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Destabilization of Conjugated Systems of α-Dicarbonyls and of Cyanogen

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We are interested in enthalpies of hydrogenation obtained by the high level composite G3 model chemistry calculation. However, G3 yields a bond dissociation energy (BDE) for H_2 that is somewhat higher than the accurately known experimental value of 104.2 kcal mol^{-1}.

For A + B $\rightarrow$ C + D, the enthalpy of reaction is given by eq. 1, where 627.5 kcal mol^{-1} $hartree^{-1}$ is the conversion factor from hartrees to kcal mol^{-1} and H^{298} is the energy in hartrees for the assembly of the species involved from the separated nuclei and electrons.

$$\Delta H_{rxn} = 627.5(H^{298}[C] + H^{298}[D] - H^{298}[A] - H^{298}[B]) \text{ kcal mol}^{-1} \qquad (1)$$

For H–H $\rightarrow$ 2 $H^{\cdot}$, BDE = 627.5{2($H^{298}[H^{\cdot}]$ – ($H^{298}[H_2]$} = 627.5{2(–0.498642) – (–1.164074) = 104.66 kcal mol^{-1}, where the H^{298} values are from reference 1. The result is 0.46 kcal mol – 1 greater than the well established experimental values of 104.20.

Because our G3 simulations of hydrogenations involve $H^{298}[H_2]$ multiple times we require a value of $H^{298}[H_2]$ that is consistent with experiment. Therefore we calibrated its value to –1.163350 hartrees, which results in the correct BDE[H–H]. Using reported[1] G3 values of H^{298} for all other species in reactions 1–16 below, we obtain the results shown. G3 calculations of various experimentally known enthalpies of hydrogenation (ΔH_{hyd}) of relevant alkenes, alkynes, ketones, imines and nitriles were tested with the calibrated $H^{298}[H_2]$ and the results obtained are in good agreement with experiment. Experimental values are derived from enthalpies of formation given in reference 2 in kcal mol^{-1}.

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(1) *Computational Chemistry Comparison and Benchmark Database*, release 15, 2010. NIST Standard Reference Database 101, National Institute of Standards and Technology: Gaithersburg, MD 20899, USA. (http://cccbdb.nist.gov/).
(2) All experimental values from: Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry Webbook*; NIST Standard Reference Database No. 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD 20899, USA. (http://webbbok.nist.gov/).

1) $CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3$
$\Delta H_{hyd} = 627.5(-79.718912 + 78.503424 + 1.163550) = -32.72$ vs. experimental -32.5 ± 0.1

2) $CH_2{=}CHCH_3 + H_2 \rightarrow CH_3CH_2CH_3$
$\Delta H_{hyd} = 627.5(-118.988320 + 117.777080 + 1.163350) = -30.05$ vs. experimental -29.90 ± 0.12

3) *trans*-$CH_3CH{=}CHCH_3 + H_2 \rightarrow CH_3CH_2CH_2CH_3$
$\Delta H_{hyd} = 627.5(-158.256913 + 157.050304 + 1.163350) = -27.15$ vs. experimental -27.45 ± 0.16

4) *cis*-$CH_3CH{=}CHCH_3 + H_2 \rightarrow CH_3CH_2CH_2CH_3$
$\Delta H_{hyd} = 627.5(-158.256913 + 157.048208 + 1.163350) = -28.46$ vs. experimental -28.20 ± 0.16

5) $CH_3C{\equiv}CH + H_2 \rightarrow CH_3CH_2CH_3$
$\Delta H_{hyd} = 627.5(-118.988320 + 116.550504 + 1.163350) = -69.73$ vs. experimental -69.34 ± 0.24

6) $C{\equiv}O + H_2 \rightarrow H_2C{=}O$
$\Delta H_{hyd} = 627.5(-114.427250 + 113.264064 + 1.163350) = +0.10$ vs. experimental -0.4 ± 0.4

7) $CH_3C(O)H + H_2 \rightarrow CH_3CH_2OH$
$\Delta H_{hyd} = 627.5(-154.899442 + 153.709879 + 1.163550) = -16.45$ vs. experimental -15.2 ± 0.6

8) $CH_3C(O)CH_3 + H_2 \rightarrow CH_3CH(OH)CH_3$
$\Delta H_{hyd} = 627.5(-194.175950 + 192.990776 + 1.163350) = -13.69$ vs. experimental -13.7 ± 0.3

