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Improved Benson Increments for the Estimation of Standard Enthalpies of Formation and Enthalpies of Vaporization of Alkyl Ethers, Acetals, Ketals, and Ortho Esters

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This work was undertaken for the evaluation and revision of group-additivity values necessary for predicting standard enthalpies of formation and enthalpies of vaporization of ethers, acetals, ketals, and ortho esters by means of Benson's group-additivity methodology. The database on the standard molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ has been extended with measurements on several acetals, ketals, and ortho esters using the transpiration method. The standard molar enthalpies of formation $\Delta_f H_m^\circ$ (g,298.15K) of alkyl ethers, acetals, ketals, and ortho esters were derived using the data for the $\Delta_f H_m^\circ$ (l or cr,298.15K) from the literature and the present results for the enthalpies of vaporization or sublimation. The current database of experimental data for enthalpies of formation and enthalpies of vaporization at 298.15 K have been used to reevaluate the values of the Benson's increments for of alkyl ethers, acetals, ketals, and ortho esters. The group-additivity parameters and strain corrections useful in the application of the Benson's correlation are presented in tabular form, together with a description of their evaluation.

1. Introduction

Structural-additive methods, based on the classical theory of structure, make it possible to address a number of vital practical issues: the understanding of interrelations between the structure and energetics of organic molecules, the detection and explanation of anomalies in the structures and properties of certain substances, the verification of experimental data with mutual consistency, and the prediction of substance properties that have not been investigated experimentally.

Thermodynamic properties of organic compounds in general can be predicted using quantitative structure−property relationships where the property of interest is a function of molecular descriptors that can be derived in either nonempirical (ab initio) or empirical ways. An example of an empirical technique is the well-known group-additivity procedure (76-Ben, 96-Coh), in which the property is estimated as the sum of contributions from the individual structural elements that compose the compound of interest. The success of empirical additive schemes, such as Benson's tables, in calculating thermochemical properties of organic compounds suggests that most of the group-additive values (GAVs) applied by this procedure are reliable. In fact, the experimental database for deriving a plethora of increments is not extensive enough to take into account a diversity of possible combinations of atoms. Thus, because of rigorous constraints, some gaps in the database have been filled with approximations. The reliability of these values, however, is questionable. Accurate and reliable experimental data are needed to establish or refine empirical estimation schemes. It is recognized that there is a lack of thermochemical information for branched molecules in each class of organic compounds. Because of this scarcity of experimental data, a number of additive parameters, such as those for a tertiary C−(G)(C)2(H) or quaternary C−(G)(C)3 carbon atom attached to a functional group (G), have generally been evaluated only from the data for one or two branched compounds. These parameters have to be checked for their validity. In this context, systematic investigations of branched esters (96-Ver/Bec), amines (97-Ver), nitriles (94-Rak/Ver), alcohols (98-Ver), ketones (95-Nol/Ver), imines (97-Ver/Mor), and fluoroalkanes (97-Sch/Ver) have been performed in our laboratory in the past decade. This paper extends our previous studies on the systematic evaluation of the group-additivity contributions for alkyl ether derivatives, containing the functional group OR (with R = alkyl). Interest in this chemical family has grown in the past decade, because alkyl ether derivatives are successfully utilized as fuel additives. Results for many alkylation reactions that produce tertiary alkyl ethers have been reported in the literature recently. Following this trend, about 30 alkyl ethers (with an emphasis on branched species), 35 acetals and ketals, and 10 ortho esters have been investigated in our laboratory since 1990. The additional thermochemical information derived from these studies has prompted the reevaluation and extension of the existing (96-Cohen) group-additivity values for alkyl ether derivatives. We report here the Benson's group-additivity increments that have been improved for estimations of the standard enthalpies of formation as well as the standard enthalpies of vaporization of alkyl ethers, acetals, ketals, and ortho esters, using the contemporary experimental database.

Data for the enthalpies of vaporization of linear and some branched alkyl ethers have been published by a number of groups (see Table 5 below). Additionally, some new experimental results on branched alkyl ethers have been reported just recently (02-Ver/Kra). Surprisingly, however, only very few experimental vapor pressure and vaporization enthalpy measurements on acetals, ketals, and ortho esters are available in the literature (see Table 7). That is why, in this work, we performed an extensive experimental

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study on these chemical families of OR-containing compounds and derived vaporization enthalpies that were then applied for calculations of the gaseous enthalpies of formation as well as for a reevaluation of the group-additivity contributions according Benson's methodology.

2. Experimental Section

Materials. For the synthesis of acetals, ketals, and ortho esters the well-known acid-catalyzed acetalization of carbonyl compounds with alcohols in the presence of a water binding orthoformic acid alkyl ester was used (98-Ver/Pen, 95-Rak/Ver). All liquid samples were purified by several fractional distillations on a spinning band column. All solid compounds were purified by several recrystallizations. The purities of the samples were determined by GC (≥99.9%).

Measurements of the Enthalpies of Vaporization or Sublimation. The enthalpies of vaporization or sublimation of oxygen-containing compounds were determined using the method of transference in a saturated N_2 stream. The method has been described before (00-Ver) and shown to give results that are in excellent agreement with those of other established techniques for determining vapor pressures of pure substances and enthalpies of vaporization from the temperature dependence of the vapor pressure. For each experiment, about 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-tube of length 20 cm and diameter 0.5 cm. A nitrogen stream was passed through the U-tube at constant temperature (±0.1 K), and the transported amount of material was condensed in a cooled trap. The mass of condensed product was determined by GC analysis using an internal standard (hydrocarbons). Assuming that Dalton's law of partial pressures applied to the saturated nitrogen stream is valid, values of the vapor pressure p can be calculated according to

$$p = mRT_a/V(N_2)M \tag{1}$$

where R is the ideal gas constant (8.314 51 $J\cdot mol^{-1}\cdot K^{-1}$), m is the mass of transported compound, $V(N_2)$ is the volume of transporting gas, M is the molar mass of the compound, and T_a is the temperature of the soap bubble meter. The volume of the gas transferred through the tube, $V(N_2)$, was determined from the flow rate and time measurements. The flow rate was maintained constant with the help of a high-precision needle valve (Hoke). The accuracy of the $V(N_2)$ determinations from the flow rate was assessed to be ±0.001 dm^3.

The vapor pressure p at each saturation temperature was calculated from the mass of sample collected within a definite time period. The thermodynamic relation for the equilibrium existing between the vapor and the liquid phase of a pure substance is

$$\frac{dp}{dT} = \frac{\Delta_l^g H_m^\circ}{T\Delta_l^g V_m} \tag{2}$$

where $\Delta_l^g V_m$ is the difference in molar volume between the vapor phase and the liquid phase. At low pressure, the volume of the liquid phase can be neglected in comparison with that of the vapor, and the in case of nonassociating or weakly associating vapors at sufficiently low pressures, the ideal gas law can be adopted, neglecting contributions arising from the second virial coefficients. The result is the Clausius−Clapeyron equation

$$-\frac{R\,d(\ln p)}{d\left(\frac{1}{T}\right)} = \Delta_l^g H_m^\circ \tag{3}$$

