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Use of DFT Methods for the Calculation of the Entropy of Gas Phase Organic Molecules: An Examination of the Quality of Results from a Simple Approach

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Entropy values for organic molecules can be calculated with useful accuracy using Gaussian 94 at the B3LYP/6-31G** level, provided the values are corrected for the number of low lying conformations by adding an entropy of mixing term. This has been tested by calculations on 128 organic compounds, with particular focus on relatively large molecules with up to 10 carbon atoms. The overall standard deviation is 1.28 (cal/K)/mol in entropy, equivalent to 0.38 kcal/mol in free energy at 25 °C, with only seven deviations greater than two standard deviations and only two greater than three standard deviations.

Introduction

Calculation of the free energy of formation of an organic compound requires both the enthalpy of formation and the standard entropy. In many cases neither is available, and entropy data seem to be less abundant than enthalpy data. For simple compounds there are excellent additivity methods[1,2] for estimating standard entropies of gaseous molecules. For more complex molecules with multiple functional groups there are often no values of the group contributions that would be required. Modern molecular orbital theory provides a way to calculate the vibrational frequencies of a molecule and thus to calculate the entropy by statistical mechanics. Programs such as Gaussian 94[3] provide a facility for calculating the entropy in this way, but the output carries warnings that the approximations involved may lead to serious errors. With readily available modern computers it is practical to carry out such calculations of entropy so it is of interest to examine how well these methods can work. It is important in such an examination to include large molecules because as molecules get larger the contribution of vibrations and internal rotations to the total entropy becomes larger, and thus the test of the approximations becomes more sensitive. A set of 128 molecules will be examined, including 35 C_5 compounds, 42 C_6, 21 C_7, 4 C_8, 2 C_9, and 5 C_{10} compounds. Calculated values will be compared to literature values, making extensive use of the compilation by Stull et al.[4]

East and Radom[5] carried out an extensive study of different levels of ab initio molecular orbital theory and different methods for calculating third law entropies and showed that entropies could be calculated to within 1 (J/K)/mol. Their methods involved fairly high levels of theory (ranging from MP2/6-31G(d) to MP2/6-311+G(2df,p)) and for their E2 and E3 approaches[6] rather elaborate treatment of the internal rotations. Their calculations were limited to relatively small molecules, the largest being toluene. Block et al.[7] suggested that the rigid rotor−harmonic oscillator approximation (used in calculations of the entropy by Gaussian 94) was adequate provided that one allowed for the entropy of mixing when a compound had more than one accessible conformation. Their work was concerned with small alcohols and derived radicals, the largest being 1-propanol or 2-propanol. My interest is in studying the reactions of organic molecules, and this leads to a need for free energies of formation of thermochemical accuracy, i.e., uncertainties ≤2 kcal/mol. This has led to an examination of methods for deriving enthalpies[8] and entropies from relatively small molecular orbital calculations. This paper will report an examination of how well a simple approach can do with molecules of up to 10 carbons. The approach will use the rigid rotor harmonic oscillator approximation, and make an approximate correction for the entropy of mixing when there is more than one conformation. Calculations will be at the B3LYP/6-31G**//B3LYP/6-31G**[9,10] level, using the implementation of DFT in Gaussian 94.

As such calculations become more commonly used, it is becoming common practice to use a molecular modeling program to set up the initial coordinates. Unless the resulting file is edited to impose exact symmetry on the molecule, the resulting optimized geometry will nearly but not exactly express the internal symmetry and the symmetry will not be recognized. The program tests for exact symmetry. This can lead to significant errors in entropy. It is essential to use the correct rotational symmetry number whether this is imposed by specifying exact symmetry or by correcting the value of entropy calculated using a symmetry number of 1.