9) $CH_3C(O)CH_2CH_3 + 2\ H_2 \rightarrow CH_3CH_2CH_2CH_3 + H_2O$
$\Delta H_{rxn} = 627.5(-158.256913 - 76.378266 + 232.260896 + 1.163350) = -29.86$ vs. experimental -30.81 ± 0.28

10) $CH_3C(O)C(O)CH_3 + 4\ H_2 \rightarrow CH_3CH_2CH_2CH_3 + 2\ H_2O$
$\Delta H_{rxn} = 627.5\{-158.256913 + 2(-76.378266) + 306.255567 + 4(1.163350)\} = -65.56$ vs. experimental -67.53

11) $CH_3C(O)C(O)CH_3 + 2\ H_2 \rightarrow CH_3C(O)CH_2CH_3 + H_2O$
$\Delta H_{rxn} = 627.5\{-232.260896 - 2(-76.378266) + 2(1.163350)\} = -35.70$ vs. experimental -36.7

12) $2\ CH_3C(O)CH_2CH_3 + 2\ H_2 \rightarrow 2\ CH_3CH_2CH_2CH_3 + O_2$
$\Delta H_{rxn} = 627.5\{2(-158.256913) - 150.\ 244899 + 2(232.260896) + 2(1.163350)\} = +56.33$ vs. experimental $+53.98 \pm 0.23$

13) $CH_3C(O)C(O)CH_3 + 2\ H_2 \rightarrow CH_3CH_2CH_2CH_3 + O_2$
$\Delta H_{rxn} = 627.5\{-158.256913) - 150.\ 244899 + 306.255567 + 2(1.163350)\} = +50.49$ vs. experimental $+48.07$

14) $CH_2{=}NCH_3 + H_2 \rightarrow CH_3NHCH_3$
$\Delta H_{hyd} = 627.5(-135.015697 + 133.815891 + 1.163350) = -22.88$ vs. experimental -21.7

15) $CH_3C{\equiv}N + 2\ H_2 \rightarrow CH_3CH_2NH_2$
$\Delta H_{hyd} = 627.5\{-135.028174 + 132.655084 + 2(1.163350)\} = -29.11$ vs. experimental -29 ± 1

16) $CH_3CH(CH_3)C{\equiv}N + 2\ H_2 \rightarrow CH_3CH(CH_3)CH_2NH_2$
$\Delta H_{hyd} = 627.5\{-213.570033 + 211.195864 + 2(1.163350)\} = -29.79$ vs. experimental -29.2 ± 0.2

Use of the calibrated value of $H^{298}[H_2]$ produces results that are in acceptable agreement with experiment, within realistically expected uncertainties in both values. Reduction of double and triple bonds between two carbons, between carbon and oxygen, and between carbon and nitrogen are modeled satisfactorily.

The G3 theoretical results of the reactions 9 and 10 indicate that reduction of the carbonyl of 2-butanone releases –29.86 kcal mol^{-1} and reduction of both carbonyls of 2,3-butanedione releases –65.56, which is 5.8 kcal mol^{-1} greater than twice the value of one unconjugated carbonyl. This confirms the experimentally derived destabilization of 5.9 kcal mol^{-1} cited in the text of the article. Reactions 12 and 13 also confirm destabilizations of 5.8 kcal mol^{-1} by the G3 calculation and 5.9 from the experimental values. Reactions 14–16 also confirm that G3 calculations yield results consistent with experimental values for reductions of imine and nitrile functions relevant to Table 1 of the article.

The results of Table 1 of the article are based on our G3 calculations of H^{298} (see below) for $N{\equiv}CC{\equiv}N$, $H_2NCH_2C{\equiv}N$, and $H_2NCH_2CH_2NH_2$ and are obtained by using the calibrated $H^{298}[H_2] = -1.163350$ hartrees.

G3 Output Energies and Structural Parameters:

Table 1 Entry 1 NCCN

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.015680 E(Thermal)= 0.019458
E(QCISD(T))= -185.185683 E(Empiric)= -0.057474
DE(Plus)= -0.008868 DE(2DF)= -0.100770
E(Delta-G3)= -0.231268 E(G3-Empiric)= -0.057474
G3(0 K)= -185.568383 G3 Energy= -185.564605
G3 Enthalpy= -185.563661 G3 Free Energy= -185.589178
1\1\GINC-ABE0287\Mixed\G3\G3\C2N2\DROGERS\03-May-2010\0\\# g3\\cyanoge
n\\0,1\N,0,-1.7323425902,0.0541007517,0.\C,0,-0.5476439574,0.016289534
1,0.\C,0,0.8330009108,-0.020738533,0.\N,0,2.0180246368,-0.0463487527,0
.\\Version=AM64L-G03RevE.01\State=1-A'\MP2/6-31G(d)=-185.1575004\QCISD
(T)/6-31G(d)=-185.1856828\MP4/6-31G(d)=-185.1938751\MP2/6-31+G(d)=-185
.1660276\MP4/6-31+G(d)=-185.2027428\MP2/6-31G(2df,p)=-185.2525165\MP4/
6-31G(2df,p)=-185.2946454\MP2/GTLarge=-185.4923119\G3=-185.568383\Freq

