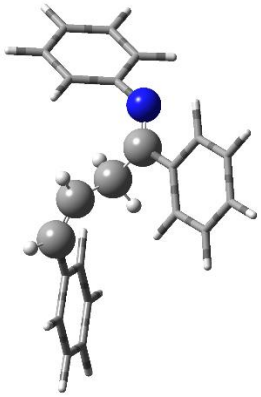
Total energy calculated in the frame of B2PLYP/6-311+G**//B3LYP/6-31+G* (*E*, a.u.) and Cartesian coordinates (Å) of some points on PES

Cartesian coordinates				Transition state
C	2.8453140	-1.5213490	-0.9240270	
C	2.1287790	-1.0991380	0.2202590	
C	2.8614720	-0.4746580	1.2529070	
C	4.2370600	-0.2671790	1.1396360	
C	4.9329390	-0.6888260	0.0005170	
C	4.2217610	-1.3206080	-1.0276300	
N	0.7832110	-1.4011940	0.4083240	
C	-0.1627810	-0.9516690	-0.3808910	
C	-0.0709790	0.1025780	-1.3744410	
C	-1.5220680	-1.5452630	-0.1372120	
C	-1.6406390	-2.8717470	0.3111700	
C	-2.8941970	-3.4510150	0.5165830	
C	-4.0576310	-2.7064890	0.2893430	
C	-3.9495320	-1.3798860	-0.1397270	
C	-2.6950660	-0.8003330	-0.3547680	
O	-1.4162040	2.2893530	-0.7627560	**TS**$_{1\rightarrow3}$, *E*(B2PLYP) = -828.6156941 a.u.,
C	-0.8708750	3.2810280	0.0493530	I_1 137cm^{-1}
C	0.4327470	3.8502170	-0.5709650	$\Delta H_1^{\ddagger}$ = 3.1 kcal mol^{-1}
C	-1.9032430	4.4265860	0.1728200	$\Delta G_1^{\ddagger}$ = 10.2 kcal mol^{-1}
C	-0.5597120	2.7336810	1.4667900	
H	2.3240170	-0.1570050	2.1428390	
H	2.3002910	-2.0141260	-1.7252160	
H	4.7709330	0.2267860	1.9502340	
H	4.7452830	-1.6602520	-1.9205390	
H	6.0059860	-0.5307580	-0.0841580	
H	0.9508670	0.3667360	-1.6559930	
H	-0.6914520	-0.0790620	-2.2589700	
H	-0.6648800	1.2283110	-0.9566330	
H	-0.7304730	-3.4341960	0.4986800	
H	-2.6173560	0.2437750	-0.6493410	
H	-2.9644190	-4.4833440	0.8559350	
H	-4.8466550	-0.7846710	-0.3004100	
H	-5.0367600	-3.1541700	0.4518300	
H	-2.8324810	4.0410440	0.6113330	
H	-1.5361150	5.2545620	0.7998000	
H	-2.1395890	4.8197480	-0.8242210	
H	0.1647130	1.9126750	1.4069990	
H	-0.1485690	3.5075970	2.1338490	
H	-1.4778100	2.3367450	1.9181380	
H	0.2221090	4.2344090	-1.5774370	
H	0.8634890	4.6647070	0.0321940	
H	1.1859150	3.0584490	-0.6634300	
C	2.8929960	1.1177670	-0.2024830	
C	1.8693470	0.2088290	0.1244990	
C	2.2129450	-1.1545710	0.1906010	
C	3.5234010	-1.5857420	-0.0267750	
C	4.5322930	-0.6669360	-0.3384170	
C	4.2043060	0.6896650	-0.4301410	
C	0.4466450	0.6448730	0.3815230	
C	0.2514530	1.9226380	0.8656010	
N	-0.4454390	-0.3597630	0.1693310	
C	-1.7905840	-0.2016430	0.0493760	
C	-2.6085150	-1.3610880	0.2448420	
C	-3.9878690	-1.3391780	0.0813040	
C	-4.6544630	-0.1625240	-0.3044160	**3**, *E*(B2PLYP) = -595.0915257 a.u.,
C	-3.8796310	0.9848110	-0.5212020	ΔH = –0.4 kcal mol^{-1}
C	-2.4959040	0.9818240	-0.3423710	
H	-1.9347050	1.8876440	-0.5442310	