Calculations

Entropies were calculated using the methods in Gaussian 94. Data files were created using PCModel,[11] endeavoring to find the lowest energy conformation in the process. Geometries were first optimized at the B3LYP/6-31G** level, and then a frequency calculation was carried out. The output was examined to ensure that there were no imaginary frequencies. This seemed to be particularly likely when there was a low barrier to rotation about a single bond. It was also necessary to ensure that the correct rotational symmetry number is used in calculating the entropy. If strict symmetry was imposed in the geometry specification, then Gaussian will calculate symmetry numbers and entropy correctly. If full geometry optimization was carried out without imposing symmetry, the final structure is likely to be almost but not perfectly symmetrical, and this approximate symmetry will not be recognized by the program, leading to an incorrect entropy. This is easily remedied by including the

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TABLE 1: Observed and Calculated Entropies[a]

compound	E: B3LYP/6-31G**[b]	n_{rot}[c]	S_{calc}[d]	S_{obs}[e]	diff[f]	n_{conf}[g]	$S_{calc\ corr}$[h]	diff[f]
acetone	−193.16421	2	72.02	70.49	−1.53	1	72.02	−1.53
methyl acetate	−268.3967	1	77.74	76.44[i]	−1.30	1	77.74	−1.30
acetylenedicarbonitrile	−261.81357	2	67.97	69.34	1.37	1	67.97	1.37
1,2-butadiene	−155.98475	1	69.18	70.03	0.85	2	70.56	−0.53
tert-butylamine	−213.82228	1	77.18	78.29[j]	1.11	1	77.18	1.11
1-butylamine	−213.8162	1	80.14	87.33[j]	7.19	27	86.70	0.63
2-butylamine	−213.81986	1	78.86	84.65[j]	5.79	9	84.61	0.04
diethylamine	−213.81301	1	79.85	84.18	4.33	9	84.22	−0.04
1-butanol	−233.67906	1	79.72	86.80	7.08	27	86.28	0.52
2-butanol	−233.68525	1	78.50	85.81	7.31	9	84.24	1.56
diethyl ether	−233.67710	2	78.31	81.90	3.59	9	82.69	−0.79
methyl propyl ether	−233.6715	1	79.80	83.52	3.72	9	84.18	−0.66
methyl isopropyl ether	−233.67460	1	79.14	80.86	1.72	3	81.33	−0.47
methyl isopropyl sulfide	−556.65674	1	83.45	85.87	2.42	3	85.64	0.23
diethyl sulfide	−556.65637	2	83.81	87.96	4.15	9	88.18	−0.22
2-butanethiol	−556.65694	1	82.13	87.65	5.52	9	87.88	−0.23
1-butanethiol	−556.65599	1	83.67	89.68	6.01	27	90.23	−0.55
methyl propyl sulfide	−556.65587	1	84.73	88.84	4.12	9	89.10	−0.26
tert-butyl mercaptan	−556.65862	1	80.44	80.79	0.35	1	80.44	0.35
diethyl disulfide	−954.85122	2	94.14	99.07	4.93	18	99.89	−0.82
undecafluoropiperidine	−1343.40671	1	115.33	116.10	0.77	1	115.33	0.77
pyridine	−248.29260	2	67.27	67.59	0.32	1	67.27	0.32
cyclopentadiene	−194.11069	2	65.33	64.00	−1.33	1	65.33	−1.33
glutaronitrile	−303.62548	1	85.54	88.10	2.57	9	89.91	−1.81
2-methylthiophene	−592.33067	1	76.79	76.62	−0.17	1	76.79	−0.17
3-methylthiophene	−592.33066	1	76.38	76.79	0.41	1	76.38	0.41