Under the assumption that

$$\begin{cases} \Delta_l^g H_m^\circ \approx \Delta_l^g H_{m,T_0}^\circ + \Delta_l^g C_{p,m}^\circ (T - T_0) \\ \Delta_l^g V_m \approx \dfrac{RT}{p} \end{cases} \tag{4}$$

which is justified at sufficiently low vapor pressures, eq 3 can be integrated, and the temperature dependence of the vapor pressure can be described by the equation

$$R \ln p = a + \frac{b}{T} + \Delta_l^g C_{p,m}^\circ \ln\left(\frac{T}{T_0}\right) \tag{5}$$

which is fitted to the experimental $p-T$ data using a and b as adjustable parameters. The following equation gives the value of the vaporization enthalpy at temperature T

$$\Delta_l^g H_m^\circ(T) = -b + T\Delta_l^g C_{p,m}^\circ \tag{6}$$

where $\Delta_l^g C_{p,m}^\circ = \Delta_l C_{p,m}^\circ - \Delta_g C_{p,m}^\circ$ is the difference between the molar heat capacities of the liquid and the gaseous phase. Values of $\Delta_g C_{p,m}^\circ$ based on the molar heat capacities $\Delta_l C_{p,m}^\circ$ and $\Delta_g C_{p,m}^\circ$ calculated according procedure developed by Domalski and Hearing (93-Dom/Hea). These values together with the coefficients a and b according to eq 5 are listed in Tables 1−4. T_0 appearing in eqs 4 and 5 is an arbitrarily chosen reference temperature. The molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ have been calculated as a function of temperature using eq 6 and are listed in Tables 1−4. To assess the uncertainty of the $\Delta_l^g H_m^\circ$(298.15K) values, the experimental data were approximated with the linear equation $\ln(p) = f(T^{-1})$ using the method of least squares. The errors in the thermodynamic functions were defined as deviations of the experimental values of $\ln(p)$ from this linear correlation. The molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ at 298.15 K derived in this manner were used to calculate the gaseous enthalpies of formation $\Delta_f H_m^\circ(g)$, as well as to evaluate the group-additivity contributions for predicting $\Delta_l^g H_m^\circ$.

3. Discussion

One of the aims of the work in our laboratory has been to build a framework of experimental data from which one can study the relation between energy content and molecular structure and calculate values for the enthalpies of formation of many hundreds of compounds without need of further experimental measurements. Among the important groups of compounds in need of experimental data suitable for a basic framework of this kind are alkyl ethers, acetals, ketals, and ortho esters. The Benson-type group-additivity values for oxygen-containing compounds were revised by Cohen (96-Coh) and Domalski and Hearing (93-Dom/Hea) using a database generally available from Pedley et al. (86-Ped/Nay). Because of the paucity of experimental data on branched alkyl ethers and both open-chained and phenyl-substituted acetals, ketals, and ortho esters at that time, the values of the additive parameters for these chemical families were derived only from very restricted numbers of compounds, and the evaluation of some necessary parameters was even not possible. New data gathered in Tables 1−7 allow more reliable GAVs to be derived for estimations of the thermochemical properties of alkyl ether

Table 1. Results for the Vapor Pressure p and Enthalpy of Vaporization $\Delta_l^g H_m^\circ$ Measured for Acetals and Ketals by the Transpiration Method

T [a]	m [b]	$V(N_2)$ [c]	p [d]	$p_{exp} - p_{calc}$	$\Delta_l^g H_m^\circ$
K	mg	dm^3	Pa	Pa	kJ·mol^{-1}
4-methyl-1,3-dioxane (1120-97-4), **86**; $\Delta_l^g H_m^\circ$(298.15 K) = (43.46 ± 0.30) kJ·mol^{-1}					
$\ln(p/Pa) = 266.415/R - 60\ 360.47/[R(T/K)] - 56.7/R \ln[(T/K)/298.15]$					
273.7	19.9	1.051	443.7	−2.8	44.84
278.2	23.4	0.844	630.4	16.8	44.59
283.2	21.8	0.573	850.2	−11.2	44.30
288.2	18.5	0.350	1169.0	−23.7	44.02
293.2	17.8	0.239	1631.0	1.1	43.74
298.2	16.3	0.159	2228.0	28.2	43.45
303.1	17.4	0.128	2935.0	17.3	43.17
308.1	16.9	0.096	3792.0	−57.3	42.89
313.1	14.8	0.063	5065.0	40.1	42.61
1.1-diethoxyethane (105-57-7), **95**; $\Delta_l^g H_m^\circ$(298.15 K) = (39.12 ± 0.33) kJ·mol^{-1}					
$\ln(p/Pa) = 270.097/R - 59\ 901.257/[R(T/K)] - 69.7/R \ln[(T/K)/298.15]$					
274.8	18.7	0.412	1063	18.1	40.75
278.6	19.4	0.329	1349	17.4	40.48
283.5	21.8	0.275	1777	−21.9	40.14
288.2	23.2	0.219	2330	−42.1	39.81
293.2	23.4	0.165	3086	−59.3	39.47
298.3	20.8	0.110	4076	−67.1	39.11
303.4	21.2	0.082	5528	133.9	38.75
308.3	17.6	0.054	6956	77.5	38.41
2-methyl-1.3-dioxolane (497-26-7), **102**; $\Delta_l^g H_m^\circ$(298.15 K) = (42.78 ± 0.61) kJ·mol^{-1}					
$\ln(p/Pa) = 260.616/R - 55\ 031.034/[R(T/K)] - 41.1/R \ln[(T/K)/298.15]$					
270.3	24.5	0.521	1502	−43.4	43.92
274.0	24.1	0.352	2105	93.7	43.77
278.6	24.6	0.261	2828	67.8	43.58
283.6	25.2	0.196	3789	−53.9	43.38
288.4	24.4	0.144	4940	−275.8	43.18
293.6	22.5	0.091	7132	−37.4	42.96
298.5	22.3	0.066	9699	134.5	42.76
303.5	23.8	0.052	13 080	384.7	42.56
308.5	22.6	0.039	16 480	−194.9	42.35
2-*n*-propyl-1.3-dioxolane (3390-13-4), **103**; $\Delta_l^g H_m^\circ$(298.15 K) = (45.21 ± 0.34) kJ·mol^{-1}					
$\ln(p/Pa) = 266.754/R - 61\ 938/[R(T/K)] - 56.10/R \ln[(T/K)/298.15]$					
278.3	32.6	2.314	320.3	−3.6	46.33
283.4	43.2	2.084	461.2	−2.6	46.04
288.3	32.0	1.084	649.6	3.7	45.76
293.3	24.5	0.589	905.5	12.1	45.48
298.4	36.6	0.637	1244.0	16.4	45.20
303.4	25.7	0.335	1656.0	0.0	44.92
308.4	19.4	0.191	2193.0	−15.2	44.64
313.4	17.2	0.128	2886.0	−26.5	44.36
2,4-dimethyl-1,3-dioxane (766-20-1), **107**; $\Delta_l^g H_m^\circ$(298.15 K) = (44.86 ± 0.60) kJ·mol^{-1}					
$\ln(p/Pa) = 258.923/R - 58\ 278.857/[R(T/K)] - 45.00/R \ln[(T/K)/298.15]$					
273.7	16.8	0.952	408.9	7.6	45.96
278.4	17.9	0.765	531.2	−32.8	45.75
283.4	18.6	0.519	796.2	−2.4	45.53
288.3	16.4	0.317	1140.0	31.9	45.31
293.3	15.6	0.216	1571.0	42.8	45.08
298.3	14.0	0.144	2108.0	26.4	44.86
303.3	15.2	0.116	2827.0	24.4	44.63
308.3	14.9	0.087	3700.0	−31.7	44.41
313.3	12.7	0.057	4798.0	−118.6	44.18
2,2-dimethoxypropane (77-76-9), **110**; $\Delta_l^g H_m^\circ$(298.15 K) = (37.63 ± 0.42) kJ·mol^{-1}					
$\ln(p/Pa) = 262.556/R - 55\ 066.835/[R(T/K)] - 58.50/R \ln[(T/K)/298.15]$					
271.9	16.3	0.167	2686	72.8	39.16
276.0	18.5	0.146	3373	−4.5	38.92
278.7	17.8	0.120	3888	−91.3	38.76
283.5	18.1	0.088	5253	−23.8	38.48
287.7	18.9	0.072	6613	−78.8	38.24
291.5	17.7	0.055	8040	−197.2	38.01
294.7	19.5	0.048	10 040	277.5	37.83
298.5	19.5	0.040	11 950	74.2	37.60
301.4	18.0	0.032	13 780	44.9	37.43
2.2-diethoxypropane (126-84-1), **111**; $\Delta_l^g H_m^\circ$(298.15 K) = (43.17 ± 0.39) kJ·mol^{-1}					
$\ln(p/Pa) = 295.905/R - 68\ 544.434/[R(T/K)] - 85.10/R \ln[(T/K)/298.15]$					
273.0	20.7	0.797	537.9	−3.0	45.31
274.7	14.0	0.478	601.1	−10.9	45.17
278.5	15.7	0.382	821.3	20.6	44.84
283.6	18.3	0.319	1124.0	−8.4	44.41
288.3	20.4	0.254	1557.0	19.7	44.01
293.3	21.1	0.191	2127.0	27.9	43.58
298.5	19.0	0.128	2829.0	−32.3	43.14
303.6	18.9	0.096	3748.0	−78.1	42.71
308.5	16.8	0.063	5058.0	58.9	42.29

