marize the derivation of *c* increments for alkyl groups. The principle used throughout is to make the calculations in sets so that the most fundamental values are least perturbed by uncertainties in the other enthalpy of formation values. The tables summarize the SM values and the FSE values assigned. The *c*[C_C_H_H_H_] and *c*[C_C_C_H_H_] values in the footnotes of Table I were determined from the *n*-alkanes listed in Table I by a least-squares procedure. These values were then held fixed for all other *c*-increment calculations. The *c*[C_C_C_C_H_] and *c*[C_C_C_C_C_] values are reported in the footnote of Table II. The *c* increments do not differ greatly from published values. The Schleyer values are −10.12, −5.13, −2.16, and −0.30; our earlier values are also similar.

Experimental FSE Values. Table III summarizes the FSE values for most of the alkanes and cycloalkanes in the Stull, Westrum, Sinke[4] and in the Pedley–Naylor–Kirby[1-3] collections plus several examples from the literature. The SM values that have been adopted are listed in the tables. For compounds of simple structure, it is possible to estimate FSE values by reference to the FSE values assigned to standards, and these expected values are listed in the last column. For the compounds for which the SM values are not now available, the FBE term is reported but no FSE value has been calculated.

Agreement is close between the values in Table III and those compounds that also appear in Tables VI and VII of the Schleyer reference.[12]

Consistency Tests. A number of tests may be made for consistency of the enthalpy of formation data and for the FSE values. These are summarized in Table IV. The first set includes all of the *n*-alkanes. Sets 2 and 3 contain all of the isoalkanes and neoalkanes. Set 4 contains all alkanes having an interior methyl group or methyl branches at each end; for these the expected FSE value is 1.40, based on the presence of two gauche interactions and assuming additivity of effects. This expectation is supported by the Wiberg ab initio results.[15] The FSE values for cyclohexanes, set 5, and cyclopentanes, set 6, are based on averages of FSE values for those examples that do not have additional steric interactions beyond those due to the rings. These ring values are well defined. Set 7 includes 40 compounds for which standard deviations have been reported for the experimental value of the enthalpy of formation and for which FSE values have been predicted. The average of the variance of these standard deviations corresponds to an average standard deviation of 0.44 while the corresponding average variance based on the differences between the predicted FSE and the experimental FSE gives a standard deviation of 0.42, Table IV; that is, the predicted FSE values are consistent with the experimental estimates. Set 8 reports the average standard deviation for all compounds for which FSE values have been predicted.

Table IV. Consistency of Experimental FSE Values and Comparison with Expected FSE Values

set		av exptl FSE	expected FSE	SD of difference[a]
1	28 *n*-alkanes (average of absolute value)	0.08	0.00	0.13
2	11 isoalkanes	0.64	0.70	0.23
3	7 neoalkanes	1.40	1.40	0.27
4	18 3-methylalkanes (or 2,*n*-dimethylalkanes	1.50	1.40	0.27
5	22 cyclohexanes	1.51	(1.40)[b]	0.47
6	16 cyclopentanes	7.56	(7.40)[b]	0.19
7	40 alkanes for which the sd of ΔH_f is reported, the avg sd of ΔH_f is 0.37[c]			0.40[a]
8	110 alkanes with assigned value of expected FSE			0.42[a,d]

[a] SD is square root of sum(FSE expected − FSE experimental)$^2/n$. The assigned FSE of *n*-alkanes is 0, of isoalkanes is 0.70, and of neoalkanes is 1.40. Other assignments based on counting gauche interactions. [b] Approximate average of compounds with fewer than about 12 carbons. [c] Square root of the average of the variance. [d] Omitting compounds having a standard deviation of the experimental ΔH_f > 0.8 kcal/mol.

The enthalpies of formation come from many sources and have been measured with variable levels of precision. Most of the values reported in the compilations appear to represent remarkably good measurements. But there are occasional serious discrepancies. In many cases discrepancies between different reported values for the same compound can be decided in favor of the value that is consistent with the observed regularities.

Experimental Formal Steric Enthalpy. 2. Olefins

DeLos F. DeTar

Department of Chemistry, Florida State University, Tallahassee, Florida 32306-3006

Received January 22, 1990

Sets of standard olefins have been selected for defining formal steric enthalpies. All possible olefins can be described in terms of 17 structural elements in addition to the four structural elements used to describe alkanes. It is possible to define definitive FBE increments for 11 of these, and reasonable estimates may be assigned to the rest. For 76 olefins for which FSE values have been assigned or estimated, the standard deviation of the difference between the experimental FSE value and the assigned or estimated value os 0.44 kcal/mol. This value is the same as the reported average uncertainties of the enthalpy of formation data (0.43).