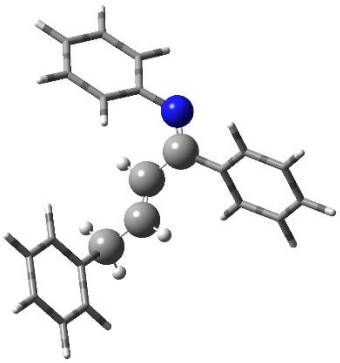
H	-2.0996450	-2.2810060	0.5266170	ΔG = 0.0 kcal mol^{-1}
H	-4.3654130	1.9099260	-0.8360680	
H	-4.5584010	-2.2529680	0.2528890	
H	-5.7353890	-0.1435770	-0.4299640	
H	-0.7312230	2.2903680	1.1365250	
H	1.0937360	2.5523450	1.1350130	
H	1.4171920	-1.8581260	0.4111850	
H	2.6524530	2.1722070	-0.3031720	
H	3.7583560	-2.6473250	0.0419030	
H	4.9699590	1.4192780	-0.6910440	
H	5.5526280	-1.0027850	-0.5166160	
C	4.2310770	-1.4020240	0.1349990	
C	3.6379140	-0.1375000	0.4110970	
C	4.4259570	1.0184000	0.1465340	
C	5.7161250	0.9093280	-0.3635180	
C	6.2835290	-0.3452880	-0.6302480	
C	5.5223720	-1.4956020	-0.3747040	
C	2.3415710	-0.0343940	0.9510930	
C	1.1077420	0.0675570	1.1008410	
C	-0.8382510	2.9137080	0.0323390	
C	-1.8423400	1.9475490	-0.1674470	
C	-3.1776500	2.3928790	-0.2028420	
C	-3.4939840	3.7456800	-0.0724300	
C	-2.4833580	4.6961740	0.1143140	**TS$_{3\rightarrow7}$**, E(B2PLYP) = -903.2793896 a.u.,
C	-1.1535660	4.2686610	0.1708430	I 254 cm^{-1}
C	-1.5283560	0.4844480	-0.3290260	$\Delta H^{\ddagger}$ = 20.0 kcal mol^{-1}
C	-0.2214340	0.1405550	-0.7330020	$\Delta G^{\ddagger}$ = 21.8 kcal mol^{-1}
N	-2.5640900	-0.3123090	-0.0454040	
C	-2.5422530	-1.6881670	-0.0346750	
C	-3.7542120	-2.3532720	-0.3737680	
C	-3.8729430	-3.7389760	-0.3373200	
C	-2.7923580	-4.5403050	0.0612650	
C	-1.5962340	-3.9094070	0.4224180	
C	-1.4621780	-2.5207560	0.3723150	
H	-0.5271770	-2.0695420	0.6845240	
H	-4.5981660	-1.7326550	-0.6663320	
H	-0.7470240	-4.5080160	0.7510360	
H	-4.8189730	-4.2021110	-0.6168400	
H	-2.8832710	-5.6240190	0.0943790	
H	-0.0109220	-0.8790790	-1.0353740	
H	0.3829350	0.8948730	-1.2252420	
H	-3.9537190	1.6463000	-0.3339640	
H	0.1980870	2.5992080	0.1047340	
H	-4.5355670	4.0609560	-0.1144370	
H	-0.3546960	4.9904130	0.3325760	
H	-2.7293040	5.7511770	0.2209390	
H	3.9996060	1.9972600	0.3501810	
H	3.6522990	-2.3015640	0.3273830	
H	6.2885810	1.8150470	-0.5583780	
H	5.9423830	-2.4793190	-0.5789640	
H	7.2925280	-0.4246270	-1.0279640	
H	0.3080030	0.1363640	1.8150990	

