

# Group Equivalents for Converting *Ab Initio* Energies to Enthalpies of Formation

Kenneth B. Wiberg

Department of Chemistry, Yale University, New Haven, Connecticut 06511  
Received 21 July 1983; accepted 23 September 1983

Group equivalents which are useful for converting energies derived from *ab initio* calculations into enthalpies of formation have been obtained. They allow  $\Delta H_f$  to be estimated from 6-31G\* energies with an uncertainty on the order of  $\pm 2$  kcal/mol.

The energies of small ring compounds are frequently difficult to obtain experimentally because of limited quantities and in many cases their high reactivity. Here *ab initio* molecular orbital (MO) calculations have proven particularly valuable in providing information on both structures and energies, and in some cases also on vibrational frequencies. Molecular mechanics or semi-empirical calculations are not as generally useful. The former method must be parametrized to account for changes in bending potentials with large variations in bond angles,<sup>1</sup> and the information needed to obtain suitable parameters is not readily available. Semi-empirical MO methods frequently have difficulty with small ring compounds,<sup>2</sup> probably because they represent minimal basis-set calculations, whereas the greater flexibility of a split valence set is particularly needed with these compounds.

Much information has become available concerning these compounds.<sup>3-7</sup> The conversion of the calculated energy to the enthalpy of formation normally requires the use of an isodesmic reaction in order to cancel the correlation energy.<sup>8</sup> It is known that the cancellation is most effective if closely related compounds are used in the hypothetical reaction.<sup>9</sup>

In this case, the procedure is actually a group equivalent scheme,<sup>10</sup> and it should be possible to develop a set of group equivalents which could be used to convert the calculated energies into classical energies of formation at 0 K. One would then still have to adjust the values for the zero-point energy and the change in  $\Delta H_f$  on going from 0 to 298 K. The information is available for many smaller molecules, but for larger ones, the

vibrational frequencies on which these quantities depend are often not available.

It is known that zero-point energies and the change in  $\Delta H_f$  may be reasonably well predicted via a group equivalent scheme. Therefore, it should be possible to combine the contributions of a given group to the calculated energy, along with the zero-point energy and  $\Delta\Delta H_f$  into a single constant. We shall now examine how well such a scheme will operate.

Table I lists the calculated energies derived using the 6-31G\* basis set and optimized geometries as well as the observed  $\Delta H_f$  for a group of 21 acyclic, monocyclic, and bicyclic alkanes and alkenes. The compounds were chosen because their heats of formation appear to be fairly well established. Compounds with unusual strain (cyclopropene and bicyclo[1.1.0]butane) or with a conjugated system (butadiene and cyclopentadiene) were excluded since correlation energy cancellation might be less complete for these cases. A few have more than one conformation, whereas the calculated values refer only to the lowest energy conformation. With these simple compounds, the correction to the energy should be small and has been neglected. A least squares analysis led to the following group equivalents (units = hartrees, 1  $H$  = 627.5 kcal/mol):

CH <sub>3</sub>	-39.59842
CH <sub>2</sub>	-39.02679
CH	-38.45274
=CH <sub>2</sub>	-39.02541
=CH	-38.45321

Table I. Results of group equivalent analysis (6-31G\*).

Compound	Energy(H)	$\Delta H_f$ (kcal/mol)		
		obs <sup>f</sup>	calc	dif
ethane	-79.22876 <sup>a</sup>	-20.24	-20.03	-0.21
propane	-118.26365 <sup>a</sup>	-24.83	-25.11	0.28
butane	-157.29840 <sup>b</sup>	-30.36	-30.10	-0.26
isobutane	-157.29896 <sup>c</sup>	-32.41	-31.99	-0.42
pentane	-196.33302 <sup>e</sup>	-35.10	-35.01	-0.09
cyclopropane	-117.05887 <sup>a</sup>	12.73	13.50	-0.77
cyclobutane	-156.09703 <sup>c</sup>	6.78	6.37	0.41
cyclopentane	-195.16124 <sup>c</sup>	-18.44	-17.11	-1.33
cyclohexane	-234.20796 <sup>c</sup>	-29.50	-29.61	0.11
bicyclo[2.1.0]pentane	-193.92697 <sup>b</sup>	37.70 <sup>g</sup>	36.95	0.75
bicyclo[2.2.0]hexane	-232.96520 <sup>b</sup>	29.90 <sup>g</sup>	29.77	0.13
bicyclo[2.2.1]heptane	-272.06101 <sup>c</sup>	-12.40 <sup>h</sup>	-13.54	1.14
bicyclo[2.2.2]octane	-311.10353 <sup>c</sup>	-23.67 <sup>i</sup>	-23.41	-0.26
ethylene	-78.03172 <sup>a</sup>	12.50	11.99	0.51
propene	-117.07147 <sup>a</sup>	4.88	3.50	1.38
1-butene	-156.10586 <sup>c</sup>	-0.20	-1.27	1.07
1,4-pentadiene	-193.94093 <sup>b</sup>	25.30	27.05	-1.75
cyclopentene	-193.97717 <sup>d</sup>	8.23	6.04	2.19
trans-2-butene	-156.11041 <sup>d</sup>	-4.82	-4.49	-0.33
cyclobutene	-154.89962 <sup>b</sup>	37.45	37.89	-0.44
bicyclo[2.1.0]pent-2-ene	-192.71022 <sup>d</sup>	79.70 <sup>g</sup>	80.61	-0.91
rms error =				0.90

