

Bond-Bond Interactions in Organic Oxygen Compounds

Part I. A Bond-Bond Interaction Scheme for Aliphatic Alcohols, Ethers, and Acetals

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The heats of formation of gaseous alcohols, ethers, and acetals are expressed as linear functions of structural parameters. The root-mean-square difference between the calculated and experimental values is ± 0.0135 kcal·mole⁻¹bond⁻¹ for 26 gaseous alcohols and ethers. The energy contributions of *gauche-n*-butane and *gauche-gauche* prime *n*-pentane structures in branched oxygen compounds are close to those in branched hydrocarbons. The energetic effect of the interaction between a fifth-neighbor hydrogen atom and the lone-pair electrons of an oxygen atom is about half of that between fifth-neighbor hydrogen atoms. A preliminary calculation gives the value, 13.4 ± 0.5 kcal·mole⁻¹, for O—C—O interaction and the value, -2.8 ± 0.5 kcal·mole⁻¹, for Δ_{OCO} increments in acetals.

The bond-bond interaction scheme of Allen¹ was recently reported by Kalb *et al.*² to correlate closely with the experimental heats of formation of gaseous and liquid paraffin hydrocarbons. McCullough and Good³ earlier applied this scheme to a number of alkanethiols and alkyl sulfides and disulfides and found that the correlation is remarkably good. Skinner⁷ applied Allen's scheme to alkenes, cycloalkenes and a limited number of alcohols, alkyl bromides, and amines quite successfully.

The present study was undertaken to determine whether the available heats of formation of saturated aliphatic alcohols, ethers, and acetals correlate with their structure. The aim was also to obtain more information about steric interactions in these molecules and to compare these with those in saturated hydrocarbons.

It is worth mentioning that Cox⁴ derived a bond energy scheme for aliphatic and benzenoid compounds including alcohols and ethers from the premise that the energy of a carbon-oxygen bond depends on the state of hybridization of the carbon atom. However, the number of accurately known experimental heats of formation data has greatly increased subsequently and a new approach is needed to clarify what kind of experimental data are now required for organic oxygen compounds in the field of thermochemistry.

GENERAL TREATMENT

Our general approach was to adjust the coefficients in the equation

$$\begin{aligned} \Delta H_a^\circ(g) - \sum E_b(g) = & n_1 \Gamma_{\text{CCC}} + n_2 \Gamma_{\text{CCO}} + n_3 \Gamma_{\text{COC}} + n_4 \Gamma_{\text{OCO}} \\ & + n_5 \Delta_{\text{CCC}} + n_6 \Delta_{\text{CCO}} + n_7 \Delta_{\text{OCO}} + n_8 S_{15}^{\text{HH}} \\ & + n_9 S_{15}^{\text{HO}} + n_{10} S_{16}^{\text{HH}} \end{aligned} \quad (1)$$

where $\Delta H_a^\circ(g)$ is the heat of atomization and $\sum E_b(g)$ the sum of bond energies of the compound in question at 25°C. Γ_{CCC} , Γ_{CCO} , etc., are the coefficients to be determined, and n_1 , n_2 , etc., are the structural parameters. n_1 is the number of pairs of next-nearest-neighbor carbon atoms, n_2 the number of pairs of next-nearest-neighbor carbon and oxygen atoms, n_3 the number of pairs of next-nearest-neighbor carbon atoms connected by an oxygen atom, n_4 the number of pairs of next-nearest-neighbor oxygen atoms, n_5 the number of sets of three carbon atoms bonded to a fourth carbon atom, n_6 the number of CCO trios bonded to a carbon atom, n_7 the number of OCO trios bonded to a carbon atom, n_8 the minimum number of fifth-neighbor H···H interactions of the *gauche*-butane type, n_9 the minimum number of fifth-neighbor interactions between hydrogen atoms and lone-pair electrons of oxygen atoms, and n_{10} the minimum number of interactions of the *gauche-gauche* prime pentane type² in which sixth-neighbor hydrogen atoms are forced to come into close proximity.

