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_].

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Experimental Formal Steric Enthalpy. 3. Alcohols and Ethers

DeLos F. DeTar

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

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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]

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Table I. *c* Increments for Alcohols and Ethers[e]

structural element (increment)	definition[a] of structural element	*c* increment[b]	no.[c] of examples	Benson[d] *b* increments
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		-1.91
c[C_C_C_C_C_]	$(C)C(C)_3$	-0.217		0.50
c[O_C_H_]	(C)OH	-40.77	29	-37.9
c[O_C_C_]	(C)O(C)	-30.25	7	-23.2
c[C_H_H_H_O_]	$CH_3(O)$	-6.819	7	(-10.08)
c[C_C_H_H_O_]	$(C)CH_2(O)$	(-5.147)		-8.1
c[C_C_C_H_O_]	(C)CH(C)(O)	-4.34	15	-7.2
c[C_C_C_C_O_]	$(C)C(C)_2(O)$	-3.87	5	-6.6
c[C_H_H_O_O_]	$CH_2(O)_2$	-9.07	4	-16.1
c[C_C_H_O_O_]	$(C)CH(O)_2$	-9.93	3	-16.3
c[C_C_C_O_O_]	$(C)C(C)(O)_2$	-12.33	2	-18.6
c[C_H_O_O_O_]	$CH(O)_3$	-16.30	2	
c[C_C_O_O_O_]	$(C)C(O)_3$	-19.39	1	
c[C_O_O_O_O_]	$C(O)_4$			

[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 occurrences of the group in the data set. [d] Reference 11. [e] The Benson values are based on setting *c*[C_H_H_H_O_] equal to *c*[C_C_H_H_H_]; values in this study are based instead on setting *c*[C_C_H_H_O_] equal to *c*[C_C_C_H_H_]. Benson values apply to enthalpies of formation of populations of conformers while *c* increments apply to formal bond enthalpy.

Table II. Compounds Used To Evaluate *c*[O_C_C_] and *c*[O_C_H_] Based on Gas-Phase Enthalpies of Formation at 25 °C[f]