<sup>a</sup>Reference 3.<sup>b</sup>Reference 4.<sup>c</sup>Reference 5.<sup>d</sup>Reference 6.<sup>e</sup>Unpublished data.<sup>f</sup>Data are from ref. 12 unless otherwise specified. Values are given in kcal/mol.<sup>g</sup>Reference 13.<sup>h</sup>W. V. Steele, *J. Chem. Thermodyn.*, **10**, 919 (1978).<sup>i</sup>S.-w. S. Wong and E. F. Westrum, Jr., *J. Am. Chem. Soc.*, **93**, 5317 (1971).

The calculated enthalpies of formation obtained using these constants are included in the table. The rms error was only 0.9 kcal/mol with a range of  $\Delta H_f$  of 115 kcal/mol. Relatively little information is available for compounds having a quaternary carbon or a vinyl carbon bearing no hydrogens. A value for the former may be derived from neopentane ( $E = -196.33381$ )<sup>11</sup> and isobutene ( $E = -156.11058$ )<sup>11</sup> may be used to give a value for the latter. The constants are  $-37.87597$  and  $-37.88189$ , respectively. They must be considered tentative since both are derived from single compounds.

It is interesting to note that the value for a  $\text{CH}_2$  group is essentially the same for an alkane, or a  $=\text{CH}_2$  group of an alkene. The same is found for a CH group. Using just three types of groups, the equivalents become

$\text{CH}_3$	-39.59841
$\text{CH}_2$	-39.02671
CH	-39.45291

and the rms error increases only slightly, to 1.0 kcal/mol. Thus, the small difference between the

two  $\text{CH}_2$  and two CH constants is not significant. On the basis of the limited information available for carbons bearing no hydrogens, it is not clear whether or not they could be accommodated using a single constant. In the absence of further information, we will list two values for this type of carbon (Table II).

The five constants were applied to a larger variety of compounds giving the results shown in Table III. The enthalpies of formation are not known for most of these compounds. In the cases where they are known, the differences between estimated and observed values are on the order of  $\pm 1$  to 3 kcal/mol. It is gratifying to note the good agreement for as large a molecule as cubane. One may reasonably conclude that 6-31G\* energies allow the estimation of  $\Delta H_f$  for most

Table II. Group equivalents.

Group	Basis Set	
	4-31G	6-31G*
$\text{CH}_3$	-39.54195	-39.59841
$\text{CH}_3$ (sat)	-38.96948	-39.02671
$\text{CH}_2$ (olefinic)	-38.97225	" "
$\text{CH}_2$ (sat)	-38.39546	-38.45291
CH (olefinic)	-38.39726	" "
C (sat)	-37.81735	-37.87600
C (olefinic)	-37.81888	-37.88026

**Table III.** Calculated enthalpies of formation (6-31G\*).

Compound	Energy(H)	$\Delta H(\text{calc})$	$\Delta H(\text{obs})^g$	Dif.
cyclopropene	-115.82305 <sup>a</sup>	68.7	66.2	2.5
bicyclo[1.1.0]but-1(3)-ene	-153.58015 <sup>c</sup>	146.7		
tetrahydrene	-153.59788 <sup>d</sup>	134.1		
bicyclo[1.1.0]butane	-154.87169 <sup>b</sup>	54.9	51.9	3.0
1,3-butadiene	-154.91965 <sup>d</sup>	24.9	26.1	-1.2
cyclopentadiene	-192.79172 <sup>a</sup>	29.3	31.9	-2.6
bicyclo[2.1.0]pent-1(4)-ene	-192.62148 <sup>c</sup>	137.5		
bicyclo[2.1.0]pent-1(2)-ene	-192.63036 <sup>c</sup>	131.2		
bicyclo[2.1.0]pent-1(5)-ene	-192.63312 <sup>c</sup>	129.5		
[1.1.1]propellane	-192.69106 <sup>b</sup>	88.5		
bicyclo[1.1.1]pentane	-193.90569 <sup>a</sup>	50.4		
bicyclo[2.2.0]hex-1(4)-ene	-231.71870 <sup>a</sup>	93.3		
bicyclo[3.1.0]hex-1(5)-ene	-231.72055 <sup>c</sup>	92.1		
[2.1.1]propellane	-231.72188 <sup>b</sup>	86.0		
bicyclo[2.2.0]hex-2(3)-ene	-231.76788 <sup>c</sup>	61.0	62.5 <sup>f</sup>	-1.5
bicyclo[2.1.1]hex-2-ene	-231.77417 <sup>c</sup>	57.0		
1,5-hexadiene	-232.97615 <sup>a</sup>	23.0	20.2 <sup>g</sup>	2.8
bicyclo[2.1.1]pentane	-232.98929 <sup>a</sup>	14.7		
norbornadiene	-269.65216 <sup>b</sup>	57.7	57.4 <sup>h</sup>	0.3
[2.2.1]propellane	-270.75955 <sup>b</sup>	79.1		
[2.2.2]propellane	-309.80908 <sup>b</sup>	64.8		
windowpane	-347.56427 <sup>a</sup>	144.5		
cubane	-307.39361 <sup>d</sup>	144.1	148.7	-4.6