The following values were used for the heats of atomization of elements: $\Delta H_a^\circ(\text{C}, g)$ 170.9 kcal·atom⁻¹, $\Delta H_a^\circ(\text{H}, g)$ 52.09 kcal·atom⁻¹, and $\Delta H_a^\circ(\text{O}, g)$ 59.56 kcal·atom⁻¹.⁷ The bond energies of the C—C and C—H bonds, 78.84 and 99.29 kcal·mole⁻¹·bond⁻¹, respectively, were those adopted by Allen.¹ The energy of the O—H bond, 110.77 kcal·mole⁻¹·bond⁻¹, is based on the heat of formation of gaseous water and that of the C—O bond, 78.16 kcal·mole⁻¹·bond⁻¹, on the heat of formation of gaseous methanol, -47.96 kcal/mole.²¹

Owing to the limited number of reliable data for acetals, the machine computation has been restricted to acyclic alcohols and ethers. Table 1 lists all of the compounds for which accurate standard heats of formation in the gaseous state are available. Also the values of S_{15}^{HH} , S_{15}^{HO} , and S_{16}^{HH} parameters are shown in Table 1.

The optimum coefficients were determined on an IBM 1130 computer at the Computer Center, University of Turku, Turku, using a linear regression program with a least-squares criterion. The program generated the $\Delta H_a^\circ(g) - \sum E_b(g)$ vector, the optimum coefficients and their covariance matrix. Table 2 lists the optimum coefficients and their standard errors, and the root-mean-square deviation of each correlation. As the heats of combustion on which the heats of formation are based vary between 31 and 50 kcal·mole⁻¹·bond⁻¹, the rms deviation (Table 2) corresponds to differences of 0.03 to 0.05 % between calculated and experimental data. Differences between calculated and experimental results are presented in Table 1.

Heats of formation of some acetals together their S_{15}^{HH} and S_{15}^{HO} parameters are shown in Table 3. Using the general treatment these values

Table 1. Comparison of calculated and experimental data.

Compound	$-\Delta H_f^\circ(\text{g})$ kcal·mole ⁻¹	$\Delta H_a^\circ(\text{g})$ Obs.	$-\sum E_b(\text{g})$ Calc.	Diff. ^a	S'_{15}^{HH}	S_{15}^{HO}	S_{16}^{HH}
EtOH	56.19 ²⁴	5.89	5.62	-0.27	0	0	0
PrOH	61.31 ^b	8.68	8.36	-0.32	0	0	0
i-PrOH	65.09 ^c	12.46	12.52	+0.06	0	0	0
BuOH	65.84 ^d	10.88	11.10	+0.22	0	0	0
i-BuOH	67.72 ^e	12.76	12.94	+0.18	0	1	0
s-BuOH	70.06 ^f	15.10	15.00	-0.10	0	1	0
t-BuOH	74.84 ^{7,10}	19.88	20.05	+0.17	0	0	0
Pentanol	71.94 ^{5,g}	14.65	13.84	-0.81	0	0	0
3-Me-1-BuOH	72.60 ^{5,g}	15.31	15.26	-0.05	1	0	0
2-Me-2-BuOH	79.11 ^{5,g}	21.82	21.86	+0.04	1	1	0
2-Pentanol	75.17 ^{5,g}	17.88	17.74	-0.14	0	0	0
2-Me-1-BuOH	72.20 ^{5,g}	14.91	15.01	+0.10	1	1	0
Hexanol	75.94 ^{5,g}	16.34	16.57	+0.23	0	0	0
Nonanol	92.03 ^{5,g}	25.42	24.79	-0.63	0	0	0
Decanol	95.85 ^{5,g}	26.91	27.52	+0.61	0	0	0
CH ₃ OCH ₃	43.99 ¹¹	5.86	5.72	-0.14	0	0	0
CH ₃ OCH ₂ CH ₃	51.73 ¹¹	11.27	11.35	+0.08	0	0	0
CH ₃ CH ₂ OCH ₂ CH ₃	59.93 ^h	17.14	16.97	-0.17	0	0	0
CH ₃ OCH ₂ CH ₂ CH ₃	56.82 ¹¹	14.03	14.09	+0.06	0	0	0
CH ₃ OCH(CH ₃) ₂	60.24 ¹¹	17.45	17.58	+0.13	1	0	0
CH ₃ OC(CH ₃) ₃	70.0 ¹⁴	24.88	24.43	-0.45	2	0	0
(CH ₃ CH ₂ CH ₂) ₂ O	69.99 ¹⁵	22.54	22.45	-0.09	0	0	0
(CH ₃) ₂ CHOCH(CH ₃) ₂	76.4 ¹⁴	28.95	29.42	+0.47	2	0	0
(CH ₃) ₂ CHOC(CH ₃) ₃	85.6 ¹⁴	35.82	35.82	(±0.00) ⁱ	1	0	1
(CH ₃ CH ₂ CH ₂ CH ₂) ₂ O	79.84 ¹⁵	27.73	27.92	+0.19	0	0	0
(CH ₃ CH ₂ CH(CH ₃)) ₂ O	86.18 ¹⁵	34.07	33.98	-0.09	3	1	0