1,2-pentadiene	−195.30131	1	76.98	79.70	2.73	3	79.16	0.54
1,4-pentadiene	−195.30905	2	75.13	79.70	4.57	9	79.51	0.19
2-methyl-1,3-butadiene	−195.32253	1	74.22	75.44	1.22	2	75.60	−0.16
cis-1,3-pentadiene	−195.32199	1	75.95	77.50	1.55	2	77.33	0.17
2,3-pentadiene	−195.30538	1	77.69	77.60	−0.09	1	77.69	−0.09
cyclopentene	−195.33880	1	69.43	69.23	−0.20	1	69.43	−0.20
3-methyl-1-butene	−196.54997	1	77.66	79.70	2.05	3	79.84	−0.14
cis-2-pentene	−196.55248	1	79.62	82.76	3.14	3	81.80	0.96
cyclopentane	−196.57104	10	69.92	70.00	0.08	1	69.92	0.08
2-methyl-1-butene	−196.55387	1	78.36	81.15	2.79	3	80.55	0.60
2-methyl-2-butene	−196.55779	1	79.05	80.92	1.87	1	79.05	1.87
1-pentene	−196.54949	1	78.50	82.65	4.15	9	82.87	−0.22
trans-2-pentene	−196.55479	1	78.86	81.36	2.50	3	81.05	0.31
2-pentanone	−271.79829	1	88.37	89.91	1.54	3	90.56	−0.65
3-pentanone	−271.79932	2	86.33	88.44	2.11	1	86.33	2.11
pentanal	−271.78497	1	86.13	91.53	5.40	27	92.69	−1.16
valeric acid	−347.04072	1	90.76	94.79[k]	4.03	27	97.32	−2.53
thiacyclohexane	−594.766982	1	77.10	77.26	0.16	1	77.10	0.16
cyclopentanethiol	−594.757901	1	82.73	86.38	3.65	6	86.30	0.08
pentane	−197.78848	2	79.21	83.40	4.19	9	83.59	−0.19
isopentane	−197.78788	1	79.70	82.12	2.42	3	81.88	0.24
neopentane	−197.78979	12	72.44	73.23	0.79	1	72.44	0.79
2,2-dimethyl-1-propanol	−272.99734	1	84.17	88.67[k]	4.50	3	86.35	2.32
1-pentanol	−272.99564	1	87.20	96.21	9.01	81	95.95	0.26
ethyl propyl sulfide	−595.97289	1	92.61	98.97	6.36	9	96.98	1.99
tert-amyl mercaptan	−595.97247	1	88.04	92.48	4.44	9	92.41	0.07
1-pentanethiol	−595.97253	1	91.50	99.28	7.78	81	100.24	−0.96
butyl methyl sulfide	−595.97238	1	92.50	98.43	5.93	27	99.06	−0.63
hexafluorobenzene	−827.59694	12	91.88	91.59	−0.29	1	91.88	−0.29
o-dichlorobenzene	−1151.44210	2	81.72	81.61	−0.11	1	81.72	−0.11
m-dichlorobenzene	−1151.44590	2	82.04	82.09	0.05	1	82.04	0.05
p-dichlorobenzene	−1151.44607	4	80.67	80.47	−0.20	1	80.67	−0.20
o-difluorobenzene	−430.71504	2	76.63	76.94	0.31	1	76.63	0.31
m-difluorobenzene	−430.72132	2	76.49	76.57	0.08	1	76.49	0.08
p-difluorobenzene	−430.72017	4	75.16	75.43	0.27	1	75.16	0.27
benzoquinone	−381.45774	4	76.59	76.65	0.06	1	76.59	0.06
bromobenzene	−2803.36171	2	77.55	77.53	−0.02	1	77.55	−0.02
chlorobenzene	−691.85294	2	74.86	74.92	0.06	1	74.86	0.06
fluorobenzene	−331.49023	2	72.08	72.33	0.25	1	72.08	0.25
nitrobenzene	−436.75851	2	81.81	82.00[k]	0.18	1	81.81	0.18
benzene	−232.25821	12	64.07	64.34	0.27	1	64.07	0.27
phenol	−307.47847	1	74.59	75.43	0.84	1	74.59	0.84
thiophenol	−630.44523	1	80.22	80.51	0.29	1	80.22	0.29
aniline	−287.61650	1	75.54	76.28	0.74	1	75.54	0.74
2-picoline	−287.61619	1	78.69	77.68	−1.01	1	78.69	−1.01
3-picoline	−287.61387	1	78.65	77.67	−0.98	1	78.65	−0.98
cyclohexene	−234.66268	1	73.86	74.27	0.41	2	75.24	−0.97