C	2.7592240	-1.8276680	-0.5813820
C	3.0099270	-1.0974800	0.5967290
C	4.3484310	-0.7764690	0.9001440
C	5.3906410	-1.1355300	0.0460780
C	5.1214200	-1.8438950	-1.1294340
C	3.8031740	-2.1940720	-1.4336890
C	1.9543600	-0.6846770	1.5403980
C	0.6729700	-0.3499610	1.2964200
C	0.6109460	2.6057150	-0.1644530
C	-0.7369010	2.2093850	-0.1130210
C	-1.7275850	3.2102120	-0.0885660
C	-1.3815800	4.5583760	-0.1177710
C	-0.0353330	4.9402340	-0.1714340
C	0.9573310	3.9595030	-0.1948500
C	-1.1372830	0.7694910	-0.0881500
C	-0.0388370	-0.2906120	-0.0376590
N	-2.3930930	0.5026510	-0.1446720
C	-2.9368760	-0.7906690	-0.0798390
C	-3.7218700	-1.2453360	-1.1554080
C	-4.3406050	-2.4940140	-1.1002370
C	-4.2194400	-3.2980410	0.0388490
C	-3.4661240	-2.8387030	1.1224210
C	-2.8258500	-1.5984480	1.0668420
H	-2.2529740	-1.2411650	1.9180990
H	-3.8339370	-0.6071370	-2.0276250
H	-3.3727590	-3.4471460	2.0188470
H	-4.9316360	-2.8354060	-1.9467460
H	-4.7141050	-4.2645340	0.0841300
H	-0.4994990	-1.2603230	-0.2606790
H	0.6810020	-0.0963140	-0.8419540
H	-2.7680640	2.9057740	-0.0489460
H	1.4036040	1.8659140	-0.1750120
H	-2.1618070	5.3152660	-0.0982230
H	2.0058480	4.2433780	-0.2356440
H	0.2347540	5.9930990	-0.1937670
H	4.5664650	-0.2304150	1.8156710
H	1.7484670	-2.1450550	-0.8156850
H	6.4132730	-0.8676920	0.2999980
H	3.5853490	-2.7647250	-2.3331340
H	5.9318750	-2.1306390	-1.7945180
H	0.0707570	-0.0663490	2.1590340
H	2.2841930	-0.6091420	2.5769230



8, *E*(B2PLYP) = -903.9174604 a.u.,
ΔH = –32.7 kcal mol^{-1}
ΔG = –26.9 kcal mol^{-1}

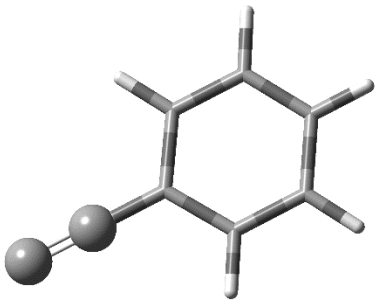
C	-3.3274290	1.2096820	0.1722580
C	-3.3038090	0.0897920	-0.6725280
C	-4.3596240	-0.8280540	-0.5968740
C	-5.4146740	-0.6351960	0.3006940
C	-5.4280220	0.4842070	1.1359610
C	-4.3802580	1.4083310	1.0675790
C	-2.1406800	-0.1262550	-1.6307760
C	-0.9073670	-0.6447190	-0.9336360
C	1.3291120	-2.9148080	-0.8869040
C	1.7140400	-1.9282490	0.0362140
C	2.3601050	-2.3264470	1.2189450
C	2.6003760	-3.6751840	1.4792960
C	2.2129980	-4.6499580	0.5536470
C	1.5835420	-4.2647430	-0.6328320
C	1.5011550	-0.4710380	-0.2246260
C	0.2788290	-0.0122530	-0.9229250
N	2.4415640	0.3268090	0.1627750
C	2.3365120	1.7265610	0.0956290
C	3.3504140	2.4472590	-0.5616310
C	3.3239300	3.8415030	-0.5863120
C	2.3100920	4.5445910	0.0745210
C	1.3182580	3.8349120	0.7576960



10, *E*(B2PLYP) = -903.9202614 a.u.,
ΔH = –35.4 kcal mol^{-1}
ΔG = –29.9 kcal mol^{-1}