The first paper in this series[1] summarizes the principles of the calculation of experimental values of formal steric enthalpy from enthalpy of formation data.[2-4] Equation 1 defines FSE as the correction to the formal bond enthalpy FBE,$\Sigma n_i c_i$, that is needed to reproduce the value

---

(1) DeTar, D. F. *J. Org. Chem.*, previous paper in this issue.

(2) Pedley, J. B.; Rylance, J. *Sussex-N.P.L. Computer Analyzed Thermochemical Data Organic and Organometallic Compounds*; University of Sussex: Sussex, UK, 1977.

0022-3263/91/1956-1470$02.50/0 © 1991 American Chemical Society

Table I. Increments for Calculating Formal Bond Enthalpies of Olefins

structural element (increment)	definition[a] of structural element	value[b] of *c* increment	no.[c] of examples	Benson[d] *b* increment
c[C_C_H_H_H_]	$CH_3(C)$	-10.033		-10.20
c[C_C_C_H_H_]	$(C)CH_2(C)$	-5.147		-4.93
c[C_C_C_C_H_]	$(C)CH(C)_2$	-2.258		-1.90
c[C_C_C_C_C_]	$(C)C(C)_3$	-0.217		0.50
c[C_C_CDH_H_]	$(=C)CH_2(C)$	(-5.147)		-4.76
c[CDCDH_H_]	$(C=)=CDH_2$	6.314	14	6.26
c[CDC_CDH_]	$(C=)=CDH(C)$	8.640	14	8.59
c[CDC_C_CD]	$(C=)=CD(C)_2$	10.139	12	10.34
c[C_CDH_H_H_]	$(=C)CH_3$	(-10.033)		(-10.20)
c[C_C_C_CDH_]	$(=C)CH(C)_2$	(-2.258)		-1.48
c[C_C_C_C_CD]	$(=C)C(C)_3$	(-0.217)		1.68
c[CDCDCDH_]	$(C=)=CDH(C=)$	6.76	6	6.78
c[CDC_CDCD]	$(C=)=CD(C)(C=)$	8.48	3	8.88
c[CDCDCDCD]	$(C=)=CD(C=)_2$	(-0.217?)		4.6
c[CDCDCD]	$(C=)=CD=(=C)$	33.82	7	34.20
c[C_CDCDH_H_]	$(=C)CH_2(C=)$	(-5.147)		
c[C_C_CDCDH_]	$(=C)CH(C)(C=)$	(-2.258?)		
c[C_C_C_CDCD]	$(=C)C(C)_2(C=)$	(-0.217?)		
c[C_CDCDCDH_]	$(=C)CH(C=)_2$	(-2.258?)		
c[C_C_CDCDCD]	$(=C)C(C)(C=)_2$	(-0.217?)		
c[C_CDCDCDCD]	$(=C)C(C=)_3$	(-0.217?)		

[a] Attached groups are indicated in parentheses; these are not counted as atoms in the structural element. [b] Values in parentheses are defined values. [c] Number of examples available and used. [d] Reference 8.

Table II. Compounds Used To Define *c*[CDCDH_H_] and *c*[CDC_CDH_] Based on Gas-Phase Enthalpies of Formation at 25 °C (All Values Are in kcal/mol)[h]

compound	formula	ΔH_f(exptl)[a]	ref[b]	FBE[c]	SM[d]	ΔH_f(calcd)[e]	FSE(exptl)[f]	FSE(assigned)[g]
ethylene	C_2H_4	12.55	P	12.63	0.00	12.63	-0.08	0.00
ethylene	C_2H_4	12.50	S	12.63	0.00	12.63	-0.13	0.00
1-butene	C_4H_8	0.02	P	-0.23	0.09	-0.14	0.16	0.00
1-butene	C_4H_8	-0.03	S	-0.23	0.09	-0.14	0.11	0.00
1-pentene	C_5H_{10}	-5.09	P	-5.37	0.36	-5.01	-0.08	0.00
1-pentene	C_5H_{10}	-5.00	S	-5.37	0.36	-5.01	0.01	0.00
1,5-hexadiene	C_6H_{10}	20.10	P	19.61	0.50	20.11	-0.01	0.00
1-hexene	C_6H_{12}	-10.40	P	-10.52	0.57	-9.95	-0.45	0.00
1-hexene	C_6H_{12}	-9.96	S	-10.52	0.57	-9.95	-0.01	0.00
(*E*)-3-hexene	C_6H_{12}	-13.00	P	-13.08	0.18	-12.90	-0.10	0.00
(*E*)-3-hexene	C_6H_{12}	-13.01	S	-13.08	0.18	-12.90	0.11	0.00
1-heptene	C_7H_{14}	-14.89	P	-15.67	0.79	-14.88	-0.01	0.00
1-heptene	C_7H_{14}	-14.89	S	-15.67	0.79	-14.88	-0.01	0.00
1-octene	C_8H_{16}	-19.46	P	-20.81	1.00	-19.81	0.35	0.00
1-octene	C_8H_{16}	-19.82	S	-20.81	1.00	-19.81	-0.01	0.00
1-decene	$C_{10}H_{20}$	-29.49	P	-31.11	1.43	-29.68	0.19	0.00
1-decene	$C_{10}H_{20}$	-29.47	S	-31.11	1.43	-29.68	0.21	0.00