TABLE 1 (Continued)

compound	*E*: B3LYP/6-31G**[b]	n_{rot}[c]	S_{calc}[d]	S_{obs}[e]	diff[f]	n_{conf}[g]	$S_{\mathrm{calc\ corr}}$[h]	diff[f]
1-methylcyclopentene	−234.66232	1	77.02	78.00	0.98	2	78.40	−0.40
3-methylcyclopentene	−234.65666	1	76.13	79.00	2.87	2	78.89	0.11
4-methylcyclopentene	−234.65655	1	76.09	78.60	2.52	2	77.46	1.14
cyclohexanone	−309.90523	1	79.64	80.04	0.40	1	79.64	0.40
cyclohexane	−235.89675	3	72.53	71.28	−1.25	1	72.53	−1.25
thiacycloheptane	−634.07351	1	84.44	86.50	2.06	1	84.44	2.06
2,3-dimethyl-1-butene	−235.86955	1	85.19	87.39	2.21	3	87.37	0.02
3,3-dimethyl-1-butene	−235.86556	1	82.46	82.16	−0.30	1	82.46	−0.30
3-methylpentane	−237.10282	1	87.22	90.77	3.55	9	91.59	−0.82
2,2-dimethylbutane	−237.10330	1	84.68	85.62	0.95	3	86.86	−1.24
hexane	−237.10501	2	86.70	92.83	6.13	27	93.26	−0.43
2,3-dimethylbutane	−237.10210	2	85.00	87.42	2.42	3	87.19	0.23
2-methylpentane	−237.10430	1	86.95	90.95	4.00	9	91.33	−0.38
hexanol	−312.31215	1	94.66	105.52	10.86	243	105.60	−0.08
diisopropyl ether	−312.31625	2	91.22	93.27	2.05	9	95.60	−2.33
dipropyl ether	−312.30992	2	93.68	100.98	7.30	81	102.42	−1.45
cyclohexanol	−311.11109	1	80.27	78.32	−1.95	1	80.27	−1.95
methyl pentyl sulfide	−635.28894	1	99.68	107.73	8.05	81	108.43	−0.70
dipropyl sulfide	−635.28938	2	99.03	107.16	8.13	81	107.77	−0.61
hexanethiol	−635.28907	1	98.47	108.58	10.11	243	109.40	−0.82
diisopropyl sulfide	−635.28811	2	95.32	99.30	3.98	9	99.70	−0.40
dipropyl disulfide	−1033.48411	2	108.92	118.30	9.38	162	119.05	−0.75
triethylamine	−292.43058	3	92.09	96.90	4.81	7	95.96	0.94
hexadecafluoroheptane	−1864.15115	2	153.35	158.88	5.53	1	153.35	5.53
α,α,α-trifluorotoluene	−569.29445	1	90.54	89.05	−1.49	1	90.54	−1.49
benzonitrile	−324.50008	2	77.18	76.73	−0.45	1	77.18	−0.45
benzaldehyde	−345.58268	1	79.46	80.31	0.85	1	79.46	0.85
p-fluorotoluene	370.81038	1	84.32	83.09	−1.23	1	84.32	−1.23
toluene	−271.57878	1	79.68	76.64	−3.04	1	79.68	−3.04
cycloheptatriene	−271.52196	1	75.40	75.44	0.04	1	75.40	0.04
p-cresol	−346.79838	1	84.72	83.09	−1.63	1	84.72	−1.63
benzyl alcohol	−346.78387	1	84.46	89.29[k]	4.83	3	86.65	2.64
anisole	−346.78332	1	81.79	83.31[l]	1.52	3	83.98	−0.67
1-heptyne	−273.92570	1	91.79	97.44	5.65	27	98.35	−0.91
trans-1,2-dimethylcyclopentane	−275.20728	1	86.28	87.67	1.39	1	87.66	0.01
trans-1,3-dimethylcyclopentane	−275.20688	1	86.77	87.67	0.90	1	88.15	−0.48
cis-1,2-dimethylcyclopentane	−275.20015	1	84.85	87.51	2.67	1	84.85	2.67
cis-1,3-dimethylcyclopentane	−275.20346	1	86.47	87.67	1.20	1	86.47	1.20
cycloheptane	−275.19925	1	81.38	81.82	0.44	1	81.38	0.44
1,1-dimethylcyclopentane	−275.20510	1	84.76	85.87	1.11	1	84.76	1.11
1-heptanol	−351.62348	1	102.09	114.83	12.74	729	115.21	−0.38
tert-butyl isopropyl ether	−351.62921	1	98.25	99.89	1.64	3	100.43	−0.54
heptanethiol	−674.60559	1	106.19	117.89	11.70	729	119.31	−1.42
butyl propyl sulfide	−674.60590	1	107.93	117.90	9.97	243	118.86	−0.96
methyl benzoate	−460.14066	1	93.00	95.14[l]	2.14	1	93.00	2.14
ethylbenzene	−310.89107	1	85.18	86.15	0.97	2	86.56	−0.41
m-xylene	−310.89924	2	89.61	85.49	−4.12	1	89.61	−4.12
di-*tert*-butyl ether	−390.94173	2	99.53	102.12	2.59	1	99.53	2.59
α-methylstyrene	−348.97963	1	87.99	91.70	3.72	2	89.37	2.34
2,2,4,4-tetramethylpentane	355.04226	2	100.68	103.13	2.45	1	100.68	2.45
naphthalene	−385.90538	8	77.82	80.22	2.40	1	77.82	2.40
decalin (trans)	−391.95885	1	90.52	89.52	−1.00	1	90.52	−1.00
m-diethylbenzene	−389.52843	2	100.50	104.99	4.49	9	104.87	0.12
durene, 1,2,4,5-tetramethylbenzene	−389.53918	4	96.47	100.03	3.56	1	96.47	3.56
1,2,3,4-tetramethylbenzene	−389.53390	2	101.25	99.55	−1.70	1	101.25	−1.70