compound	formula	ΔH_f(expt)[a]	ref[b]	FBE[c]	SM	ΔH_f(calcd)[d]	FSE(exptl)[e]	FSE(assigned)
ethanol	C_2H_6O	-56.21	P	-55.95	0.00	-55.95	-0.26	0.00
ethanol	C_2H_6O	-56.12	S	-55.95	0.00	-55.95	-0.17	0.00
ethylene glycol	$C_2H_6O_2$	-92.61	P	-91.83	0.00	-91.83	-0.78	0.00
1-propanol	C_3H_8O	-60.97	P	-61.10	0.12	-60.98	0.00	0.00
1-propanol	C_3H_8O	-61.55	S	-61.10	0.12	-60.98	-0.57	0.00
1-propanol	C_3H_8O	-61.28	W	-61.10	0.12	-60.98	-0.29	0.00
1-butanol	$C_4H_{10}O$	-65.73	P	-66.24	0.33	-65.91	0.18	0.00
1-butanol	$C_4H_{10}O$	-65.59	S	-66.24	0.33	-65.91	0.32	0.00
1-butanol	$C_4H_{10}O$	-65.65	W	-66.24	0.33	-65.91	0.25	0.00
2-methyl-1-propanol	$C_4H_{10}O$	-67.85	P	-68.24	0.05	-68.19	0.34	0.20
2-methyl-1-propanol	$C_4H_{10}O$	-67.69	W	-68.24	0.05	-68.19	0.50	0.20
diethyl ether	$C_4H_{10}O$	-60.25	P	-60.61	0.47	-60.14	-0.11	0.00
1,4-butanediol	$C_4H_{10}O_2$	-101.98	P	-102.13	0.47	-101.66	-0.32	0.00
1-pentanol	$C_5H_{12}O$	-70.43	P	-71.39	0.53	-70.86	0.43	0.00
1-pentanol	$C_5H_{12}O$	-71.40	W	-71.39	0.53	-70.86	-0.51	0.00
2-methyl-1-butanol	$C_5H_{12}O$	-72.18	P	-73.39	0.15	-73.24	1.06	0.90
2-methyl-1-butanol	$C_5H_{12}O$	-72.30	W	-73.39	0.15	-73.24	0.94	0.90
3-methyl-1-butanol	$C_5H_{12}O$	-72.01	P	-73.39	0.18	-73.21	1.20	0.70
3-methyl-1-butanol	$C_5H_{12}O$	-72.20	W	-73.39	0.18	-73.21	1.01	0.70
ethyl *n*-propyl ether	$C_5H_{12}O$	-65.06	P	-65.76	0.69	-65.07	0.01	0.00
1-hexanol	$C_6H_{14}O$	-75.48	P	-76.54	0.79	-75.75	0.27	0.00
1-hexanol	$C_6H_{14}O$	-76.39	S	-76.54	0.79	-75.75	-0.64	0.00
1-hexanol	$C_6H_{14}O$	-75.90	W	-76.54	0.79	-75.75	-0.17	0.00
di-*n*-propyl ether	$C_6H_{14}O$	-70.00	P	-70.90	0.91	-69.99	0.00	0.00
di-*n*-propyl ether	$C_6H_{14}O$	-70.00	S	-70.90	0.91	-69.99	-0.01	0.00
1-heptanol	$C_7H_{16}O$	-80.40	P	-81.69	1.00	-80.69	0.29	0.00
1-heptanol	$C_7H_{16}O$	-80.03	S	-81.69	1.00	-80.69	0.66	0.00
1-octanol	$C_8H_{18}O$	-84.97	P	-86.83	1.22	-85.61	0.64	0.00
1-octanol	$C_8H_{18}O$	-85.34	S	-86.83	1.22	-85.61	0.27	0.00
2-ethyl-1-hexanol	$C_8H_{18}O$	-87.31	P	-88.83	0.62	-88.21	0.90	1.40
di-*n*-butyl ether	$C_8H_{18}O$	-79.68	P	-81.20	1.33	-79.87	0.19	0.00
di-*n*-butyl ether	$C_8H_{18}O$	-79.80	S	-81.20	1.33	-79.87	0.07	0.00
1-nonanol	$C_9H_{20}O$	-89.94	P	-91.98	1.43	-90.55	0.61	0.00
1-decanol	$C_{10}H_{22}O$	-94.74	P	-97.13	1.65	-95.48	0.74	0.00
1-decanol	$C_{10}H_{22}O$	-96.38	S	-97.13	1.65	-95.48	-0.90	0.00

[a] kcal/mol, gas phase 298 K. [b] P, ref 2; S, ref 4; W, ref 5; A is average. [c] FBE from sum of *c* increments in Table I. [d] FBE + SM. [e] ΔH_f(exptl) − ΔH_f(calcd). [f] For 36 entries the variance of the difference FSE(exptl) − FSE(assigned) is 0.20 (SD 0.4); for 19 entries for which the standard deviation of the experimental data are given, their variance is 0.10 (SD 0.3) and for the same set the variance of FSE(exptl) − FSE(assigned) is 0.16 (SD 0.4).

As discussed in part 1,[6] eq 1 defines the relationship between the observed enthalpy of formation and the formal steric enthalpy.[7-9] The left-hand side is the enthalpy of formation of the single conformer of lowest energy; SM corrects for the contribution due to multiple conformers of higher energy. The first term on the right-hand side is the formal bond enthalpy (FBE) expressed as a sum of group increments; FSE is the formal steric enthalpy. In

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Table III. Compounds Used To Evaluate *c*[C_H_H_H_O_] Based on Gas-Phase Enthalpies of Formation at 25 °C[f]

compound	formula	ΔH_f(exptl)	ref[b]	FBE[c]	SM	ΔH_f(calcd)	FSE(exptl)[e]	FSE(assigned)
dimethyl ether	C_2H_6O	−43.98	P	−43.89	0.00	−43.89	−0.09	0.00
dimethyl ether	C_2H_6O	−43.99	S	−43.89	0.00	−43.89	−0.10	0.00
ethyl methyl ether	C_3H_8O	−51.72	P	−52.25	0.25	−52.00	0.28	0.00
ethyl methyl ether	C_3H_8O	−51.73	S	−52.25	0.25	−52.00	0.28	0.00
methyl *n*-propyl ether	$C_4H_{10}O$	−56.93	P	−57.40	0.48	−56.92	0.00	0.00
methyl *n*-propyl ether	$C_4H_{10}O$	−56.82	S	−57.40	0.48	−56.92	0.10	0.00
methyl *n*-butyl ether	$C_5H_{12}O$	−61.69	P	−62.54	0.69	−61.85	0.16	0.00

[a–e] See Table II. [f] For seven entries the variance of the difference FSE(exptl) − FSE(assigned) is 0.16, SD 0.4; the variance based on standard deviations of experimental ΔH_f values are reported for four compounds is 0.16.