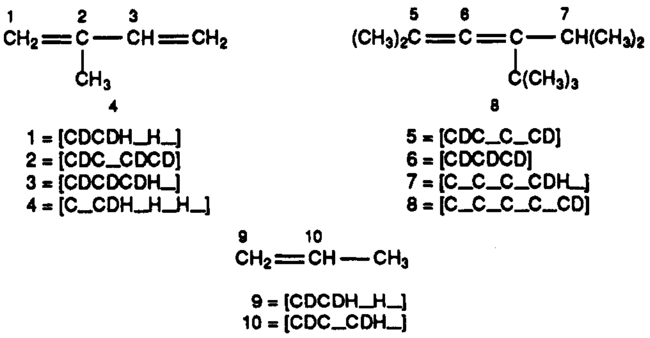
[a] Units are kcal/mol for the gas phase at 25 °C. [b] P is ref 2, S is ref 4. [c] FBE based on *c* increments of Table I. [d] SM, see text; for chains longer than five carbons the increment is 0.215 kcal/mol per extra CH_2 group.[11,12] [e] FBE + SM. [f] ΔH_f(exptl) - ΔH_f(calcd). [g] Assigned FSE value. [h] For 17 entries the variance of the difference of FSE(exptl) - FSE(assigned) is 0.03 (SD 0.17); for nine entries for which the standard deviation of the experimental ΔH_f is reported, the variance is 0.05 (SD 0.2) and for this smaller set the variance of the difference of FSE(exptl) - FSE(assigned) is 0.08 (SD 0.3).

on the left-hand side, which is the enthalpy of formation of the single conformer of lowest energy, ΔH_f is the enthalpy of formation of the population of conformers and SM corrects for the effect of conformers having energies above the minimum.[5-7]

$$\Delta H_f - \mathrm{SM} = \Sigma n_i c_i + \mathrm{FSE} \qquad (1)$$

The first step is to calculate a definitive set of *c* increments for olefins. This requires assignments of FSE values to representative sets of olefins and assignments of representative SM values. Also required are the *c* increments for the alkane structural elements; these were derived in part 1.[1] Estimation of SM values of olefins has been based on calculations for compounds with one or with two rotatable bonds (pentenes, for example). Torsions for C—C═C—C— were eclipsed; others were staggered. The following energies were assigned: C—C—C—C s-trans 0,

Scheme I. Representative Olefin Structural Elements



---

(3) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London and New York, 1970.

(4) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley & Sons, Inc.: New York, 1969.

(5) DeTar, D. F. *Comput. Chem.* **1988**, *12*, 1-14.

(6) DeTar, D. F.; Binzet, S.; Darba, P. *J. Org. Chem.* **1985**, *50*, 2826-36.

(7) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377-86.

Table III. Compounds Used To Define *c*[CDC_C_CD] and *c* Increments of Alkyl Groups Attached to Olefinic Carbon Atoms Based on Gas-Phase Enthalpies of Formation at 25 °C