[a] All at 25 °C; entropies in (cal/K)/mol; compounds are listed in order of increasing numbers of atoms, with carbon having highest priority and then H, Br, Cl, F, N, O, and S. [b] Energy of the optimized structure used for calculation of frequencies and entropy; B3LYP/6-31G**//B3LYP/6-31G**. [c] Rotational symmetry number. [d] Calculated entropy from Gaussian 94, corrected for the rotational symmetry number. [e] Observed entropy; taken from Stull et al.[4] unless otherwise noted. [f] diff $= S_{\mathrm{obs}} - S_{\mathrm{calc}}$. [g] $n_{\mathrm{conf}} =$ number of low-energy conformations used in calculating the entropy of mixing. [h] Calculated entropy, corrected for the entropy of mixing contribution from low-energy conformations and for the presence of enantiomers where appropriate. [i] Reference 19. [j] Reference 20. [k] Calculated from the entropy of the liquid, the heat of vaporization, and the vapor pressure as described in the text. [l] Reference 17.

contribution for the rotational symmetry number. The problem is particularly severe for the rare case of a linear molecule, where slight deviations from perfect linearity will lead to the use of the formula for a nonlinear molecule and a calculated entropy seriously in error. The point is that the program will optimize to almost the correct geometry, but not recognize the symmetry unless the symmetry is exact. Either the structure specification must impose exact symmetry or the final result must be corrected for the proper symmetry number.

For all compounds with more than one low lying conformation a correction for the entropy of mixing was included:

$$S^{\circ} = \sum_{i}^{n} x_i S_i + \Delta S_{\mathrm{mix}}$$

It will be assumed that S_i is effectively the same for all conformations and that the entropy of mixing can be approximated as

TABLE 2: Estimated and Calculated Entropies[a]

compound	*E*: B3LYP/6-31G**[b]	n_{rot} [c]	S_{calc} [d]	S_{est}	diff[e]	n_{conf} [f]	$S_{\text{calc corr}}$ [g]	diff[f]
1-chloro-3-methylbutane	−657.38193	1	87.39	95.56	8.17	9	91.76	3.80
4-vinylcyclohexene	−312.05814	1	86.21	96.40	10.19	4	88.97	7.43
				90.35[h]	4.14			2.76
1-bromopentane	−2768.89198	1	91.20	97.70	6.50	27	97.75	−0.05
2-chloro-2-methylbutane	−657.38681	1	85.02	88.06	3.04	3	87.20	0.86
2,3-dibromo-2-methylbutane	−5339.99946	1	96.15	98.60	2.45	3	98.34	0.26
N,*N*-diethylaniline	−444.86726	1	103.57	92.40	−11.17	9	107.94	−15.54
				109.17[h]	−5.60			−1.23
N-methylaniline	−326.92508	1	83.09	81.60	−1.49	1	83.09	−1.49
N,*N*-dimethylaniline	−366.23104	1	90.66	87.50	−3.16	1	90.66	−3.16
4-ethylheptane	−355.04721	1	108.61	118.52	9.91	243	119.54	−1.02