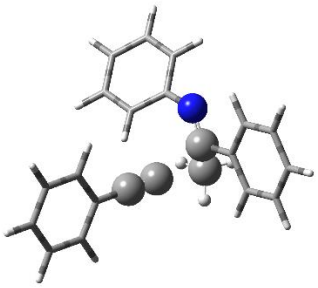
C	1.3237870	2.4383560	0.7664630
H	0.5602880	1.8896300	1.3111590
H	4.1498460	1.8960440	-1.0490800
H	0.5349940	4.3698360	1.2900370
H	4.1073250	4.3824860	-1.1117440
H	2.3011470	5.6312890	0.0673370
H	0.3672200	0.9476920	-1.4295550
H	2.6720640	-1.5630930	1.9249370
H	0.8520140	-2.6248210	-1.8181810
H	3.0917060	-3.9667600	2.4042050
H	1.2926210	-5.0143640	-1.3645380
H	2.4033390	-5.7012630	0.7547020
H	-4.3606900	-1.6995680	-1.2489630
H	-2.5144080	1.9314060	0.1258700
H	-6.2261880	-1.3575570	0.3427820
H	-4.3841160	2.2849240	1.7108230
H	-6.2486160	0.6379520	1.8320450
H	-1.0287980	-1.5806330	-0.3892660
H	-2.4472220	-0.8499250	-2.3997080
H	-1.9011910	0.8093270	-2.1514430

C	0.0517430	1.2074850	-0.0000600
C	-0.7009520	-0.0000740	-0.0003500
C	0.0518140	-1.2075420	-0.0000530
C	1.4459160	-1.2048130	0.0000610
C	2.1631350	0.0000550	0.0000550
C	1.4458300	1.2048860	0.0000630
C	-2.1203660	-0.0000950	-0.0000440
C	-3.3751570	0.0000820	0.0002430
H	-0.4939190	-2.1477240	0.0000090
H	-0.4940980	2.1476060	0.0000180
H	1.9823570	-2.1538290	0.0001610
H	1.9822240	2.1539330	0.0001670
H	3.2516620	0.0001030	0.0001580



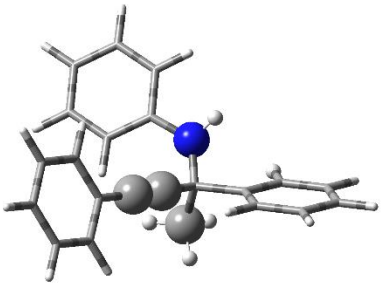
4, *E*(B2PLYP) = -307.594805 a.u.,
ΔH = –7.6 kcal mol^{-1}
ΔG = –2.1 kcal mol^{-1}

C	-3.5321730	-0.6466760	-1.2074010
C	-3.1521740	-0.2506570	0.0982410
C	-4.1766430	-0.1634520	1.0719430
C	-5.5035360	-0.4559330	0.7566590
C	-5.8588440	-0.8460030	-0.5402990
C	-4.8601600	-0.9379550	-1.5177450
C	-1.7938580	0.0453920	0.4142880
C	-0.6124310	0.3048930	0.6834800
C	1.0155290	3.0450730	1.0059390
C	1.4663630	2.0303830	0.1459620
C	1.8880350	2.4009760	-1.1402140
C	1.8573380	3.7344660	-1.5551580
C	1.4111580	4.7360010	-0.6873840
C	0.9900290	4.3807160	0.5980460
C	1.5473740	0.5765490	0.5775850
C	1.8109130	0.3475360	2.0666840
N	2.0888900	-0.2183000	-0.3283410
C	2.2750560	-1.5745630	-0.1763710
C	3.4270370	-2.1652600	-0.7580980
C	3.6455590	-3.5402070	-0.7108100
C	2.7150280	-4.3930690	-0.0998770
C	1.5598660	-3.8304750	0.4575860
C	1.3378190	-2.4530910	0.4291100
H	0.4218110	-2.0370270	0.8374890
H	4.1413400	-1.5064790	-1.2474430
H	0.8135200	-4.4756440	0.9204440
H	4.5482370	-3.9537170	-1.1600660



TS$_{4\rightarrow5}$, *E*(B2PLYP) = -903.2750798 a.u.,
I 188 cm^{-1}
$\Delta H^{\ddagger}$ = 13.7 kcal mol^{-1}
$\Delta G^{\ddagger}$ = 20.9 kcal mol^{-1}