compound	formula	ΔH_f(exptl)[a]	ref[b]	FBE[c]	SM[d]	ΔH_f(calcd)[e]	FSE(exptl)[f]	FSE(assigned)[g]
propene	C_3H_6	4.78	P	4.92	0.00	4.92	−0.14	0.00
propene	C_3H_6	4.88	S	4.92	0.00	4.92	−0.04	0.00
(*Z*)-2-butene	C_4H_8	−1.70	P	−2.79	0.00	−2.79	1.09	1.00
(*Z*)-2-butene	C_4H_8	−1.67	S	−2.79	0.00	−2.79	1.12	1.00
(*E*)-2-butene	C_4H_8	−2.72	P	−2.79	0.00	−2.79	0.07	0.00
(*E*)-2-butene	C_4H_8	−2.67	S	−2.79	0.00	−2.79	0.12	0.00
2-methylpropene	C_4H_8	−4.04	P	−3.61	0.00	−3.61	−0.43	0.00
2-methylpropene	C_4H_8	−4.04	S	−3.61	0.00	−3.61	−0.43	0.00
2-methyl-1-butene	C_5H_{10}	−8.44	P	−8.76	0.09	−8.67	0.23	0.00
2-methyl-1-butene	C_5H_{10}	−8.68	S	−8.76	0.09	−8.67	−0.01	0.00
2-methyl-2-butene	C_5H_{10}	−9.99	P	−11.32	0.00	−11.32	1.33	1.00
2-methyl-2-butene	C_5H_{10}	−10.17	S	−11.32	0.00	−11.32	1.15	1.00
(*E*)-2-pentene	C_5H_{10}	−7.62	P	−7.93	0.09	−7.84	0.22	0.00
(*E*)-2-pentene	C_5H_{10}	−7.59	S	−7.93	0.09	−7.84	0.25	0.00
3-methyl-1-butene	C_5H_{10}	−6.60	P	−7.37	0.05	−7.32	0.72	0.00
3-methyl-1-butene	C_5H_{10}	−6.92	S	−7.37	0.05	−7.32	0.40	0.00
2-ethyl-1-butene	C_6H_{12}	−13.38	P	−13.91	0.18	−13.73	0.35	0.00
(*Z*)-2-hexene	C_6H_{12}	−12.50	P	−13.08	0.30	−12.78	0.28	1.00
(*Z*)-2-hexene	C_6H_{12}	−12.51	S	−13.08	0.30	−12.78	0.27	1.00
(*E*)-2-hexene	C_6H_{12}	−12.88	P	−13.08	0.30	−12.78	−0.10	0.00
(*E*)-2-hexene	C_6H_{12}	−12.88	S	−13.08	0.30	−12.78	−0.10	0.00
2-methyl-1-pentene	C_6H_{12}[h]	−14.20	P	−13.91	0.36	−13.55	−0.65	0.00
2-methyl-2-pentene	C_6H_{12}[h]	−15.99	P	−16.47	0.00	−16.47	0.48	1.00
3,3-dimethyl-1-butene	C_6H_{12}[h]	−14.46	P	−15.36	0.00	−15.36	0.90	0.55
3-methyl-1-pentene	C_6H_{12}[h]	−11.83	P	−12.52	0.30	−12.22	0.39	1.25
(*E*)-3-methyl-2-pentene	C_6H_{12}[h]	−15.08	P	−16.47	0.09	−16.38	1.30	1.00
(*Z*)-3-methyl-2-pentene	C_6H_{12}[h]	−14.89	P	−16.47	0.09	−16.38	1.49	1.00
(*E*)-4-methyl-2-pentene	C_6H_{12}[h]	−14.70	P	−15.08	0.00	−15.08	0.38	0.00
2,4-dimethyl-1-pentene	C_7H_{14}	−20.03	P	−21.05	0.12	−20.93	0.90	0.70

[a-g] See Table II. [h] Some Stull values are inconsistent with hydrogenation data of ref 10. See text. For 29 entries the variance of FSE(exptl) − FSE(assigned) is 0.16 (SD 0.4); for 18 entries for which the standard deviation of the experimental ΔH_f is reported, the variance is 0.09 (SD 0.3) and for this smaller set the variance of the difference of FSE(exptl) − FSE(assigned) is 0.20 (SD 0.44).

Table IV. Compounds Used To Define *c*[CDCDCDH_], *c*[CDC_CDCD], and *c*[CDCDCD] Based on Gas-Phase Enthalpies of Formation at 25 °C[h]