Table 1. (Continued)

T[a]	m[b]	$V(N_2)$[c]	p[d]	$p_{exp} - p_{calc}$	$\Delta_l^g H_m^\circ$
K	mg	dm^3	Pa	Pa	kJ·mol^{-1}
2,2-dimethyl-1,3-dioxolane (2916-31-6), **116**; $\Delta_l^g H_m^\circ$(298.15 K) = (41.08 ± 0.16) kJ·mol^{-1}					
$\ln(p/\mathrm{Pa}) = 267.854/R - 57\,925.274/[R(T/\mathrm{K})] - 56.50/R \ln[(T/\mathrm{K})/298.15]$					
278.3	43.5	0.537	2129	28.1	42.20
283.2	22.5	0.199	2905	27.6	41.92
288.2	19.0	0.123	3905	−9.8	41.64
293.2	19.1	0.092	5192	−67.9	41.36
298.2	25.3	0.092	6839	−144.9	41.08
303.2	28.2	0.077	9060	−109.5	40.79
308.2	29.6	0.061	11 940	28.4	40.51
313.2	38.6	0.061	15 540	222.2	40.23
318.2	37.0	0.046	19 690	180.2	39.95
2-methyl-2-ethyl-1,3-dioxolane (126-39-6), **117**; $\Delta_l^g H_m^\circ$(298.15 K) = (42.82 ± 0.29) kJ·mol^{-1}					
$\ln(p/\mathrm{Pa}) = 271.808/R - 61\,905.414/[R(T/\mathrm{K})] - 64.00/R \ln[(T/\mathrm{K})/298.15]$					
274.1	18.0	0.813	473.9	−6.6	44.36
278.4	19.7	0.642	655.4	6.9	44.09
283.3	21.4	0.501	910.6	10.2	43.77
288.4	21.8	0.376	1240.0	−9.2	43.45
293.4	25.4	0.314	1729.0	29.8	43.13
298.4	23.1	0.220	2243.0	−39.6	42.81
303.4	22.1	0.156	3025.0	−5.1	42.49
308.3	17.3	0.094	3923.0	−33.2	42.17
313.3	15.1	0.062	5190.0	50.9	41.85
2-methyl-2-*n*-propyl-1,3-dioxolane (4352-98-1), **118**; $\Delta_l^g H_m^\circ$(298.15 K) = (46.16 ± 0.34) kJ·mol^{-1}					
$\ln(p/\mathrm{Pa}) = 282.336/R - 67\,480.549/[R(T/\mathrm{K})] - 71.50/R \ln[(T/\mathrm{K})/298.15]$					
278.3	27.1	2.537	215.6	−2.9	47.58
283.4	36.5	2.286	316.6	0.7	47.22
288.3	27.2	1.189	448.6	5.1	46.87
293.3	20.5	0.646	616.5	−1.7	46.51
298.3	31.0	0.698	858.8	8.8	46.15
303.3	22.1	0.367	1158.0	4.3	45.79
308.3	16.9	0.210	1545.0	−2.1	45.44
313.2	14.8	0.141	2018.0	−21.4	45.09
2-methyl-2-*n*-pentyl-1,3-dioxolane (4352-95-8), **119**; $\Delta_l^g H_m^\circ$(298.15 K) = (53.99 ± 0.28) kJ·mol^{-1}					
$\ln(p/\mathrm{Pa}) = 305.337/R - 79\,809.604/[R(T/\mathrm{K})] - 86.60/R \ln[(T/\mathrm{K})/298.15]$					
278.2	3.63	3.116	18.94	0.0	55.72
283.4	5.21	2.861	29.19	−0.2	55.27
288.3	6.22	2.266	43.70	−0.1	54.84
293.3	5.47	1.331	65.08	0.5	54.41
298.2	6.61	1.119	93.22	0.2	53.99
303.3	5.30	0.624	133.80	−0.1	53.54
308.3	5.46	0.452	190.00	1.3	53.11
313.3	4.76	0.284	263.20	0.9	52.68
318.2	4.48	0.199	353.60	−4.0	52.25
2-methyl-2-isopropyl-1,3-dioxolane (4405-16-7), **120**; $\Delta_l^g H_m^\circ$(298.15 K) = (43.90 ± 0.24) kJ·mol^{-1}					
$\ln(p/\mathrm{Pa}) = 268.180/R - 64\,327.624/[R(T/\mathrm{K})] - 68.50/R \ln[(T/\mathrm{K})/298.15]$					
273.7	4.58	0.864	110.2	1.1	45.58
278.4	5.03	0.667	152.8	0.0	45.26
283.3	5.33	0.498	213.0	−1.0	44.92
288.2	5.80	0.393	290.3	−5.3	44.59
293.4	6.32	0.301	409.1	−1.4	44.23
298.4	6.87	0.236	563.7	8.1	43.89
303.2	7.08	0.186	734.9	0.6	43.56
2,2-diisopropyl-1,3-dioxolane (4421-10-7), **121**; $\Delta_l^g H_m^\circ$(298.15 K) = (49.93 ± 0.30) kJ·mol^{-1}					
$\ln(p/\mathrm{Pa}) = 292.479/R - 73\,934.389/[R(T/\mathrm{K})] - 80.50/R \ln[(T/\mathrm{K})/298.15]$					
278.3	10.4	3.446	49.63	0.6	51.53
283.5	14.6	3.164	74.70	1.1	51.11
288.5	16.7	2.506	106.80	−0.2	50.71
293.5	13.6	1.472	146.90	−6.3	50.31
298.5	16.8	1.237	214.60	−1.5	49.91
303.6	13.3	0.690	304.50	1.9	49.49
308.6	13.3	0.500	418.30	3.1	49.09
313.6	11.3	0.314	568.40	5.8	48.69
318.5	10.5	0.220	749.30	0.4	48.30

[a] Temperature of saturation. N_2 gas flow of 0.22−0.69 cm^3 s^{-1}. [b] Mass of transferred sample condensed at T = 243 K. [c] Volume of nitrogen used to transfer mass m of sample. [d] Vapor pressure at temperature T calculated from m and the residual vapor pressure at T = 243 K.

derivatives. The GAVs evaluated in this work are based solely on experimental data, not on calculated values. The approach used to determine the GAVs for calculating the enthalpies of formation was similar to that of Cohen (96-Coh). We adopted his revised values for the alkane groups in the liquid and the gaseous phases (see Table 8). With