Table IV. Compounds Used To Evaluate *c*[C_C_C_H_O_] and *c*[C_C_C_C_O_] Based on Gas-Phase Enthalpies of Formation at 25 °C[f]

compound	formula	ΔH_f(exptl)[a]	ref[b]	FBE[c]	SM	ΔH_f(calcd)[d]	FSE(exptl)[e]	FSE(assigned)
2-propanol	C_3H_8O	−65.20	P	−65.18	0.00	−65.18	0.00	0.00
2-propanol	C_3H_8O	−65.15	S	−65.18	0.00	−65.18	0.00	0.00
2-propanol	C_3H_8O	−65.11	W	−65.18	0.00	−65.18	0.03	0.00
1,2-propanediol	$C_3H_8O_2$	−100.69	P	−101.06	0.12	−100.94	0.25	0.00
2-butanol	$C_4H_{10}O$	−70.00	P	−70.32	0.25	−70.07	0.07	0.20
2-butanol	$C_4H_{10}O$	−69.86	S	−70.32	0.25	−70.07	0.21	0.20
2-butanol	$C_4H_{10}O$	−69.94	W	−70.32	0.25	−70.07	0.14	0.20
2-methyl-2-propanol	$C_4H_{10}O$	−74.67	W	−74.74	0.00	−74.74	0.07	0.00
2-methyl-2-propanol	$C_4H_{10}O$	−74.69	P	−74.74	0.00	−74.74	0.06	0.00
methyl isopropyl ether	$C_4H_{10}O$	−60.23	P	−61.48	0.08	−61.40	1.17	1.15
methyl isopropyl ether	$C_4H_{10}O$	−60.24	S	−61.48	0.08	−61.40	1.17	1.15
2-methyl-2-butanol	$C_5H_{12}O$	−79.06	P	−79.89	0.09	−79.80	0.74	0.90
2-methyl-2-butanol	$C_5H_{12}O$	−78.65	S	−79.89	0.09	−79.80	1.15	0.90
2-methyl-2-butanol	$C_5H_{12}O$	−78.80	W	−79.89	0.09	−79.80	1.00	0.90
2-pentanol	$C_5H_{12}O$	−74.74	P	−75.47	0.46	−75.01	0.27	0.20
2-pentanol	$C_5H_{12}O$	−75.00	W	−75.47	0.46	−75.01	0.01	0.20
methyl *tert*-butyl ether	$C_5H_{12}O$	−67.76	P	−71.04	0.00	−71.04	3.28	2.30
methyl *tert*-butyl ether	$C_5H_{12}O$	−70.00	S	−71.04	0.00	−71.04	1.04	2.30

[a–e] See Table II. [f] For 20 entries the variance of FSE(exptl) − FSE(expected) is 0.19 (SD 0.4); the variance of the reported ΔH_f values for eight entries is 0.13 (SD 0.4) and the variance of FSE(exptl) − FSE(expected) is 0.13 for this set.

Table V. Compounds Used To Evaluate Remaining *c* Increments of Table I Based on Gas-Phase Enthalpies of Formation at 25 °C[f]