^a $\Delta H_f^\circ(\text{g, exptl}) - \Delta H_f^\circ(\text{g, calc.})$ ^b 61.55 ± 0.14 ⁵ and 61.07 ± 1.05 ^{6,7} ^c 64.88 ± 0.14 ⁵ ^d 65.15 ± 0.22 ^{6,7} and 65.29 ⁸ ^e 65.57 ± 0.25 ⁵ ^f 65.81 ± 0.15 ⁹ and 66.14 ± 0.25 ^{7,10} ^g 67.61 ± 0.25 ⁵ and 67.84 ± 0.30 ^{7,10} ^h 70.08 ± 0.24 ⁵ and 70.03 ± 0.32 ^{7,10} ⁱ For heats of vaporization, see Ref. 25. ^h 60.28 ± 0.19 ¹² ⁱ 59.70 ¹² (Stohmann in Ref. 12) and 59.82 ± 0.44 ¹³ ^j Because this is the only compound including S_{16}^{HH} -interaction, the difference vanishes automatically.

lead to the following equations assuming (as first approximation) that the ring of 1,3-dioxanes is nearly strainless:

$$\Gamma_{\text{OCO}} = 12.83 + [\text{RS}]^* = 13.43 \quad (\text{I})$$

$$\Gamma_{\text{OCO}} = 12.74 + [\text{RS}]^* = 13.34 \quad (\text{II})$$

$$\Gamma_{\text{OCO}} + \Delta_{\text{OCO}} = 10.62 + [\text{RS}]^* = 11.22 \quad (\text{III})$$

$$\text{CH}_3\text{CH}(\text{OCH}_2\text{CH}_3)_2 \quad \Gamma_{\text{OCO}} + \Delta_{\text{OCO}} = 10.02 \quad (\text{IV})$$

$$\begin{array}{c} \text{OCH}(\text{CH}_3)_2 \\ \diagup \\ \text{CH}_3\text{CH} \\ \diagdown \\ \text{OCH}(\text{CH}_3)_2 \end{array} \quad \Gamma_{\text{OCO}} + \Delta_{\text{OCO}} = 10.20 \quad (\text{V})$$

$$(\text{CH}_3)_2\text{C}(\text{OCH}_3)_2 \quad \Gamma_{\text{OCO}} + 2\Delta_{\text{OCO}} = 7.95 \quad (\text{VI})$$

* $[\text{RS}] = 0.6$ kcal·mole⁻¹ assumed for apparent ring strain when the strain energy is $0.6 - RT \approx 0$.²⁸

Table 2. Optimum coefficients determined in this work and those presented by Kalb *et al.*² and Skinner.⁷