Table 2. Results for the Vapor Pressure p and Enthalpy of Vaporization $\Delta_l^g H_m^\circ$ Measured for Phenyl-Substituted Acetals and Ketals by the Transpiration Method

T [a] K	m [b] mg	$V(N_2)$ [c] dm^3	p [d] Pa	$p_{exp} - p_{calc}$ Pa	$\Delta_l^g H_m^\circ$ kJ·mol^{-1}
phenyldimethoxymethane (1125-88-8), **127**; $\Delta_l^g H_m^\circ$(298.15 K) = (60.91 ± 0.49) kJ·mol^{-1} $\ln(p/\text{Pa}) = 314.565/R - 84\,163.453/[R(T/\text{K})] - 78.00/R \ln[(T/\text{K})/298.15]$					
278.1	1.600	3.300	7.89	−0.18	62.47
278.3	0.658	1.290	8.31	0.09	62.46
280.1	1.550	2.703	9.34	−0.44	62.32
283.2	0.730	0.860	13.83	0.73	62.07
285.0	1.966	2.071	15.45	−0.02	61.93
288.2	1.981	1.625	19.85	−0.82	61.68
288.3	0.860	0.645	21.68	0.83	61.68
290.0	3.674	2.429	24.62	0.38	61.54
293.2	1.510	0.739	33.29	1.28	61.29
293.2	0.850	0.430	32.18	0.17	61.29
295.0	2.366	1.100	35.02	−2.30	61.15
298.0	0.620	0.215	46.95	−0.99	60.92
298.2	1.526	0.492	50.51	1.77	60.90
300.0	2.866	0.825	56.55	0.08	60.76
302.9	0.630	0.143	71.71	0.44	60.54
303.2	2.040	0.443	74.95	1.97	60.51
304.9	2.991	0.570	85.37	1.95	60.38
308.2	2.258	0.344	106.81	−0.79	60.12
308.2	0.665	0.108	100.30	−7.30	60.12
313.2	3.107	0.321	157.81	1.52	59.73
318.3	4.467	0.321	226.89	1.45	59.34
phenyldiethoxymethane (774-48-1), **128**; $\Delta_l^g H_m^\circ$(298.15 K) = (62.76 ± 0.59) kJ·mol^{-1} $\ln(p/\text{Pa}) = 337.746/R - 93\,980.475/[R(T/\text{K})] - 104.7/R \ln[(T/\text{K})/298.15]$					
283.3	4.79	16.180	4.12	0.2	64.32
288.5	3.93	8.630	6.32	−0.1	63.77
293.3	4.72	6.970	9.38	−0.5	63.27
298.3	4.55	4.240	14.82	−0.4	62.75
303.3	5.05	3.030	23.00	−0.1	62.22
308.4	4.70	1.850	34.97	0.3	61.69
313.5	5.39	1.400	53.07	1.9	61.16
318.5	4.95	0.920	74.09	0.3	60.63
323.4	2.41	0.310	107.00	2.8	60.12
328.5	2.28	0.220	142.40	−4.8	59.59
2-phenyl-1,3-dioxolane (936-51-6), **129**; $\Delta_l^g H_m^\circ$(298.15 K) = (62.64 ± 0.68) kJ·mol^{-1} $\ln(p/\text{Pa}) = 298.913/R - 85\,300.69/[R(T/\text{K})] - 76.00/R \ln[(T/\text{K})/298.15]$					
284.9	0.123	1.360	1.49	0.06	63.65
290.0	0.134	1.003	2.21	−0.08	63.26
295.0	0.141	0.687	3.39	−0.17	62.88
295.0	0.138	0.615	3.69	0.13	62.88
298.2	0.273	1.000	4.50	−0.19	62.64
300.0	0.175	0.533	5.42	−0.04	62.50
303.2	0.409	1.000	6.75	−0.35	62.26
304.9	0.180	0.340	8.72	0.57	62.13
308.2	0.621	1.000	10.24	−0.35	61.88
310.0	0.137	0.170	13.26	1.08	61.74
313.2	0.931	1.002	15.36	−0.20	61.50
314.9	0.192	0.170	18.64	0.97	61.37
314.9	0.124	0.113	18.17	0.50	61.37
318.2	1.299	1.003	21.43	−1.09	61.12
323.2	1.900	1.000	31.34	−0.82	60.74
328.2	2.730	1.001	45.03	−0.30	60.36
333.2	3.830	1.007	63.18	0.08	59.98
2-phenyl-5,5-dimethyl-1,3-dioxane (776-88-5), **130**; $\Delta_{cr}^g H_m^\circ$(298.15 K) = (69.18 ± 0.82) kJ·mol^{-1} $\ln(p/\text{Pa}) = 321.786/R - 94\,580.961/[R(T/\text{K})] - 85.20/R \ln[(T/\text{K})/298.15]$					
307.9	0.588	1.830	4.14	−0.03	68.35
312.9	0.892	1.830	6.29	−0.08	67.92
317.9	0.981	1.301	9.72	0.12	67.50
322.9	0.841	0.731	14.83	0.60	67.07
328.0	0.964	0.610	20.37	−0.60	66.64
333.0	1.058	0.457	29.85	−0.37	66.21
338.0	1.027	0.306	43.29	0.29	65.78
phenyldimethoxyethane (4316-35-2), **131**; $\Delta_l^g H_m^\circ$(298.15 K) = (54.01 ± 0.82) kJ·mol^{-1} $\ln(p/\text{Pa}) = 305.821/R - 81\,852.912/[R(T/\text{K})] - 93.40/R \ln[(T/\text{K})/298.15]$					
268.0	0.365	1.677	3.24	−0.24	56.82
272.8	0.476	1.292	5.49	0.06	56.37
277.6	0.477	0.833	8.54	0.20	55.93
278.7	0.515	0.798	9.62	0.45	55.82
283.7	0.533	0.575	13.82	−0.18	55.36
288.5	0.582	0.408	21.27	0.62	54.91
293.7	0.878	0.405	32.32	1.40	54.42
298.9	0.790	0.266	44.28	−1.20	53.94
303.2	0.891	0.225	59.04	−2.76	53.53

Table 2. (Continued)