compound	formula	ΔH_f(exptl)[a]	ref[b]	FBE[c]	SM	ΔH_f(calcd)[d]	FSE(exptl)[e]	FSE(assigned)
dimethoxymethane	$C_3H_8O_2$	−83.27	P	−83.21	0.08	−83.13	−0.14	0.00
1,1-dimethoxyethane	$C_4H_{10}O_2$	−93.14	P	−94.10	0.23	−93.87	0.73	1.35
trimethoxymethane	$C_4H_{10}O_3$	−127.13	P	−127.51	0.15	−127.36	0.23	0.00
2,2-dimethoxypropane	$C_5H_{12}O_2$	−102.68	P	−106.53	0.32	−106.21	3.53	2.70
diethoxymethane	$C_5H_{12}O_2$	−99.14	P	−99.93	0.28	−99.65	0.51	0.00
1,1,1-trimethoxyethane	$C_5H_{12}O_3$	−136.88	P	−140.63	0.30	−140.33	3.45	3.45
1,1-diethoxyethane	$C_6H_{14}O_2$	−108.39	P	−110.82	0.46	−110.36	1.97	1.35
3,5,7-trioxanonane	$C_6H_{14}O_3$	−138.89	P	−139.25	0.55	−138.70	−0.19	0.00
2,2-diethoxypropane	$C_7H_{16}O_2$	−120.84	P	−123.26	0.55	−122.71	1.87	2.70
tris(ethoxymethane) (ethyl orthoformate)	$C_7H_{16}O_3$	−151.86	P	−152.59	0.96	−151.63	−0.23	0.00

[a–e] See Table II. [f] The variance of FSE(exptl) − FSE(assigned) is 0.26 (SD 0.5) while the variance of the reported standard deviations of the experimental ΔH_f values in 0.22 (SD 0.5).

this study I derive the *c* increments from FSE values assigned to appropriate standards and then calculate FSE values of other alcohols and ethers.

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

The definitions of FSE values require two key quantities, appropriate FSE values for the standard molecules and suitable SM values. The values presented in these studies may be considered provisional since there is no established method for evaluating conformer populations and the overall SM correction for a given molecule. Fortunately, although population fractions themselves are rather sensitive to assumptions, SM values are less so due to compensation effects described in part 1.[6]

Calculations of SM values were derived by use of a consistent set of energies and based on compounds with one or two rotatable bonds using either three or nine staggered conformers. The following energies were assigned: C–C–C–C trans 0, gauche 0.70 kcal/mol; C–C–O–C trans 0, gauche 1.15; C–C–C–O trans 0, gauche 0.20; C–O–C–O trans 0, gauche 0.60; O–C–C–O trans 0, gauche 0; in every case the g^+g^- value was assigned the sum of the gauche values plus 1.90. This rule assigns 3.30 kcal/mol for the g^+g^- conformer of C–C–C–C–C, the value indicated in the Wiberg study.[10] For longer chains the increment per methylene group was 0.215.

Table I lists the 12 additional structural groups needed to describe all classes of alcohols and ethers. Also included are the four alkane functional groups that occur in many of the listed compounds. Since the *c* increments are underdetermined, it is necessary to make one arbitrary assignment. I have chosen to set *c*[C_C_H_H_O_[equal to *c*[C_C_C_H_H_]. It is also assumed that the appro-

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Table VI. Experimental Formal Steric Enthalpies of Alcohols and Ethers Based on Gas-Phase Enthalpies of Formation at 25 °C (All ΔH_f Values Are in Units of kcal/mol)