[a] All at 25 °C; entropies in (cal/K)/mol. Estimated values from ref 4 unless otherwise noted. [b] Energy of the optimized structure used for calculation of frequencies and entropy; B3LYP/6-31G**//B3LYP/6-31G**. [c] Rotational symmetry number. [d] Calculated entropy from Gaussian 94, corrected for the rotational symmetry number. [e] diff = $S_{\text{est}} - S_{\text{calc}}$. [f] n_{conf} = number of low-energy conformations used in calculating the entropy of mixing. [g] Calculated entropy, corrected for the entropy of mixing contribution from low-energy conformations. [h] Estimated using group contributions from the tables in ref 2.

$$\Delta S_{\text{mix}} = -R\sum_{i=1}^{n} x_i \ln(x_i) \approx R \ln(n)$$

where

$$x_i = \frac{c_i}{\sum_{i=1}^{n} c_i} \approx \frac{1}{n}$$

n is the number of conformations and c_i is the concentration of the *i*th conformation.

As was pointed out by Block et al.,[7] the result is insensitive to the exact amounts of each conformer, though high-energy conformers should not be included. We have taken 1 kcal/mol as the cutoff; conformations more than 1 kcal/mol higher in energy than the lowest will not be counted. Getting the correct number of conformations is most important when the number is small. The difference in entropy of mixing between 1 and 2 conformations is important ($\Delta S_{\text{mix}} = 0$ or 1.38 (cal/K)/mol); the difference between 240 and 242 is not ($\Delta S_{\text{mix}} = 10.91$ or 10.92 (cal/K)/mol). Only distinguishable conformations count, so rotation about bonds to terminal symmetrical groups (CH_3, CF_3, $C(CH_3)_3$, etc.) does not contribute to the number of conformations, while rotations about interior bonds or bonds to unsymmetrical terminal groups do contribute, normally three per bond. Acyclic compounds were checked using PCModel, comparing gauche and anti conformations. If the gauche was more than 1 kcal/mol higher in energy than the anti, then no conformations resulting from rotation about that bond were counted; if the difference was less than l kcal/mol then 3 were counted. The number of conformations used is given in Table 1. For disulfides, where the preferred torsional angle about the S−S bond is 90°,[12] we count only two conformations from rotation about the S−S bond. In using this approximation for ΔS_{mix}, we are assuming not only that the concentrations of each low energy conformation are approximately the same but also that the entropy of each such conformation is approximately the same.

For cyclic molecules there may be additional complications. Some rings have very low barriers to pseudorotation, so that there are not well-defined conformations. The simple conformation counting assumes that there are substantial barriers separating the conformations (though low enough that the conformations are populated). If the barrier to interconversion becomes small relative to *kT*, then a more elaborate treatment is necessary. For the present purpose such molecules are assumed to be pseudorotating, and the pseudorotation is assumed to be adequately treated by the normal approximations of treating vibrations as harmonic. This is a drastic approximation, justified by the results shown below. Thus, for the various methyl- and dimethylcyclopentanes the number of conformations is taken as one.

For cyclopentane, Gaussian reports a very low frequency (22.2 cm^{-1}) associated with the pseudorotation of the ring. When there is a pseudorotation with a negligible barrier, as here, the full symmetry of the molecule is expressed, and one must correct for the symmetry number of 10, even though for rigid rotation of the entire molecule the symmetry number would be 1. When this is done, the calculated entropy is in good agreement with experiment. In the case of symmetrical molecules capable of pseudorotation, which have very low calculated frequencies, corrections of this sort should be made.