compound	formula	ΔH_f(exptl)[a]	ref[b]	FBE[c]	SM[d]	ΔH_f(calcd)[e]	FSE(exptl)[f]	FSE(assigned)[g]
propadiene	C_3H_4	45.53	P	46.45	0.00	46.45	−0.92	0.00
propadiene	C_3H_4	45.92	S	46.45	0.00	46.45	−0.53	0.00
1,2-butadiene	C_4H_6	38.79	P	38.74	0.00	38.74	0.05	0.00
1,2-butadiene	C_4H_6	38.77	S	38.74	0.00	38.74	0.03	0.00
1,3-butadiene	C_4H_6	26.29	P	26.15	0.00	26.15	0.14	0.00
1,3-butadiene	C_4H_6	26.33	S	26.15	0.00	26.15	0.18	0.00
1,2-pentadiene	C_5H_8	33.63	P	33.59	0.18	33.77	−0.14	0.00
(*E*)-1,3-pentadiene	C_5H_8	18.19	P	18.44	0.00	18.44	−0.25	0.00
(*E*)-1,3-pentadiene	C_5H_8	18.60	S	18.44	0.00	18.44	0.16	0.00
1,4-pentadiene	C_5H_8	25.24	P	25.04	0.18	25.22	0.02	0.00
1,4-pentadiene	C_5H_8	25.20	S	25.04	0.18	25.22	−0.02	0.00
2,3-pentadiene	C_5H_8	31.81	P	31.03	0.00	31.03	0.78	0.00
2-methyl-1,3-butadiene	C_5H_8	18.04	P	17.84	0.00	17.84	0.21	0.50
2-methyl-1,3-butadiene	C_5H_8	18.10	S	17.84	0.00	17.84	0.27	0.50
3-methyl-1,2-butadiene	C_5H_8	31.00	S	30.21	0.00	30.21	0.79	0.00
2,3-dimethyl-1,3-butadiene	C_6H_{10}	10.78	P	9.52	0.00	9.52	1.26	1.00

[a-g] See Table II. [h] For 16 entries the variance of the FSE(exptl) − FSE(assigned) is 0.17 (SD 0.4); for nine entries for which the standard deviation of the experimental ΔH_f values are reported, their variance is 0.06 (SD 0.24) and for this set the variance of the FSE(exptl) − FSE(assigned) is 0.19 (SD 0.44).

gauche 0.70; C—C=C—C— H-eclipsed 0, C-eclipsed 0.57; no extra increments for 1,5-interactions. Calculations were based on Boltzmann populations of 3 or of 9 conformers. For longer chains the 0.215 methylene increment was used.[1]

Although four structural elements suffice to define the formal bond enthalpies of alkanes and cycloalkanes, 17 additional structural elements are needed to describe all possible olefins. These are listed in Table I along with the alkane structural elements. The structural elements are denoted by an extension of the Benson nomenclature (ref 8, p 272). The first symbol defines the main atom; the rest define the ligands. Examples are shown in Scheme I. There is a possible ambiguity in the use of a single symbol CD to represent an sp^2 carbon atom as a ligand. This could be removed by using different symbols to indicate explicitly whether the ligand atom CD is attached to the main atom CD by a double bond or by a single bond. In the present context, the potential ambiguity can be resolved by inspection and by a rigorous algorithm.

Most olefins beyond the simple examples of Scheme I include the alkane structural elements. These have been determined in part 1[1] and are included in Table I. Since the system of equations based on eq 1 is underdetermined for the olefin structural elements, it is necessary to assign one arbitrary *c* increment. Benson chose to define the increment for the olefinic methyl group as equal to that

---

(8) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley & Sons: New York, 1976.

Table V. Experimental Formal Steric Enthalpies of Olefins Based on Gas-Phase Enthalpies of Formation at 25 °C