compound	formula	ΔH_f(exptl)[a]	ref[b]	FBE[c]	SM	ΔH_f(calcd)[d]	FSE(exptl)[e]	FSE(predicted)
methanol	CH_4O	-48.12	A	-47.59	0.00	-47.59	-0.49	0.00
ethylene oxide	C_2H_4O	-12.58	A	-40.54	0.00	-40.54	27.96	
methyloxirane	C_3H_6O	-22.40	A	-49.77	0.00	-49.77	27.60	
oxetane	C_3H_6O	-19.24	P	-45.69	0.00	-45.69	26.45	
1,3-dioxolane	$C_3H_6O_2$	-71.22	P	-79.86	0.00	-79.86	8.64	
1,3,5-trioxane	$C_3H_6O_3$	-111.35	P	-117.96	0.00	-117.96	6.61	
1,3-propanediol	$C_3H_8O_2$	-93.71	P	-96.98	0.22	-96.76	3.05	0.00
1,2,3-propanetriol	$C_3H_8O_3$	-141.66	P	-136.94	0.22	-136.72	-4.94	
tetrahydrofuran	C_4H_8O	-51.67	P	-50.84	0.00	-50.84	-0.83	
1,3-dioxane	$C_4H_8O_2$	-81.81	P	-85.01	0.00	-85.01	3.20	
1,4-dioxane	$C_4H_8O_2$	-75.39	A	-81.09	0.00	-81.09	5.79	
2-methyl-1,3-dioxolane	$C_4H_8O_2$	-84.13	P	-90.76	0.00	-90.76	6.63	
1,3,5,7-tetraoxacyclooctane	$C_4H_8O_4$	-148.23	P	-157.28				
1,3-butanediol	$C_4H_{10}O_2$	-103.54	P	-106.21	0.33	-105.88	2.34	0.00
2,3-butanediol	$C_4H_{10}O_2$	-115.27	P	-110.29	0.19	-110.10	-5.17	0.00
diethylene glycol	$C_4H_{10}O_3$	-136.52	P	-132.38	0.67	-131.71	-4.81	0.00
erythritol	$C_4H_{10}O_4$	-185.28	P	-182.05	0.47	-181.58	-3.70	
3,3-dimethyloxetane	$C_5H_{10}O$	-35.42	P	-60.83	0.00	-60.83	25.41	
cyclopentanol	$C_5H_{10}O$	-57.98	P	-65.70	0.00	-65.70	7.72	
tetrahydropyran	$C_5H_{10}O$	-53.39	P	-55.99	0.00	-55.99	2.60	
1,3-dioxepane	$C_5H_{10}O_2$	-82.84	P	-90.16	0.00	-90.16	7.32	
cis-2,4-dimethyl-1,3-dioxolane	$C_5H_{10}O_2$	-91.44	P	-99.98	0.00	-99.98	8.54	
trans-2,4-dimethyl-1,3-dioxolane	$C_5H_{10}O_2$	-90.94	P	-99.98	0.00	-99.98	9.04	
2-methyl-1,3-dioxane	$C_5H_{10}O_2$	-95.08	P	-95.90	0.00	-95.90	0.82	
4-methyl-1,3-dioxane	$C_5H_{10}O_2$	-90.08	P	-94.24	0.00	-94.24	4.16	
2-(hydroxymethyl)tetrahydrofuran	$C_5H_{10}O_2$	-88.24	P	-95.95	0.00	-95.95	7.71	
1,3,6-trioxacyclooctane	$C_5H_{10}O_3$	-111.64	P	-120.41				
1,3,5,7,9-pentaoxacyclodecane	$C_5H_{10}O_5$	-186.38	P	-196.60				
3-methyl-2-butanol	$C_5H_{12}O$	-75.22	A	-77.47	0.09	-77.38	2.28	0.90
3-pentanol	$C_5H_{12}O$	-75.76	A	-75.47	0.38	-75.09	-0.61	0.40
1,5-pentanediol	$C_5H_{12}O_2$	-107.34	P	-107.28	0.68	-106.60	-0.75	0.00
pentaerythritol	$C_5H_{12}O_4$	-185.64	P	-183.89	0.00	-183.89	-1.76	
cyclohexanol	$C_6H_{12}O$	-69.40	A	-70.85	0.00	-70.85	0.45	1.40
1,3-dioxacyclooctane	$C_6H_{12}O_2$	-80.50	P	-95.31				
cis-2,4-dimethyl-1,3-dioxane	$C_6H_{12}O_2$	-101.65	P	-105.13	0.00	-105.13	3.48	
2-methoxytetrahydropyran	$C_6H_{12}O_2$	-95.51	P	-97.84	0.00	-97.84	2.33	
4,5-dimethyl-1,3-dioxane	$C_6H_{12}O_2$	-97.78	P	-101.38	0.00	-101.38	3.60	
5,5-dimethyl-1,3-dioxane	$C_6H_{12}O_2$	-100.41	P	-100.15	0.00	-100.15	-0.26	
paraldehyde	$C_6H_{12}O_3$	-151.00	P	-150.64	0.00	-150.64	-0.36	
diisopropyl ether	$C_6H_{14}O$	-76.25	A	-79.06	0.11	-78.95	2.75	2.30