In a number of cases (neopentyl alcohol, nitrobenzene, benzyl alcohol, and valeric acid) experimental values for the entropy of the liquid were available but had not been extended to the gas. In such cases a value was calculated using the heat of vaporization and the vapor pressure at 25° (estimated if necessary from an Antoine equation[13]).

$$S°(\text{g}) = S°(\text{l}) + \Delta H_{\text{vap}}/T_{\text{vap}} + R \ln(p)\ (p \text{ in atm})$$

In the case of valeric acid, examining the original reference[4,14] showed that the value for the entropy of gaseous valeric acid depended on an old value[15] for the heat of vaporization. When a new value of the heat of vaporization[16] was used, the value calculated for the entropy of gaseous valeric acid was in better accord with the expectation from group additivity.[17,18]

Results and Discussion

The results of this investigation are found in Table 1, which gives the observed and calculated entropy values. Both the value calculated by the Gaussian 94 program (corrected by using the proper symmetry number) and the value corrected for the entropy of mixing different conformations are given to demonstrate the importance of this correction. Experimental values were mostly taken from Stull et al.,[4] which is the last major compilation of gas phase entropy values to have been published. The emphasis was on higher molecular weight compounds and on compounds with functional groups; numerous small hydrocarbons for which entropy values are available were not examined. The goal of this work was to develop a method capable of giving useful results for moderately large molecules containing functional groups.

When the entropy of mixing correction is made, the agreement between calculated values and literature values is very good: the standard deviation is 1.28 (cal/K)/mol. For any calculational procedure it is also important to examine the cases where there are large deviations, because these may indicate restrictions on where the method may safely be applied. Deviations greater than two standard deviations were observed only for hexadecafluoroheptane, toluene, benzyl alcohol, *cis*-1,2-dimethylcyclopentane, *m*-xylene, di-*tert*-butyl ether, and durene; deviations greater than three standard deviations were observed only for hexadecafluoroheptane and *m*-xylene. Of these, all except toluene and *m*-xylene were low; the problems with these two may be the inadequate treatment of almost free rotations, though this does not explain why several entropy values were seriously low. This number of deviations is in accord with expectation for a normal distribution and 128 data points.

For 12 compounds (cyclopentane, 2-pentanone, 3-pentanone, butyl propyl sulfide, *p*-fluorotoluene, α,α,α-trifluorotoluene, hexadecafluoroheptane, *trans*-1,3-dimethylcyclopentane, ethylbenzene, *m*-xylene, *m*-diethylbenzene, 1,2,3,4-tetramethylbenzene) there were calculated frequencies ≤ 34 cm^{-1} corresponding to entropy contributions >5.5 (cal/K)/mol. Many of these will be torsional frequencies, yet for some of these compounds the entropy calculated in this work is in satisfactory agreement with the literature value; for some it is too high and for some it is too low. Thus, the presence of a low frequency is not a reliable flag for difficulties.

Both molecular mechanics and molecular orbital calculations showed that alternative conformations of hexadecafluoroheptane were at least 2 kcal/mol higher than the lowest energy conformation and the barriers to rotation about the internal C−C bonds were high. Thus, rather surprisingly, only one conformation is important for this molecule.

It is worth stressing that the method being examined in this paper treats all internal modes as harmonic oscillator vibrations. For those molecules with free or essentially free rotors this may lead to values for the entropy that are in error. For compounds with a methyl, ethyl, or trifluoromethyl group rotating against a double bond, this simple method is likely to be unreliable, and more elaborate treatments should be considered.

The key finding from this investigation is that entropy values good enough for many purposes can be obtained by the standard procedures in Gaussian 94, provided that one takes care to make appropriate corrections for rotational symmetry and the number of low-energy conformations.

While there is no doubt that more elaborate calculational methods (for instance East and Radom's E2 or E3 procedures) will give better calculated entropy values, for many purposes the quality of the calculated value reported here will be quite adequate. There is little point in putting a great deal of effort into improving a value of the entropy if it is only to be combined with an enthalpy of formation with a substantial uncertainty.

Stull et al.[4] included some estimated entropy values in order to be able to generate more comprehensive tables. A few of these compounds have also been examined in this work, with the results in Table 2. In most cases the estimates were in very good agreement with the calculations from this work. In the two cases of vinylcyclohexene and *N*,*N*-diethylaniline there is significant disagreement. For both of these compounds the estimates of entropy are relatively old; new estimates are obtained using Benson's tables (making the unavoidable assumption that $[N(C_b)(C)_2]$ will be approximately equal to $[N(C)_3]$) that are in better agreement with DFT calculations.

Conclusions

The procedures described in this work allow calculation of standard entropies of organic molecules with a standard deviation of 1.28 (cal/K)/mol in entropy or 0.38 kcal/mol in free energy at 25 °C.

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