H	2.8823180	-5.4678540	-0.0680310
H	1.7694610	-0.7159100	2.3070630
H	2.8238760	0.7127160	2.2979230
H	1.0918690	0.8646010	2.7034420
H	2.2392890	1.6146260	-1.7996400
H	0.6479880	2.7886940	1.9939660
H	2.1864150	3.9920320	-2.5607540
H	0.6277290	5.1444620	1.2841350
H	1.3874660	5.7761040	-1.0076960
H	-3.9062890	0.1388450	2.0802650
H	-2.7606140	-0.7210050	-1.9687280
H	-6.2673800	-0.3792250	1.5291240
H	-5.1187900	-1.2405310	-2.5313240
H	-6.8941890	-1.0744650	-0.7847760
C	3.4180050	-0.4262070	-0.9334410
C	2.6648680	-1.1304690	0.0275620
C	3.2923500	-2.1476030	0.7743320
C	4.6368210	-2.4510860	0.5616340
C	5.3763240	-1.7471550	-0.3942260
C	4.7622400	-0.7348990	-1.1387910
C	1.2859640	-0.8113010	0.2405400
C	0.1167980	-0.5293090	0.4088320
C	-1.8541220	-2.4471980	-0.3322330
C	-2.2768720	-1.1907970	0.1163150
C	-3.6523020	-0.9039240	0.1143180
C	-4.5785360	-1.8504010	-0.3276770
C	-4.1466610	-3.1040660	-0.7712160
C	-2.7822250	-3.3976880	-0.7706310
C	-1.2872250	-0.1236350	0.6429700
C	-1.5260410	0.0346440	2.1725300
N	-1.6214340	1.1330560	-0.0660670
C	-0.8748050	2.3220200	-0.0668780
C	-1.2421360	3.3123950	-1.0040320
C	-0.5895700	4.5406360	-1.0476780
C	0.4518360	4.8260910	-0.1567320
C	0.8257460	3.8502920	0.7675610
C	0.1804230	2.6104050	0.8170350
H	0.5238750	1.8702610	1.5278040
H	-2.0579620	3.1096040	-1.6959230
H	1.6402620	4.0427800	1.4620980
H	-0.8990450	5.2803820	-1.7823270
H	0.9610970	5.7851990	-0.1883030
H	-0.8644910	0.7838760	2.6113010
H	-2.5609720	0.3394990	2.3504710
H	-1.3463810	-0.9220660	2.6724010
H	-3.9997850	0.0667740	0.4566360
H	-0.7950330	-2.6836340	-0.3440180
H	-5.6383150	-1.6076380	-0.3229820
H	-2.4320130	-4.3670870	-1.1164650
H	-4.8671850	-3.8421460	-1.1143510
H	2.7174060	-2.6916730	1.5183040
H	2.9390030	0.3607370	-1.5084870
H	5.1085760	-3.2381130	1.1445100
H	5.3320390	-0.1831330	-1.8820850
H	6.4241810	-1.9854750	-0.5572300
H	-2.0405010	0.9459880	-0.9694550



6, *E*(B2PLYP) = -903.8858109 a.u.,
ΔH = –13.0 kcal mol^{-1}
ΔG = –7.5 kcal mol^{-1}

Computational details

The modeling of interactions between (*E*)-*N*,1-diphenylethanimine and phenylacetylene has been carried out within the anionic model, which neglects the presence of a remote cation and considers the solvation medium as a polarizable continuum only. We demonstrated, that in the presence of the nearest solvation shell of non-dissociated base, *i.e.* with a much more comprehensive definition of the superbase system, the main transformations of both ethynylation and C-vinylation occur at a significant distance from the cationic center, reaching 2.5–5.0Å, *i.e.* periphery of the reaction complex.[1,2,3] For these reasons we used a simple anionic model. Moreover, the modeling reaction pair is a large system, and the anionic model can be the only model that has a reasonable ratio of characteristics of the calculation accuracy and the resource consumption.