1,2-diethoxyethane	$C_6H_{14}O_2$	-97.56	P	-101.15	0.62	-100.53	2.97	0.00
1,6-hexanediol	$C_6H_{14}O_2$	-110.23	P	-112.42	0.89	-111.53	1.30	0.00
triethylene glycol	$C_6H_{14}O_4$	-173.28	P	-172.92	1.02	-171.90	-1.38	0.00
8-oxatricyclo[3.2.1.0^{1,5}]octane	$C_7H_{10}O$	6.43	P	-63.73	0.00	-63.73	70.16	
2,4,10-trioxaadamantane	$C_7H_{10}O_3$	-119.31	P	-135.51	0.00	-135.51	16.20	
2,4,8,10-tetraoxaspiro[5.5]undecane	$C_7H_{12}O_4$	-150.45	P	-159.95	0.00	-159.95	9.50	
cis-2-methylcyclohexanol	$C_7H_{14}O$	-78.15	P	-77.99	0.00	-77.99	-0.16	
trans-2-methylcyclohexanol	$C_7H_{14}O$	-84.25	P	-77.99	0.00	-77.99	-6.26	
cis-3-methylcyclohexanol	$C_7H_{14}O$	-83.87	P	-77.99	0.00	-77.99	-5.88	
trans-3-methylcyclohexanol	$C_7H_{14}O$	-78.66	P	-77.99	0.00	-77.99	-0.67	
cis-4-methylcyclohexanol	$C_7H_{14}O$	-83.05	P	-77.99	0.00	-77.99	-5.06	
trans-methylcyclohexanol	$C_7H_{14}O$	-87.76	P	-77.99	0.00	-77.99	-9.77	
cis,cis-2,4,6-trimethyl-1,3-dioxane	$C_7H_{14}O_2$	-106.38	P	-114.36	0.00	-114.36	7.98	
1-heptanol	$C_7H_{16}O$	-79.91	A	-81.69	1.00	-80.69	1.39	0.00
isopropyl *tert*-butyl ether	$C_7H_{16}O$	-85.54	A	-88.63	0.00	-88.63	3.03	
1,3-diethoxypropane	$C_7H_{16}O_2$	-104.25	P	-106.30	1.33	-104.97	0.72	0.00
3,5,7,9-tetraoxaundecane	$C_7H_{16}O_4$	-177.10	P	-178.57	0.59	-177.98	0.88	0.00
3-oxabicyclo[3.2.2]nonane	$C_8H_{14}O$	-53.18	P	-65.65	0.00	-65.65	12.47	
2-(ethoxyethoxy)tetrahydropyran	$C_8H_{16}O_3$	-134.56	P	-146.23				
1,4,7,10-tetraoxacyclododecane	$C_8H_{16}O_4$	-150.81	P	-162.18				
di-*sec*-butyl ether	$C_8H_{18}O$	-86.23	A	-89.36	0.23	-89.13	2.87	2.30
di-*tert*-butyl ether	$C_8H_{18}O$	-86.86	A	-98.19	0.00	-98.19	10.99	
acetaldehyde diisopropyl acetal	$C_8H_{18}O_2$	-125.74	P	-123.69				
3,5,7,9,11-pentaoxatridecane	$C_8H_{18}O_5$	-216.52	P	-217.89	0.63	-217.26	0.74	0.00
tetraethylene glycol	$C_8H_{18}O_5$	-211.04	P	-213.47	1.37	-212.10	1.06	0.00
1-nonanol	$C_9H_{20}O$	-91.21	A	-91.98	1.43	-90.55	-1.92	0.00
dibutoxymethane	$C_9H_{20}O_2$	-119.81	P	-120.52	1.14	-119.38	-0.43	0.00
1-adamantanol	$C_{10}H_{16}O$	-74.33	P	-82.30	0.00	-82.30	7.97	
2-adamantanol	$C_{10}H_{16}O$	-71.53	P	-79.88	0.00	-79.88	8.35	
1,4,7,10,13-pentaoxacyclpentadecane	$C_{10}H_{20}O_5$	-191.09	P	-202.72				
methyl *n*-decyl ether	$C_{11}H_{24}O$	-91.09	P	-93.43	1.98	-91.45	0.36	0.00
1,1-dibutoxypropane	$C_{11}H_{24}O_2$	-132.10	P	-136.56	1.41	-135.15	3.05	0.00
1-dodecanol	$C_{12}H_{26}O$	-104.35	P	-107.42	2.08	-105.34	0.99	0.00
1-diamantol	$C_{14}H_{20}O$	-74.28	P	-91.33	0.00	-91.33	17.05	
3-diamantol	$C_{14}H_{20}O$	-71.13	P	-88.91	0.00	-88.91	17.78	
4-diamantol	$C_{14}H_{20}O$	-75.79	P	-91.33	0.00	-91.33	15.54	
tetradecanol	$C_{14}H_{30}O$	-126.05	P	-117.71	2.50	-115.21	-10.84	0.00