T^{a}	m^{b}	$V(N_2)^{c}$	p^{d}	$p_{exp} - p_{calc}$	$\Delta_l^g H_m^\circ$
K	mg	dm^3	Pa	Pa	$kJ \cdot mol^{-1}$
1-phenyl-1,1-dimethoxypropane (25310-92-3), **132**; $\Delta_l^g H_m^\circ(298.15\ K) = (58.92 \pm 0.28)\ kJ \cdot mol^{-1}$ $\ln(p/Pa) = 325.455/R - 89\,006.156/[R(T/K)] - 100.90/R \ln[(T/K)/298.15]$					
288.2	28.90	36.75	11.15	0.0	59.93
293.5	19.70	15.97	17.42	0.0	59.39
298.2	18.40	10.18	25.43	−0.2	58.92
303.1	14.10	5.18	38.27	0.7	58.42
308.2	14.50	3.70	54.95	0.0	57.91
313.3	11.80	2.11	78.38	−0.9	57.39
318.2	9.69	1.229	110.50	−0.7	56.90
323.2	10.50	0.943	155.90	1.1	56.40
328.2	9.13	0.600	213.10	0.2	55.89
2-phenyl-2-methyl-1,3-dioxolane (3674-77-9), **133**; $\Delta_{cr}^g H_m^\circ(298.15\ K) = (82.89 \pm 0.89)\ kJ \cdot mol^{-1}$ $\ln(p/Pa) = 386.407/R - 110\,142.041/[R(T/K)] - 91.40/R \ln[(T/K)/298.15]$					
293.0	0.680	2.447	4.19	−0.09	83.36
297.9	1.286	2.531	7.67	0.17	82.91
303.0	1.520	1.781	12.88	−0.28	82.45
307.9	1.350	0.879	23.18	1.06	82.00
313.0	2.180	0.895	36.75	−0.47	81.53
318.0	2.330	0.585	60.10	−0.73	81.08
324.0	2.330	0.329	106.95	−0.19	80.53
2-phenyl-2,5,5-trimethyl-1,3-dioxane (5406-58-6), **134**; $\Delta_{cr}^g H_m^\circ(298.15\ K) = (66.39 \pm 0.80)\ kJ \cdot mol^{-1}$ $\ln(p/Pa) = 341.610/R - 96\,385.581/[R(T/K)] - 100.60/R \ln[(T/K)/298.15]$					
302.0	2.80	2.706	12.43	−0.32	66.00
306.7	3.15	2.039	18.56	−0.48	65.53
311.7	4.59	1.901	29.00	0.29	65.03
316.3	5.10	1.473	41.58	0.28	64.57
322.6	6.55	1.157	68.00	1.45	63.93
326.7	7.19	0.946	91.31	1.64	63.52
331.9	10.10	0.906	133.88	4.73	63.00
342.7	11.10	0.505	264.07	0.52	61.91
353.7	20.30	0.495	492.59	−22.32	60.80
2,2-diphenyldimethoxymethane (2235-01-0), **135**; $\Delta_{cr}^g H_m^\circ(298.15\ K) = (106.7 \pm 1.2)\ kJ \cdot mol^{-1}$ $\ln(p/Pa) = 410.202/R - 131\,790.187/[R(T/K)] - 84.30/R \ln[(T/K)/298.15]$					
301.8	0.28	75.24	0.040	0.003	106.35
313.1	0.48	33.06	0.158	−0.010	105.40
317.4	0.79	32.00	0.268	−0.022	105.03
321.4	1.73	42.39	0.443	−0.033	104.70
323.0	1.03	18.72	0.597	0.020	104.56
332.8	1.42	7.98	1.931	0.122	103.74
337.7	0.87	2.99	3.160	0.046	103.32
342.9	2.92	5.70	5.560	0.126	102.88
352.5	3.74	2.85	14.242	−0.221	102.07
2,2-diphenyldiethoxymethane (6397-77-9), **136**; $\Delta_{cr}^g H_m^\circ(298.15\ K) = (97.2 \pm 1.1)\ kJ \cdot mol^{-1}$ $\ln(p/Pa) = 424.619/R - 137\,029.997/[R(T/K)] - 133.70/R \ln[(T/K)/298.15]$					
275.4	0.015	238.90	0.0006	0.0001	100.21
283.0	0.036	201.90	0.0017	−0.0001	99.19
286.8	0.054	173.60	0.0030	−0.0001	98.68
293.0	0.153	209.30	0.0070	−0.0004	97.86
298.6	0.174	104.60	0.0161	0.0003	97.11
302.9	0.207	66.90	0.0299	0.0024	96.53
308.3	0.216	38.25	0.0546	0.0010	95.81
308.5	0.138	26.48	0.0503	−0.0047	95.78
312.8	0.294	33.77	0.0841	−0.0075	95.21
313.5	0.544	57.62	0.0912	−0.0083	95.12
317.8	0.396	22.17	0.1726	0.0099	94.54
321.9	0.477	15.95	0.2891	0.0328	93.99
2,2-diphenyl-1,3-dioxolane (4359-34-6), **137**; $\Delta_{cr}^g H_m^\circ(298.15\ K) = (99.7 \pm 1.1)\ kJ \cdot mol^{-1}$ $\ln(p/Pa) = 325.250/R - 109\,110.521/[R(T/K)] - 31.60/R \ln[(T/K)/298.15]$					
275.6	0.008	301.60	0.000 28	0.000 00	100.40
283.3	0.024	263.50	0.000 99	0.000 09	100.16
291.3	0.042	165.30	0.002 76	−0.000 14	99.91
297.0	0.059	106.20	0.006 05	−0.000 35	99.73
300.1	0.031	36.30	0.009 36	−0.000 35	99.63
303.3	0.025	19.01	0.014 22	−0.000 57	99.53
308.9	0.045	17.30	0.028 63	−0.001 60	99.35
314.7	0.040	6.84	0.063 56	0.001 93	99.17
319.0	0.053	5.12	0.112 80	0.010 12	99.03

Table 2. (Continued)

T [a] K	m [b] mg	$V(N_2)$ [c] dm^3	p [d] Pa	$p_{exp} - p_{calc}$ Pa	$\Delta_l^g H_m^\circ$ kJ·mol^{-1}
2,2-diphenyl-1,3-dioxolane (4359-34-6), **137**; $\Delta_l^g H_m^\circ(298.15\ K) = (84.44 \pm 0.64)\ kJ\cdot mol^{-1}$ $\ln(p/Pa) = 314.038/R - 102\ 387.753/[R(T/K)] - 60.20/R \ln[(T/K)/298.15]$					
331.2	3.28	44.650	0.82	−0.02	82.45
335.2	1.82	17.070	1.18	−0.02	82.21
340.2	1.66	9.720	1.89	0.04	81.91
345.2	1.74	6.620	2.90	0.08	81.61
350.2	0.77	2.010	4.20	−0.02	81.31
355.2	1.34	2.310	6.38	0.12	81.00
360.2	1.36	1.640	9.08	−0.07	80.70
365.2	1.07	0.880	13.28	0.06	80.40
370.1	1.10	0.660	18.34	−0.42	80.11

[a] Temperature of saturation. N_2 gas flow of 0.22−0.69 cm^3 s^{-1}. [b] Mass of transferred sample condensed at $T = 243$ K. [c] Volume of nitrogen used to transfer mass m of sample. [d] Vapor pressure at temperature T calculated from m and the residual vapor pressure at $T = 243$ K.

these values, we derived GAVs for the alkyl ethers (Table 8) using the database listed in the Tables 5 and 6. With these values fixed, we evaluated GAVs for acetals, ketals, ortho esters, and ortho carbonates (see Table 8) using compounds selected from the database listed in Table 7.

The previous compilations (96-Coh and 93-Dom/Hea) do not provide GAVs for calculating vaporization enthalpies at 298.15 K. However, a similar approach for this property was developed by Ducros et al. (80-Duc/Gru). We adopted their GAVs for the alkane groups (see Table 8) and carried out the evaluation of the further increments in the same way as for the calculation of the GAVs for enthalpies of formation.

According to the common definitions, $\Delta_f H_m^\circ(g) = \Delta_f H_m^\circ(l) + \Delta_l^g H_m^\circ$. Hence, the enthalpy of formation of a molecule in the gaseous phase is independent of intermolecular interactions. Thus, a gaseous increment reflects a certain amount of intramolecular energy ascribed to a defined structural fragment of a molecule. The enthalpies of formation of substances in condensed states and the enthalpies of phase transitions depend to a great extent on intermolecular interactions. However, the energy of intermolecular interactions is much smaller than the energy of intramolecular interactions, and in many cases, the enthalpies of formation of condensed phases and of phase transitions can be presented as a sum of the values for the structural fragments of the molecules. Therefore, the enthalpies of formation of molecules in the liquid state adhere well to the principles of additivity, as has been demonstrated in Domalski and Hearing (93-Dom/Hea) and Cohen (96-Coh). Moreover, a number of gaseous and liquid increments exhibit similar trends, and their differences are generally not larger than 3−5 kJ·mol^{-1}. Taking this fact into account, the use of GAVs helps to explain the interrelations of structure and energetics. The discussion here will consider predominantly GAVs in the gaseous phase, where explanations of the anomalies in the structures and properties of certain molecules seem to be much easier than in condensed phases.