<sup>a</sup>Reference 4.<sup>b</sup>Reference 5.<sup>c</sup>Reference 6.<sup>d</sup>Unpublished data.<sup>e</sup>Data from ref. 12 unless otherwise specified (kcal/mol).<sup>f</sup>Reference 13.<sup>g</sup>R. B. Turner, B. J. Mallon, M. Tichy, W. v. E. Doering, W. R. Roth, and G. Schroder, *J. Am. Chem. Soc.*, **95**, 8605 (1973).<sup>h</sup>D. W. Rogers, L. S. Choi, R. S. Girellini, T. J. Holmes, and N. L. Allinger, *J. Phys. Chem.*, **84**, 1810 (1980).

hydrocarbons with an uncertainty on the order of 2 kcal/mol.

Benzene ( $E = -230.70305$  H,<sup>11</sup> est  $\Delta H_f = 9.1$ , obs = 19.8 kcal/mol) is a notable exception. It is not surprising that the correlation energy per CH group is different for a delocalized system such as benzene than for the other alkenes.

The group equivalents are, of course, basis-set dependent. Values have been derived for the 4-31G basis set using the compounds in Table I and related compounds, but excluding bicyclo[2.1.0]pentane and bicyclo[2.1.0]pent-2-ene which gave relatively large errors. With this basis set, it appears desirable to give separate values for the two types of CH<sub>2</sub> and CH groups. The group equivalents are given in Table II, and lead to an rms error of 2.0 kcal/mol. They should be considered as tentative, and will be examined for a larger range of structures. They are useful for the less strained compounds, but lead to fairly large errors with the compounds having large strain energies per carbon. It is known that polarization functions are needed in order to obtain satisfactory energies for these compounds.<sup>5</sup> There are not sufficient data to allow us to propose group equivalents for the 3-21G basis set. Values were not derived for the STO-3G basis

set since it is known that it leads to an incorrect ordering of energies of alkanes and alkenes.<sup>8</sup>

This investigation was supported by the Office of Basic Energy Sciences, Department of Energy.

## References

1. U. Burkert and N. L. Allinger, *Molecular Mechanics*, ACS Monograph 177, 1982.
2. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4907 (1977).
3. R. A. Whiteside, J. S. Binkley, R. Krishnan, D. J. DeFrees, H. B. Schlegel, and J. A. Pople, *Carnegie-Mellon Quantum Chemistry Archive*, Carnegie-Mellon University, Pittsburgh, 1980.
4. K. B. Wiberg and J. J. Wendoloski, *J. Am. Chem. Soc.*, **104**, 5679 (1982).
5. K. B. Wiberg, *J. Am. Chem. Soc.*, **105**, 1227 (1983).
6. K. B. Wiberg, G. Bonneville, and R. Dempsey, *Isr. J. Chem.*, **23**, 85 (1983).
7. C. Van Alsenoy, J. N. Scarsdale, and L. Schaefer, *J. Comput. Chem.*, **3**, 53 (1982); *J. Chem. Phys.*, **74**, 6278 (1981).
8. J. A. Pople, *Mod. Theor. Chem.*, **4**, 1 (1977).
9. P. George, M. Trachtman, A. M. Brett, and C. W. Bock, *J. Chem. Soc. Perkin Trans.*, **2**, 1036 (1977).
10. J. L. Franklin, *Ind. Eng. Chem.*, **10**, 1070 (1949).
11. Unpublished results.
12. J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic, London, 1970.
13. W. R. Roth, F.-G. Klärner, and H.-W. Lennartz, *Chem. Ber.*, **113**, 1818 (1980).