[a–e] See Table II.

priate set of structural elements may be described in terms of a main atom plus atoms in the first rank out, the ligands. In particular it is assumed that a single *c*[C_H_H_H_O_], etc., will be sufficient to correlate enthalpies of formation data for both alcohols and ethers. I mention this point because at least one force field, MM2(85), uses different reference bond lengths for the set of groups, depending on whether the groups occur in alcohols or in ethers, and still different reference values for the set if they occur in glycols. This implies that a more complex set of structural groups has been used, some of which depend on atoms in the second rank out.

The last column indicates the number of instances available for each group. The available data are insufficient to provide definitive values for *c*[C_H_O_O_O_], *c*[C_C_O_O_O_], and $_c$[C_O_O_O_O_].

Tables II–V list the compounds used to derive the *c* increments reported in Table I. The differences between the assigned FSE values and the experimental FSE values calculated by eq 1 and using the *c* increments of Table I have standard deviations of about 0.4 kcal/mol. Data for the compounds of the acetal and orthoester families (Table V) are less certain.

The FSE values were assigned to the standards as follows: A molecule of a straight-chain compound in the extended form is assumed to have a FSE of 0. For other molecule energies due to gauche interactions were based on the values listed above and were summed for the conformer of lowest energy.

Table VI reports experimental FSE values for most of the other alcohols and ethers for which enthalpy of formation data for the gas phase are available. On the basis of the generalities observed for alkanes and cycloalkanes, FSE values for the cyclohexanols should correspond to those found for the acyclic alcohols. The relatively large negative values suggest that the experimental enthalpies of formation may be in serious error. The data for some of the glycols are also strongly negative and are in error; other glycol enthalpy values are inconsistent in that additions of successive methylene groups do not produce the expected increments in the enthalpies of formation. The expected increment is −4.926 kcal/mol per added CH_2 increment as summarized in ref 4 (p 240); cf. Benson value in Table I.

The standard deviations of the several correlations are given in the footnotes of the tables.

Experimental Formal Steric Enthalpy. 4. Aldehydes, Ketones, Acids, and Esters

DeLos F. DeTar

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

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This study is a critical evaluation of experimental values of formal steric enthalpies derived from published values of enthalpies of formation of aldehydes, ketones, esters, and acids, gas phase, 25°C. These data may be useful for calibration of force fields.

As discussed in the first paper in this series,[1] eq 1 defines the relationship between the observed enthalpy of formation and the formal steric enthalpy.[2,3] The left-hand side is the enthalpy of formation of the single conformer of lowest energy; SM corrects for the contribution due to multiple conformers of higher energy. The first term on the right-hand side is the formal bond enthalpy expressed as a sum of group increments; FSE is the formal steric enthalpy. In this study I derive the *c* increments from appropriate standards having defined FSE values and from them calculate FSE values for the remaining compounds. The data come from refs 4 and 5.

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

The SM values of all compounds are based on assigning the energies of staggered conformations as follows: C_C_C_C=O trans 0, gauche 0.30, and g^+g^- as 1.90 plus the sum of the gauche interactions.

Table I lists the structural elements needed to describe monofunctional aldehydes, ketones, esters, and acids. *c* increments for alkane structural elements[1] and for alkoxyl groups[6] are also included. Since the *c* increments for each set are underdetermined, it is necessary to make one arbitrary assignment for each. I have chosen to set *c*[C_C_CKH_H_] and *c*[C_C_CEH_H_] equal to *c*[C_C_C_H_H_]. For many of the structural elements, it is necessary to go to the second rank out in making the definition. This is effected by defining three types of sp^2 carbon atoms, CD for olefins (treated elsewhere, ref 7), CE

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