compound	formula	ΔH_f(exptl)[a]	ref[b]	FBE[c]	SM[d]	ΔH_f(calcd)[e]	FSE-(exptl)[f]	FSE-(expected)[g]
cyclopropene	C_3H_4	66.23	P	12.41	0.00	12.41	53.82	
1-methylcyclopropene	C_4H_6	58.22	P	3.88	0.00	3.88	54.34	
cyclobutene	C_4H_6	37.45	P	6.99	0.00	6.99	30.46	
methylenecyclopropane	C_4H_6	47.92	P	6.16	0.00	6.16	41.76	
cyclopentadiene	C_5H_6	32.10	P	25.93	0.00	25.93	6.17	
(*Z*)-1,3-pentadiene	C_5H_8	19.46	P	18.44	0.00	18.44	1.02	1.00
(*Z*)-1,3-pentadiene	C_5H_8	18.70	S	18.44	0.00	18.44	0.26	1.00
cyclopentene	C_5H_8	8.10	P	1.84	0.00	1.84	6.26	
cyclopentene	C_5H_8	7.87	S	1.84	0.00	1.84	6.03	
methylenecyclobutane	C_5H_8	29.04	P	1.01	0.00	1.01	28.03	
(*Z*)-2-pentene	C_5H_{10}	−6.80	P	−7.93	0.09	−7.84	1.24	1.00
(*Z*)-2-pentene	C_5H_{10}	−6.71	S	−7.93	0.09	−7.84	1.13	1.00
1,3-cyclohexadiene	C_6H_8	25.38	P	20.51	0.00	20.51	4.87	
1-methylcyclopentene	C_6H_{10}	−0.91	P	−6.70	0.00	−6.70	5.79	
3-methylcyclopentene	C_6H_{10}	1.77	P	−5.31	0.00	−5.31	7.08	
4-methylcyclopentene	C_6H_{10}	3.49	P	−5.31	0.00	−5.31	8.80	
cyclohexene	C_6H_{10}	−1.20	P	−3.31	0.00	−3.31	2.11	
cyclohexene	C_6H_{10}	−1.28	S	−3.31	0.00	−3.31	2.03	
methylenecyclopentene	C_6H_{10}	2.87	P	−4.14	0.00	−4.14	7.01	
2,3-dimethyl-1-butene	C_6H_{12}	−14.96	P	−15.90	0.00	−15.90	0.94	
2,3-dimethyl-2-butene	C_6H_{12}	−16.30	P	−19.85	0.00	−19.85	3.55	
3,3-dimethyl-1-butene	C_6H_{12}	−14.46	P	−15.36	0.00	−15.36	0.90	
(*Z*)-3-hexene	C_6H_{12}	−11.38	P	−13.08	0.18	−12.90	1.52	1.00
(*Z*)-3-hexene	C_6H_{12}	−11.38	S	−13.08	0.18	−12.90	1.52	1.00
4-methyl-1-pentene	C_6H_{12}	−12.26	P	−12.52	0.18	−12.34	0.08	0.75
(*Z*)-4-methyl-2-pentene	C_6H_{12}	−13.74	P	−15.08	0.00	−15.08	1.34	1.00
2,5-bicyclo[2.2.1]heptadiene	C_7H_8	58.77	P	24.90	0.00	24.90	33.87	
1,3-cycloheptadiene	C_7H_{10}	22.54	P	15.36	0.00	15.36	7.18	
2-bicyclo[2.2.1]heptene	C_7H_{10}	21.51	P	−2.68	0.00	−2.68	24.19	
1-ethylcyclopentene	C_7H_{12}	−4.71	P	−11.84	0.09	−11.75	7.04	
1-methylcyclohexene	C_7H_{12}	−10.35	P	−11.84	0.00	−11.84	1.49	
cycloheptene	C_7H_{12}	−2.20	P	−8.46				
ethylidenecyclopentane	C_7H_{12}	−4.33	P	−11.84	0.00	−11.84	7.51	
methylenecyclohexane	C_7H_{12}	−6.02	P	−9.28	0.00	−9.28	3.26	
2,3,3-trimethyl-1-butene	C_7H_{14}	−20.43	P	−23.90	0.00	−23.90	3.47	
2,4-dimethyl-2-pentene	C_7H_{14}	−21.20	P	−23.61	0.00	−23.61	2.41	
2-ethyl-3-methyl-1-butene	C_7H_{14}	−19.00	P	−21.05	0.12	−20.93	1.93	
(*E*)-3-methyl-3-hexene	C_7H_{14}	−18.36	P	−21.61	0.18	−21.43	3.07	
(*Z*)-3-methyl-3-hexene	C_7H_{14}	−18.98	P	−21.61	0.18	−21.43	2.45	