Coefficients	This work	Kalb <i>et al.</i>		Skinner
		Seven parameters	Six parameters	
Γ_C	2.33	2.237 ± 0.097	2.323 ± 0.118	2.35
Γ_{CCC}	2.737 ± 0.038	2.745 ± 0.096	2.673 ± 0.117	2.58
Γ_{CCO}	5.623 ± 0.127	—	—	5.66
Γ_{COC}	5.725 ± 0.199	—	—	6.00 ^a
Γ_{OCO}	$13.4^b \pm 0.5$	—	—	—
Δ_{CCC}	-0.640 ± 0.210	-0.811 ± 0.081	-0.819 ± 0.099	-0.55
Δ_{CCO}	-1.465 ± 0.139	—	—	-1.43
Δ_{OCO}	$-2.8^b \pm 0.5$	—	—	—
S_{16}^{HH}	-0.669 ± 0.126	-0.545 ± 0.054	-0.687 ± 0.056	—
S_{16}^{HO}	-0.252 ± 0.200	—	—	—
S_{16}^{HH}	-1.802 ± 0.466	—	—	—
RMS deviation ^c	± 0.0135	± 0.0166	± 0.0185	—

All coefficients in kcal·mole⁻¹. ^a Skinner and Pilcher.⁷ ^b Preliminary estimations on the basis of heats of formation data for acetals. ^c In kcal·mole⁻¹·bond⁻¹.

From eqns. (I) and (II) we obtain the value, 13.4 ± 0.5 kcal·mole⁻¹, for the O—C—O interaction allowing some uncertainty and then eqns. (III—VI) give the value, -2.8 ± 0.5 kcal·mole⁻¹, for the interaction of the OCO trio bonded to a carbon atom in acetals.

Chao and Rossini recently reported heats of formation for several alkanols.⁵ Unfortunately, heat of vaporization data are available only for ten molecules of this series.²⁵ We have calculated heats of vaporization for the remaining alkanols by the expression described by Klages¹⁹ as improved by Wadsö²⁵ and employed the derived values to evaluate the heats of formation of gaseous alkanols.

DISCUSSION

Extensive discussions of the theoretical basis of the above treatment have been presented by Allen,¹ Kalb *et al.*,² Allen and Shull,²² Cignitti and Allen,²³ and Skinner.⁷ Consequently, our discussion will be restricted to some aspects that became evident in this work.

The computed coefficients yield the following equations for the direct calculation of the heats of formation of gaseous alcohols and ethers, respectively:

$$-\Delta H_f^\circ(g) = 45.64 + 2.33n_C + 2.74n_1 + 5.62n_2 - 0.64n_5 - 1.465n_6 - 0.67n_8 - 0.25n_9 - 1.80n_{10} \quad (2)$$

$$-\Delta H_f^\circ(g) = 33.47 + 2.33n_C + 2.74n_1 + 5.62n_2 + 5.725n_3 - 0.64n_5 - 1.465n_6 - 0.67n_8 - 0.25n_9 - 1.80n_{10} \quad (3)$$

n_C is the number of carbon atoms. The above equations apply to acyclic molecules.

Kalb *et al.*² have computed the optimum coefficients for gaseous alkanes, cyclohexane, alkylcyclohexanes, and decalins using equations with six and seven parameters. Their calculations led to the equations

$$-\Delta H_f^\circ(g) = 15.599K + 2.323n_c + 2.673n_1 - 0.819n_5 - 0.687n_8 - 2.552n_{10} \quad (\text{six parameters}) \quad (4)$$

$$-\Delta H_f^\circ(g) = 15.660K + 2.237n_c + 2.745n_1 - 0.811n_5 - 0.545n_8 - 2.836n_{10} - 0.392n_L \quad (\text{seven parameters}) \quad (5)$$

where K is 1 for acyclic, 0 for unicyclic and -1 for bicyclic molecules and n_L is the minimum number of fifth-neighbor interactions which are locked, that is, the $H \cdots H$ distance cannot be increased by internal rotation about any C—C bond without simultaneously decreasing the $H \cdots H$ distance in another fifth-neighbor or sixth-neighbor interaction.² We have not included the locking parameter in our study because the only molecule exhibiting locking is 2,2-dimethoxypropane in which, moreover, two of the fifth-neighbor interactions are of S_{15}^{HO} type. Consequently, we think that the value of the locking parameter in molecules of this kind is so small that more, very accurate, experimental data are needed before the value of this parameter for oxygen compounds can be taken into account.