Alkyl Ethers. Databases for the enthalpies of formation of linear as well as some branched alkyl ethers have been established by means of combustion calorimetry on liquid (75-Fen/Har) and gaseous (63-Pil, 64-Pil) samples. Combustion calorimetry has been also used to derive $\Delta_f H_m^\circ(l)$ values for *tert*-amyl methyl ether (91-Roz/Saf) and *tert*-amyl butyl ether (96-Ver/Bec) in our laboratory at the University of Freiburg. After the data had been published, we had the opportunity to check the combustion samples used in both studies for water content. Karl Fischer titration detected traces of water in the aforementioned *tert*-alkyl ethers. This report gives us an opportunity to correct our previous enthalpies of combustion $\Delta_c H_m^\circ$. For *tert*-amyl methyl ether, $\Delta_c H_m^\circ = -(4025.1 \pm 0.7)$ kJ·mol^{-1} instead of $-(4020.1 \pm 0.7)$ kJ·mol^{-1} (91-Roz/Saf) measured with 0.082 mass % of water. For *tert*-amyl butyl ether, $\Delta_c H_m^\circ = -(5975.9 \pm 2.1)$ kJ·mol^{-1} instead of $-(5971.51 \pm 2.1)$ kJ·mol^{-1} (96-Ver/Bec) measured with 0.073 mass % of water. Values for the enthalpies of formation $\Delta_f H_m^\circ(l)$ calculated from these corrected results are given in Table 5.

The use of oxygenated additives (e.g., methyl *tert*-butyl ether or methyl *tert*-amyl ether) produced from iso-olefins and alcohols is a worldwide trend for gasoline formulations aimed at reducing the emissions of exhaust gases. Various branched ethers have been suggested as fuel additives, and chemical reactions of their syntheses have been studied extensively. Reaction enthalpies, $\Delta_r H_m^\circ$, obtained from such studies can be utilized for calculation of the enthalpies of formation of branched alkyl ethers with the help of the enthalpies of formation (65-Cha/Ros) and enthalpies of vaporization (66-Wad) of alcohols and olefins (51-Pro/Mar, 91-Wib/Hao). For this purpose, we selected the following reactions, which have been investigated in the liquid phase using ion-exchange resins as catalysts

$$^{i}\mathrm{PrOH} + \text{2-methylpropene} \leftrightarrow {}^{t}\mathrm{Bu{-}O{-}}{}^{i}\mathrm{Pr}$$

T range = 298−383 K

$$\Delta_r H_m^\circ = -(22.9 \pm 1.3)\ \mathrm{kJ\cdot mol^{-1}} \qquad \text{(97-Cal/Tej)}$$

calorimetrically at 298 K

$$\Delta_r H_m^\circ = -(21.7 \pm 1.6)\ \mathrm{kJ\cdot mol^{-1}} \qquad \text{(97-Sol/Per)}$$

$$\mathrm{EtOH} + \text{2-methylpropene} \leftrightarrow {}^{t}\mathrm{Bu{-}O{-}Et}$$

T range = 314−353 K

$$\Delta_r H_m^\circ = -(34.8 \pm 1.3)\ \mathrm{kJ\cdot mol^{-1}} \qquad \text{(94-Izq/Cun)}$$

T range = 313−353 K

$$\Delta_r H_m^\circ = -(36.0 \pm 2.0)\ \mathrm{kJ\cdot mol^{-1}} \qquad \text{(97-Gom/Cun)}$$

calorimetrically at 298 K

$$\Delta_r H_m^\circ = -32.0\ \mathrm{kJ\cdot mol^{-1}} \qquad \text{(95-Sol/Per)}$$

$$\mathrm{MeOH} + \text{2-methylbuten-2} \leftrightarrow {}^{t}\mathrm{Am{-}O{-}Me}$$

calorimetrically at 298 K

$$\Delta_r H_m^\circ = -(27.1 \pm 2.5)\ \mathrm{kJ\cdot mol^{-1}} \qquad \text{(97-Sol/Per)}$$

The following reactions have been investigated (00-Chu)

Table 3. Results for the Vapor Pressure p and Enthalpy of Vaporization $\Delta_l^g H_m^\circ$ Measured for Ketals Attached to the Small Rings by the Transpiration Method

T[a]	m[b]	$V(N_2)$[c]	p[d]	$p_{exp} - p_{calc}$	$\Delta_l^g H_m^\circ$
K	mg	dm^3	Pa	Pa	kJ·mol^{-1}
1,1-dimethoxy-2-phenylcyclopropane (18523-34-7), **138**; $\Delta_l^g H_m^\circ$(298.15 K) = (63.65 ± 0.60) kJ·mol^{-1} $\ln(p/\text{Pa}) = 306.372/R - 86\,222.319/[R(T/\text{K})] - 75.70/R \ln[(T/\text{K})/298.15]$					
278.3	0.176	2.122	1.20	−0.04	65.16
278.4	0.732	8.120	1.28	0.03	65.15
281.5	1.280	10.300	1.75	0.04	64.91
283.2	0.348	2.663	1.86	−0.15	64.78
283.3	1.030	6.930	2.09	0.06	64.78
288.2	0.238	1.053	3.18	−0.05	64.41
288.4	1.220	4.910	3.49	0.19	64.39
293.2	0.292	0.813	5.04	−0.08	64.03
293.3	1.180	3.150	5.23	0.07	64.02
298.1	0.407	0.734	7.74	−0.12	63.66
298.2	1.500	2.490	8.39	0.46	63.65
303.1	0.401	0.479	11.67	−0.32	63.28
303.3	1.690	1.916	12.26	0.06	63.26
308.2	0.709	0.558	17.70	−0.45	62.89
308.4	2.160	1.613	18.62	0.18	62.88
313.2	1.650	0.859	26.79	−0.04	62.51
1-phenyl-4,7-dioxaspiro[2,4]heptane (39522-76-4), **139**; $\Delta_{cr}^g H_m^\circ$(298.15 K) = (91.70 ± 0.81) kJ·mol^{-1} $\ln(p/\text{Pa}) = 314.322/R - 93\,278.636/[R(T/\text{K})] - 73.70/R \ln[(T/\text{K})/298.15]$					
288.3	3.38	153.80	0.309	−0.003	92.37
293.4	3.60	82.19	0.616	0.007	92.02
296.4	3.67	57.88	0.891	0.000	91.81
299.4	3.82	41.22	1.301	0.007	91.61
302.1	4.34	34.30	1.780	−0.017	91.43
1-phenyl-4,7-dioxaspiro[2,4]heptane (39522-76-4), **139**; $\Delta_l^g H_m^\circ$(298.15 K) = (71.30 ± 0.71) kJ·mol^{-1} $\ln(p/\text{Pa}) = 314.322/R - 93\,278.636/[R(T/\text{K})] - 73.70/R \ln[(T/\text{K})/298.15]$					
307.3	3.66	18.37	2.80	0.00	70.63
313.4	4.82	14.33	4.73	−0.06	70.18
318.4	2.71	5.16	7.39	0.09	69.81
321.5	2.50	3.79	9.27	−0.12	69.58
325.4	15.30	16.47	13.10	0.27	69.30
333.6	3.25	1.92	23.78	−0.24	68.69
1-phenyl-6,6-dimethyl-4,8-dioxaspiro[2,5]octane (8545-55-9), **140**; $\Delta_{cr}^g H_m^\circ$(298.15 K) = (98.04 ± 0.34) kJ·mol^{-1} $\ln(p/\text{Pa}) = 333.845/R - 104\,898.303/[R(T/\text{K})] - 23.00/R \ln[(T/\text{K})/298.15]$					
298.5	0.702	67.45	0.118	−0.002	98.03
303.5	1.120	55.81	0.228	−0.003	97.92
308.2	0.460	12.03	0.435	0.018	97.81
308.6	0.853	22.09	0.439	0.001	97.80
313.2	0.434	6.51	0.757	−0.009	97.69
313.5	1.360	19.59	0.790	−0.004	97.69
318.1	0.730	5.93	1.398	0.033	97.58
319.4	3.590	25.51	1.598	0.011	97.55
323.2	2.230	10.24	2.469	0.026	97.46
323.6	2.130	9.68	2.502	−0.053	97.46
328.1	1.060	2.90	4.156	−0.042	97.35
328.6	1.600	4.12	4.402	−0.031	97.34
333.1	1.530	2.41	7.196	0.025	97.24
333.2	2.710	4.23	7.283	0.036	97.23
338.3	2.130	1.98	12.220	−0.078	97.12
cyclobutanone dimethylacetal (4415-90-1), **141**; $\Delta_l^g H_m^\circ$(298.15 K) = (41.97 ± 0.29) kJ·mol^{-1} $\ln(p/\text{Pa}) = 270.965/R - 61\,113.565/[R(T/\text{K})] - 64.20/R \ln[(T/\text{K})/298.15]$					
273.5	34.7	1.421	579.4	−11.1	43.55
278.2	38.4	1.062	829.7	14.4	43.25
283.3	30.1	0.588	1149.0	8.9	42.93
288.3	29.7	0.425	1548.0	−14.0	42.60
293.3	28.6	0.294	2135.0	22.6	42.28
298.2	29.4	0.229	2797.0	−8.8	41.97
303.1	27.7	0.163	3680.0	−5.2	41.65
308.2	25.6	0.114	4847.0	7.7	41.33
313.2	28.3	0.098	6226.0	−28.1	41.01
cyclopetanone dimethylacetal (53355−43−4), **142**; $\Delta_l^g H_m^\circ$(298.15 K) = (44.52 ± 0.35) kJ·mol^{-1} $\ln(p/\text{Pa}) = 277.130/R - 65\,866.985/[R(T/\text{K})] - 71.60/R \ln[(T/\text{K})/298.15]$					
278.2	18.1	1.564	235.3	2.2	45.95
283.2	12.2	0.736	330.5	−0.1	45.59
288.3	11.8	0.506	457.6	−7.4	45.22
293.2	16.8	0.506	645.4	8.8	44.87
298.2	14.4	0.322	868.9	3.1	44.52
303.1	9.0	0.153	1137.0	−19.0	44.17
308.2	10.0	0.123	1558.0	14.9	43.80
313.2	7.9	0.077	1963.0	−61.9	43.44
318.2	8.6	0.061	2704.0	75.0	43.08