The structural parameters of the investigated systems were optimized using the density functional theory (DFT) at the B3LYP[4,5,6] level of theory with the 6-31+G* basis set. The vibrational corrections to enthalpies and Gibbs free energies were calculated at the same level of theory (B3LYP/6-31+G*) at a standard temperature 298.15 K. For all the stationary points, the number of negative eigenvalues of the Hessian matrix was analyzed. The connection of transition states, found with the corresponding PES minima, was proved by the reaction coordinate following the local quadratic approximation (LQA) algorithm.[7] Further, the energies at the stationary points were refined using the double hybrid functional B2PLYP[8] in combination with the extended 6-311+G**. This B2PLYP//B3LYP approach was used in the investigation of the ethynylation of the carbonyl group and C-vinylation of the ketone carbanion.[9] We checked both $\mathbf{TS_{4\rightarrow 5}}$ (for ethynylation) and $\mathbf{TS_{3\rightarrow 7}}$ (for C-vinylation) transition states with the STABLE keyword as implemented in G-09, and the wave functions of these key transition states were found to be stable under the perturbations considered. In addition, according to our calculations, the dispersion correction effect results in the changes of the relative thermodynamic stability for the starting compounds only by 0.4 kcal mol^{-1} and as well leads to minor increase in the activation barriers with the difference up to 1.4 kcal mol^{-1} (Table S1).

Table S1 Gibbs free energy change during the transformation of the phenylethynide ion **4** and imine **1** into phenylacetylene **2** and imine carbanion **3** (ΔG) as well as the activation barriers for ethynylation and C-vinylation calculated relative to structures **4** and **1**.

Method	ΔG/kcal mol^{-1}	$\Delta G_1^{\ddagger}$/kcal mol^{-1}	$\Delta G_2^{\ddagger}$/kcal mol^{-1}
B2PLYP/6-311+G** //B3LYP/6-31+G*	2.1	20.9	21.8
B2PLYPD/6-311+G** //B3LYP/6-31+G*	2.5	21.9	23.2
Difference	0.4	1.0	1.4

Solvation energy in DMSO was calculated additionally by the polarizable dielectric model using the IEFPCM.[10] To estimate activation free energy in the solution, we used the approach based on results of Wertz[11] suggested in article.[12]

The Wertz method for DMSO solutions is composed of several steps. First, a solute is treated as an ideal gas and compressed from 1 atm to a hypothetical ideal gas state with the concentration

equal to that in the liquid state (d = 1.100 g ml^{-1}, 298 K, 14.08 mol l^{-1}). This entropy change can be estimated as follows:

$$\Delta S_1 = -R\ln\frac{P_2}{P_1} = -R\ln\left(22.4\cdot 14.08\right) = -47.85 \quad \text{J mol}^{-1}\ \text{K}^{-1}\ .$$

The next step is the conversion of this hypothetical state to the final liquid state. The fraction of entropy lost in the second step is defined as a coefficient α:

$$\alpha = \frac{\Delta S_2}{S_\text{g}} = \frac{S_\text{g} - S_\text{l}^0}{S_\text{g}} = \frac{S_\text{g}^0 + \Delta S_1 - S_\text{l}^0}{S_\text{g}},$$

$$\Delta S_2 = \alpha S_\text{g} = \alpha S_\text{g}^0 + \alpha\Delta S_1$$

The entropy of liquid DMSO S_l^0 = 188.78 J mol^{-1} K^{-1} (standard state).[13] The entropy of vaporization can be estimated from its normal heat of vaporization (52.9 kJ mol^{-1})[14] and boiling temperature (462 K at 1 atm) as ΔS_vap^0 = 114.2 J mol^{-1} K^{-1}, therefore, S_g^0 = 303.0 J mol^{-1} K^{-1} and α = 0.26.

The entropy change from the gas state of *any* given molecule **M** in standard state to its 1 mol l^{-1} state in DMSO is composed of three steps. The first is the compression of ideal gas **M** in standard state to a hypothetical ideal gas state with the concentration equal to that of the *solvent* liquid state (14.08 mol l^{-1}), which gives the same ΔS_1 = –47.85 J mol^{-1} K^{-1}. Conversion of the hypothetical ideal gas state to a hypothetical liquid state brings $\Delta S_2 = \alpha S_\text{g} = \alpha S_\text{g}^0 + \alpha\Delta S_1$. The fraction of entropy loss in this step is assumed to be equal to α. Finally, expansion of the hypothetical liquid state to the 1 mol l^{-1} state in DMSO results in $\Delta S_3 = R\ln\left(14.08\right) = 21.99$ J mol^{-1} K^{-1}.

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