Table 1 Entry 2 H2NCH2CN

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.061536 E(Thermal)= 0.066132
E(QCISD(T))= -187.562892 E(Empiric)= -0.070246
DE(Plus)= -0.013968 DE(2DF)= -0.142888
E(Delta-G3)= -0.237534 E(G3-Empiric)= -0.070246
G3(0 K)= -187.965992 G3 Energy= -187.961396
G3 Enthalpy= -187.960452 G3 Free Energy= -187.992528
1\1\GINC-ABE0151\Mixed\G3\G3\C2H4N2\DROGERS\04-May-2010\0\\# g3\\1,1-t
etrahydrocyanogen\\0,1\N,0,0.7348737328,-1.3967310616,-0.1114130647\C,
0,-0.0726593252,-0.21884375,0.1837619828\C,0,0.6857804634,1.0458933122
,0.2846875438\N,0,1.3396814072,2.0256772726,0.3545544394\H,0,1.4436435
435,-1.5202249662,0.6087561308\H,0,1.2314957554,-1.2649799456,-0.99019
35056\H,0,-0.8322968525,-0.1080170138,-0.5946505771\H,0,-0.6037727246,
-0.3823458476,1.1252760506\\Version=AM64L-G03RevE.01\State=1-A\MP2/6-3
1G(d)=-187.5163785\QCISD(T)/6-31G(d)=-187.5628921\MP4/6-31G(d)=-187.56

51003\MP2/6-31+G(d)=-187.5298131\MP4/6-31+G(d)=-187.5790681\MP2/6-31G(
2df,p)=-187.6512138\MP4/6-31G(2df,p)=-187.7079883\MP2/GTLarge=-187.902
1826\G3=-187.965992\FreqCoord=1.3988908798,-2.6172963788,-0.2075587863

Table 1 Entry 3 H2NCH2CH2NH2

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.106882	E(Thermal)=	0.112316
E(QCISD(T))=	-189.920338	E(Empiric)=	-0.083018
DE(Plus)=	-0.018843	DE(2DF)=	-0.185766
E(Delta-G3)=	-0.244433	E(G3-Empiric)=	-0.083018
G3(0 K)=	-190.345516	G3 Energy=	-190.340082
G3 Enthalpy=	-190.339138	G3 Free Energy=	-190.373019

1\1\GINC-ABE0493\Mixed\G3\G3\C2H8N2\DROGERS\04-May-2010\0\\# g3\\diami
noethane\\0,1\N,0,-1.7029738742,-0.3868056168,0.497720338\C,0,-0.98292
2837,0.4676765882,-0.4416329766\C,0,0.4753902812,0.5332549781,-0.02316
94737\N,0,1.0640580088,-0.8083129777,-0.1200854029\H,0,-2.6390754034,-
0.5843261839,0.1498196855\H,0,-1.2029556277,-1.2737503659,0.5406755607
\H,0,-1.4143046843,1.474392902,-0.4126294654\H,0,-1.0294144094,0.12892
59626,-1.4925585122\H,0,1.0005999503,1.2946608349,-0.6207863036\H,0,0.
5145877434,0.8429008669,1.024695279\H,0,1.2542791528,-1.0242772857,-1.
0976893571\H,0,1.9629876996,-0.8330167026,0.3567476282\\Version=AM64L-
G03RevE.01\State=1-A\MP2/6-31G(d)=-189.8584593\QCISD(T)/6-31G(d)=-189.
9203378\MP4/6-31G(d)=-189.9181851\MP2/6-31+G(d)=-189.8765662\MP4/6-31+
G(d)=-189.9370282\MP2/6-31G(2df,p)=-190.0338205\MP4/6-31G(2df,p)=-190.
1039514\MP2/GTLarge=-190.2963603\G3=-190.345516\FreqCoord=-3.246454509