Table 3. (Continued)

T [a] K	m [b] mg	$V(N_2)$ [c] dm^3	p [d] Pa	$p_{exp} - p_{calc}$ Pa	$\Delta_l^g H_m^\circ$ kJ·mol^{-1}
cyclopetanone ethylene acetal (176-32-9), **143**; $\Delta_l^g H_m^\circ$(298.15 K) = (47.47 ± 0.48) kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = 263.220/R - 63\,719.038/[R(T/\mathrm{K})] - 54.50/R \ln[(T/\mathrm{K})/298.15]$					
278.3	6.59	1.388	96.8	0.1	48.55
283.2	6.43	0.938	137.6	−1.4	48.28
288.2	8.85	0.875	200.7	2.5	48.01
293.2	8.00	0.563	279.9	1.3	47.74
298.2	4.81	0.251	375.4	−11.2	47.47
303.2	8.77	0.312	548.5	18.9	47.19
308.2	5.48	0.150	711.7	−5.2	46.92
313.2	6.13	0.125	953.3	−6.2	46.65
cyclopetanone 2,2-dimethylpropylene acetal (702-75-0), **144**; $\Delta_l^g H_m^\circ$(298.15 K) = (53.77 ± 0.51) kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = 277.509/R - 72\,764.691/[R(T/\mathrm{K})] - 63.70/R \ln[(T/\mathrm{K})/298.15]$					
283.3	1.68	1.436	17.86	0.1	54.72
288.3	1.67	0.957	26.26	−0.3	54.40
293.3	1.75	0.678	38.38	−0.6	54.08
298.1	2.35	0.606	57.18	1.5	53.78
303.2	3.25	0.591	80.92	0.8	53.45
308.2	3.20	0.423	110.90	−2.0	53.13
313.4	4.44	0.407	159.60	0.5	52.80
cyclohexanone dimethylacetal (933-40-4), **145**; $\Delta_l^g H_m^\circ$(298.15 K) = (48.64 ± 0.21) kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = 289.565/R - 72\,313.335/[R(T/\mathrm{K})] - 79.40/R \ln[(T/\mathrm{K})/298.15]$					
278.3	7.10	1.914	69.30	0.4	50.22
283.2	8.23	1.500	99.81	−0.4	49.83
288.2	11.40	1.419	143.90	−0.5	49.43
293.2	9.97	0.861	204.40	−0.6	49.03
298.2	10.20	0.622	286.80	−0.1	48.64
303.2	19.10	0.830	400.50	4.6	48.24
308.2	9.86	0.319	536.20	−3.2	47.84
cyclohexanone ethylene acetal (177-10-6), **146**; $\Delta_l^g H_m^\circ$(298.15 K) = (50.36 ± 0.56) kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = 273.332/R - 68\,902.478/[R(T/\mathrm{K})] - 62.20/R \ln[(T/\mathrm{K})/298.15]$					
278.3	1.91	0.973	36.98	−0.1	51.59
283.3	2.76	0.909	55.73	0.9	51.28
288.2	2.69	0.614	79.09	−0.2	50.98
293.2	2.25	0.366	109.80	−4.1	50.67
298.2	5.06	0.543	165.20	4.0	50.35
303.3	3.90	0.303	227.20	0.6	50.04
308.3	5.23	0.295	311.70	−0.6	49.73
cyclohexanone 2,2-dimethylpropylene acetal (707-29-9), **147**; $\Delta_l^g H_m^\circ$(298.15 K) = (59.27 ± 0.63) kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = 294.582/R - 80\,589.561/[R(T/\mathrm{K})] - 71.50/R \ln[(T/\mathrm{K})/298.15]$					
283.2	1.44	3.916	5.01	−0.2	60.34
283.3	1.09	2.935	5.15	−0.1	60.33
288.2	1.63	2.758	8.00	−0.1	59.98
288.2	1.53	2.567	8.15	0.1	59.98
293.2	1.96	2.036	13.04	0.7	59.63
293.2	1.27	1.356	12.70	0.3	59.63
298.1	1.01	0.718	19.01	0.5	59.28
298.2	2.05	1.537	17.97	−0.7	59.27
303.2	1.45	0.686	28.59	1.0	58.91
303.2	1.57	0.799	26.42	−1.2	58.91
308.1	1.83	0.643	38.34	−1.6	58.56
308.2	1.50	0.479	42.28	2.0	58.55
313.2	1.79	0.408	59.15	1.2	58.20
313.2	1.20	0.271	59.79	1.9	58.20
318.2	1.71	0.297	77.42	−4.8	57.84
323.2	3.21	0.376	114.60	−0.6	57.48
7,7-dimethoxybicyclo[2,2,1]heptane (39869-70-0), **148**; $\Delta_l^g H_m^\circ$(298.15 K) = (50.39 ± 0.22) kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = 299.905/R - 77\,133.244/[R(T/\mathrm{K})] - 89.70/R \ln[(T/\mathrm{K})/298.15]$					
283.4	2.73	0.919	48.52	0.0	51.71
288.3	2.75	0.633	70.39	0.0	51.27
293.4	3.13	0.488	103.40	1.4	50.82
298.3	3.06	0.345	142.30	−1.0	50.38
303.3	2.50	0.202	198.20	−1.9	49.93
308.3	3.73	0.216	275.40	0.0	49.48
313.2	3.68	0.158	370.90	−1.1	49.04
318.2	2.72	0.086	503.20	3.8	48.59
bicyclo[2,2,1]heptane-7-on ethylene acetal, **149**; $\Delta_l^g H_m^\circ$(298.15 K) = (54.00 ± 0.40) kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = 302.978/R - 80\,151.966/[R(T/\mathrm{K})] - 87.70/R \ln[(T/\mathrm{K})/298.15]$					
282.9	0.75	0.663	18.51	0.0	55.34
287.9	0.93	0.548	27.71	−0.1	54.90
292.9	0.84	0.332	41.03	0.0	54.46
297.9	1.30	0.357	58.83	−0.8	54.03
302.8	1.91	0.357	86.39	1.6	53.60
308.1	1.65	0.218	122.40	0.3	53.13
313.2	1.37	0.127	173.40	2.5	52.68
318.2	1.10	0.077	230.30	−4.3	52.25