4,4-dimethyl-1-pentene	C_7H_{14}	−19.50	P	−20.51	0.09	−20.42	0.92	1.40
(*E*)-4,4-dimethyl-2-pentene	C_7H_{14}	−21.22	P	−23.07	0.00	−23.07	1.85	0.00
(*Z*)-4,4-dimethyl-2-pentene	C_7H_{14}	−17.35	P	−23.07	0.00	−23.07	5.72	
5-methyl-1-hexene	C_7H_{14}	−15.70	P	−17.66	0.36	−17.30	1.60	0.70
cyclooctatetraene	C_8H_8	70.72	P	54.08				
5-isopropylidenecyclopentadiene	C_8H_{10}	32.12	P	17.11	0.00	17.11	15.01	
(*E*)-1,3-divinylcyclobutane	C_8H_{12}	34.30	P	15.10	0.00	15.10	19.20	
(*Z*)-1,3-divinylcyclobutane	C_8H_{12}	39.79	P	15.10	0.00	15.10	24.69	
(*Z*,*Z*)-1,5-cyclooctadiene	C_8H_{12}	24.16	P	13.97				
2-bicyclo[2.2.2]octene	C_8H_{12}	4.90	P	−7.82	0.00	−7.82	12.72	
4-vinylcyclohexene	C_8H_{12}	15.56	P	14.54	0.00	14.54	1.03	
7-methylenebicyclo[2.2.1]heptane	C_8H_{12}	14.39	P	−8.65	0.00	−8.65	23.04	
1-ethylcyclohexene	C_8H_{14}	−15.15	P	−16.99	0.09	−16.90	1.75	
cyclooctene	C_8H_{14}	−6.45	P	−13.60				
vinylcyclohexane	C_8H_{14}	−11.69	P	−13.04	0.00	−13.04	1.35	
(*E*)-2,2-dimethyl-3-hexene	C_8H_{16}	−25.74	P	−28.22	0.09	−28.13	2.39	
(*Z*)-2,2-dimethyl-3-hexene	C_8H_{16}	−21.34	P	−28.22	0.09	−28.13	6.79	
2,4,4-trimethyl-1-pentene	C_8H_{16}	−26.43	P	−29.04	0.00	−29.04	2.61	
2,4,4-trimethyl-2-pentene	C_8H_{16}	−25.07	P	−31.60	0.00	−31.60	6.53	
3-ethyl-2-methyl-1-pentene	C_8H_{16}	−23.97	P	−26.20				
(*Z*)-5-ethylidenebicyclo[2.2.1]heptene	C_9H_{12}	34.82	P	11.22	0.00	11.22	23.60	
2-methylbicyclo[2.2.2]oct-2-ene	C_9H_{14}	−4.45	P	−16.36	0.00	−16.36	11.91	
2-methylenebicyclo[2.2.2]octane	C_9H_{14}	−2.20	P	−13.80	0.00	−13.80	11.60	
1-isopropyl-4-methylcyclohexadiene	$C_{10}H_{16}$	−4.92	P	−5.09	0.00	−5.09	0.17	
1-methyl-4-isopropenylcyclohexene (dipentene)	$C_{10}H_{16}$	−0.62	P	−2.53	0.00	−2.53	1.91	
1-methyl-4-isopropenylcyclohexene (limonene)	$C_{10}H_{16}$	−1.53	P	−2.53	0.00	−2.53	1.00	
2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane	$C_{10}H_{16}$	−6.84	P	−23.79	0.00	−23.79	16.95	
2,6,6-trimethylbiocyclo[3.1.1]hept-2-ene	$C_{10}H_{16}$	6.76	P	−26.35	0.00	−26.35	33.11	
2-methyl-5-isopropyl-1,3-cyclohexadiene	$C_{10}H_{16}$	−2.22	P	−7.24	0.00	−7.24	5.02	
6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane	$C_{10}H_{16}$	9.25	P	−23.79	0.00	−23.79	33.04	
(*E*)-2,2,5,5-tetramethyl-3-hexene	$C_{10}H_{20}$	−39.56	P	−43.35	0.00	−43.35	3.79	
(*E*,*E*,*E*)-1,5,9-cyclododecatriene	$C_{12}H_{18}$	24.21	P	20.96				
(*E*,*E*,*Z*)-1,5,9-cyclododecatriene	$C_{12}H_{18}$	23.21	P	20.96				
1-dodecene	$C_{12}H_{24}$	−39.53	P	−41.40	1.86	−39.54	0.01	0.00
1-hexadecene	$C_{16}H_{32}$	−59.39	P	−61.99	2.72	−59.27	0.12	0.00