Skinner⁷ derived eqn. (6) for the calculation of the heats of formation of gaseous alcohols:

$$-\Delta H_f^\circ(g) = 45.59 + 2.35n_c + 2.58n_1 + 5.66n_2 - 0.55n_5 - 1.43n_6 - [S] \quad (6)$$

[S] constitutes different steric interactions. Eqn. (2) obtained in this work and eqn. (6) are in fairly good agreement when it is taken into account that the latter is based on the heats of formation of only seven gaseous alcohols. When the same coefficients in eqns. (2), (3), (4), and (5) are compared, it is observed that they are generally of the same order of magnitude. The difference in the values of S_{16}^{HH} , however, seems to be real since our value and that of Kalb *et al.*² deviate more than the limits of the combined standard errors (Table 2). The value for the S_{16}^{HH} -type interaction in the gaseous state was derived from the heat of formation of only one gaseous molecule exhibiting

Table 3. Heats of formation data for some gaseous acetals.

Compound	$-\Delta H_f^\circ(g)$ kcal·mole ⁻¹	$\Delta H_a^\circ(g) - \sum E_b(g)$	S_{15}^{HH}	S_{15}^{HO}	S_{16}^{HH}
1,3-Dioxane	83.42 ²⁶	38.26	0	0	0
4-Methyl-1,3-d	92.56 ^{26,a}	45.07	0	0	0
2-Methyl-1,3-d	94.79 ^{26,a}	47.30	0	0	0
$\text{CH}_3\text{CH}(\text{OCH}_2\text{CH}_3)_2$	108.41 ¹³	43.04	1	1	0
$(\text{CH}_3)_2\text{C}(\text{OCH}_3)_2$	102.9 ¹⁷	39.86	2	2	0
$\text{CH}_3\text{CH}(\text{OCH}(\text{CH}_3)_2)_2$	125.70 ^{27,a}	55.67	3	1	0
$\text{CH}_2(\text{OCH}_2\text{CH}_3)_2$	97.15 ¹⁶	(Calc. about 99 kcal·mole ⁻¹)			
$(\text{CH}_3)_2\text{C}(\text{OC}_2\text{H}_5)_2$	120.5 ¹⁷	(Calc. about 119 »)			


^a For heats of vaporization, see Ref. 25.

this interaction in both investigations and thus the difference in these values may be mostly of experimental origin.

The preliminary results for acetals show that the heat of formation of diethoxymethane may be in error about 2 kcal·mole⁻¹ in agreement with the communication of Sunner.¹⁸ Also the value for 2,2-diethoxypropane is obviously less accurate in accordance with the conclusion of Cox.⁴

An application of the computed bond-bond interaction scheme to saturated oxygen heterocycles showed that additional coefficients, *e.g.* for ring strain, must be taken into account. A more detailed discussion of this extension and of the Γ_{OCO} and Δ_{OCO} increments in acetals will be presented in a forthcoming paper.²⁰

The present study reveals a lack of heat of formation data for acetals. Additional heats of combustion should be measured including those for several

acetals and especially molecules in which  S_{15}^{HO} , S_{16}^{HH} and locking

interactions are present. However, the bond-bond interaction scheme derived in this work forms a basis for the prediction of heats of formation, and also heats of reaction, of saturated aliphatic alcohols, acetals and ethers. Its agreement with previous treatments is very satisfactory.

However, it is very difficult to make a choice between the heats of formation data from different laboratories. Thus, for instance, we have used for methanol and ethanol the values recommended by Natural Bureau of Standards²¹ and for the other lower alkanols the mean of two or three slightly different values in order to avoid subjective choice. For the higher alkanols we have adopted the values of Chao and Rossini, except for 3-pentanol, 3-methyl-2-butanol, heptanol and octanol for which their values seem to be in error one or more kcal·mole⁻¹. This may be due to the fact that they have assumed that the only impurities in their samples were isomeric alkanols.⁵ It is worth mentioning that from the older heats of formation data for alkanols, the values reported by Verkade and Coops⁵ for heptanol and octanol may be reliable on the basis of the derived bond-bond interaction scheme.

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