[a-g] See Table II.

of the alkane methyl group. However, there are advantages in setting the values of the methylene groups equal since this choice requires fewer steps in calculating other *c* increments. Accordingly, I have chosen to make *c*[C_C_CDH_H_] = *c*[C_C_C_H_H_]. Since the *c*[C_C_CDH_H_] value has been assigned, that value is enclosed in parentheses in Table I.

Because enthalpy of formation data are of variable quality both in terms of numbers of examples and of experimental uncertainties, it was deemed best to approach the estimation of *c* increments in a series of steps rather than to include all types in a single calculation. This approach also made it possible to eliminate specific outliers, although in most cases the *c* increments are not very sensitive to inclusion or exclusion of outliers.

The starting point was to determine values of *c*[CDCDH_H_] and *c*[DCD_CDH_]. The set of compounds used is summarized in Table II along with assigned FSE values and estimated SM values. The two *c* increments were calculated by a least-squares procedure. The small residuals shown in the column labeled "FSE experimental" shows the high quality of the enthalpies of formation and the consistency of the results obtained with eq 1 and with the assigned FSE and SM values. The overall standard deviation for this set is 0.2 kcal/mol.

The next step was to calculate *c* increments for alkyl groups attached to an olefinic carbon atom viz. *c*[C_CDH_H_H_], *c*[C_C_C_CDH_], and *c*[C_C_C_C_CD] plus the olefinic value *c*[CDC_C_CD]. As indicated above, the *c*[C_C_CDH_H_] is defined to be equal to *c*[C_C_C_H_H_]. The selected compounds are listed in Table III along with the assigned FSE values and the SM values. Examination of available data for the difference of enthalpy of formation of a *cis*-olefin and a *trans*-olefin of the structure RCH=CHR′ showed an average of 1.0 kcal/mol. This value was therefore adopted as an appropriate FSE value for the simple *cis*-olefins. It is assumed that an olefin $CH_3R_1C{=}CH_2$ having a methyl or an *n*-alkyl substituent has an FSE of 0. For the compounds flagged there were large differences between the Pedley-Rylance-Naylor-Kirby values[2,3,9] and the Stull-Westrum-Sinke values.[4] The hydrogenation data in Bartolo and Rossini[10] are consistent with the former and the Stull values have been omitted.

The least-squares evaluation of the alkyl olefin *c* increments showed that they were all quite close to the alkyl alkane values. I have therefore chosen to adopt the alkyl alkane values, and this choice is indicated by listing the alkyl olefin values in parentheses.

The last set of olefin *c* increments that can be evaluated from the experimental data are those for *c*[CDCDCDH_] (for 1,3-dienes, Scheme I), *c*[CDC_CDCD] (for alkyl-substituted 1,3-dienes), and *c*[CDCDCD] (for 1,2-dienes). The compounds used as FSE standards are listed in Table IV. There is one compound that has the [C_CDCDH_H_] structural element, 1,4-pentadiene. Since the *c* increment is close to that of *c*[C_C_C_H_H_], the alkane value was adopted. There are no compounds for which reliable FSE values can be assigned that have the remaining olefin structural elements. Therefore I tentatively assign the alkane alkyl values as indicated in parentheses and with question marks. The estimates should be good, considering the closeness of the values treated in Table III.

Table V applies the group increments of Table I to most of the remaining olefins for which enthalpies of formation are reported. In a few instances it is possible to predict a FSE value, as shown in the column "FSE expected". The three cyclohexenes have an average FSE of 1.46, effectively the same as for cyclohexanes. For four cyclopentanes the average FSE is 6.62, 1 kcal/mol smaller than that for cyclopentanes. For the 76 olefins in Tables III-V for which FSE values have been assigned or predicted, the standard deviation of the agreement is 0.44 kcal/mol. This is the same as the average estimated error (from average of variances): 0.43.

The Benson *b* increments in the last column of Table I are not directly comparable with the *c* increments, but differences are expected to be small. There are two reasons for incompatibility. The Benson values reproduce experimental enthalpies of formation while *c* increments give FBE values, and the Benson values equate *b*[C_CDH_H_H_] to *b*[C_C_H_H_H$_s$bd] while *c* increments are based on *c*[C_C_CDH_H_] being equal to *c*[C_C_C_H_H_].

---

(9) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: Cambridge, England, 1986.

(10) Bartolo, H. F.; Rossini, F. D. *J. Phys. Chem.* **1960**, *64*, 1685.

(11) DeTar, D. F. *J. Org. Chem.* **1987**, *52*, 1851-7.

(12) DeTar, D. F. *Comput. Chem.* **1976**, *1*, 35.

Experimental Formal Steric Enthalpy. 3. Alcohols and Ethers

DeLos F. DeTar

Department of Chemistry, Florida State University, Tallahassee, Florida 32306-3006

Received January 22, 1990

This study is a critical evaluation of experimental values of formal steric enthalpies of alcohols and ethers, gas phase, 25 °C, derived from published values of enthalpies of formation. These data can serve as primary values for calibration of force fields used in molecular mechanics.

This continues the work described in the first paper in this series;[6] experimental FSE values for alcohols and ethers are derived from the compilations of Cox and Pilcher[1] in the revised form of Pedley, Naylor, and Kirby[2,3] and from the compilations of Stull, Westrum, and Sinke;[4] some values for alcohols come from the compilation of Wilhoit and Zwolinksi.[5]

---

(1) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London and New York, 1970.

(2) Pedley, J. B.; Rylance, J. *Susex - N.P.L. Computer Analysed Thermochemical Data Organic and Organometallic Compounds*; University of Sussex: Sussex, UK, 1977.

(3) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: Cambridge, England, 1986.

(4) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley & Sons, Inc.: New York, 1969.

0022-3263/91/1956-1474$02.50/0 © 1991 American Chemical Society