Table 3. (Continued)

T [a] K	m [b] mg	$V(N_2)$ [c] dm^3	p [d] Pa	$p_{exp} - p_{calc}$ Pa	$\Delta_l^g H_m^\circ$ kJ·mol^{-1}
bicyclo[2,2,1]heptane-7-one 2,2-dimethylpropylene acetal, **150**; $\Delta_l^g H_m^\circ(298.15\ K) = (84.34 \pm 0.87)$ kJ·mol^{-1} $\ln(p/Pa) = 320.476/R - 92\ 848.884/[R(T/K)] - 28.50/R\ \ln[(T/K)/298.15]$					
293.4	2.72	22.240	1.65	−0.1	84.49
298.5	1.34	5.750	3.12	0.0	84.34
303.4	1.93	4.675	5.55	0.2	84.20
308.4	4.10	5.851	9.38	0.2	84.06
313.3	1.52	1.332	15.28	0.0	83.92
318.3	1.41	0.751	25.12	−0.3	83.78
323.0	1.48	0.500	39.70	−0.6	83.64

[a] Temperature of saturation. N_2 gas flow of 0.22−0.69 cm^3 s^{-1}. [b] Mass of transferred sample condensed at $T = 243$ K. [c] Volume of nitrogen used to transfer mass m of sample. [d] Vapor pressure at temperature T calculated from m and the residual vapor pressure at $T = 243$ K.

in the gaseous phase using Al_2O_3 as the catalyst

$$\text{EtOH} + \text{2-methylbuten-2} \leftrightarrow {}^t\text{Am}-\text{O}-\text{Et}$$

$$T\ \text{range} = 353-373\ \text{K}$$

$$\Delta_r H_m^\circ = -(68.2 \pm 2.4)\ \text{kJ·mol}^{-1}$$

$$\Delta_r S_m^\circ = -(207.4 \pm 6.5)\ \text{J·mol}^{-1}\text{·K}^{-1}$$

$$\text{PrOH} + \text{2-methylpropene} \leftrightarrow {}^t\text{Bu}-\text{O}-\text{Pr}$$

$$T\ \text{range} = 383-413\ \text{K}$$

$$\Delta_r H_m^\circ = -(66.2 \pm 1.8)\ \text{kJ·mol}^{-1}$$

$$\Delta_r S_m^\circ = -(175.2 \pm 4.6)\ \text{J·mol}^{-1}\text{·K}^{-1}$$

$$\text{BuOH} + \text{2-methylpropene} \leftrightarrow {}^t\text{Bu}-\text{O}-\text{Bu}$$

$$T\ \text{range} = 398-423\ \text{K}$$

$$\Delta_r H_m^\circ = -(68.0 \pm 4.8)\ \text{kJ·mol}^{-1}$$

$$\Delta_r S_m^\circ = -(179 \pm 12)\ \text{J·mol}^{-1}\text{·K}^{-1}$$

$${}^i\text{BuOH} + \text{2-methylpropene} \leftrightarrow {}^t\text{Bu- O}-{}^i\text{Bu}$$

$$T\ \text{range} = 388-411\ \text{K}$$

$$\Delta_r H_m^\circ = -(69.7 \pm 4.8)\ \text{kJ·mol}^{-1}$$

$$\Delta_r S_m^\circ = -(183 \pm 12)\ \text{J·mol}^{-1}\text{·K}^{-1}$$

$${}^i\text{PrOH} + \text{2-methylpropene} \leftrightarrow {}^t\text{Bu}-\text{O}-{}^i\text{Pr}$$

$$T\ \text{range} = 353-383\ \text{K}$$

$$\Delta_r H_m^\circ = -(70.4 \pm 2.1)\ \text{kJ·mol}^{-1}$$

$$\Delta_r S_m^\circ = -(195.1 \pm 5.5)\ \text{J·mol}^{-1}\text{·K}^{-1}$$

Even though equilibrium studies have been performed at elevated temperatures, any corrections of the reaction enthalpies are negligible (01-Ver/Hei, 01-Vere/Hei), taking into account the individual error bars of about (1.5−3) kJ·mol^{-1} typical of the equilibrium measurements. In further calculations, it was assumed that the enthalpy of reaction hardly changes on passing from the average temperature of the experimental range to $T = 298.15$ K. Enthalpies of formation of the branched alkyl ethers calculated from the enthalpies of reactions listed above are given in Table 5.

Generally, the molecular structure of an alkyl ether can be described in terms of an increment for the O−(C)$_2$ group and the sum of increments for the adjacent hydrocarbon chain. The hydrocarbon increments necessary in this work are listed in the Table 8. According to Benson, the following increments are necessary for the estimation of the thermochemical properties of the alkyl ethers: O−(C)$_2$, C−(O)-(H)$_2$(C), C−(O)(H)(C)$_2$, C−(O)(C)$_3$. We included in a correlation a set (see Table 5) of 19 experimental data (**1**−**4**, **9**, **10**, **11**, **15**, **19**, **24**, **27**, **32**−**34**, **36**, **37**, **41**, **45**, **55**) for $\Delta_f H_m^\circ$(l), a set of 18 experimental data (**1**−**4**, **10**, **11**, **15**, **19**, **24**, **27**, **32**−**34**, **36**, **37**, **41**, **45**, **55**) for $\Delta_f H_m^\circ$(g), and a set of 52 experimental data (**1**−**54**, excluding **18** and **40**) for $\Delta_l^g H_m^\circ$ and treated them using the method of least squares. The average standard deviation for all compounds involved was at the level of 0.8 kJ·mol^{-1} for all three properties correlated.

In addition to the increments, some corrections for nonbonded interactions are required, because of the spatial interactions of parts of a molecule whose proximity is not implicit in bonding alone. The most common is the 1,4 or gauche correction, the interaction of two methyl groups within the alkyl chain of an ether. For example, the $\Delta_f H_m^\circ$ values in the liquid or gaseous state of all *tert*-amyl ethers (**45**−**54**) have to be adjusted by a gauche correction of 4 kJ·mol^{-1}. New additional experimental data on branched species have allowed us to specify this kind of interaction more properly. In comparison to the definition applied in Cohen (96-Coh), we suggested that no such corrections are necessary for predicting the enthalpies of formation of branched alkyl ethers with the structures C_{quat}−O−C_{second} (e.g., ^{s}Bu−O−Et) and C_{quat}−O−C_{quat} (e.g., ^{s}Bu−O−^{s}Bu), where C_{quat} and C_{second} denote quaternary and secondary C atoms in the alkyl chain connected directly to the oxygen. However, more strained alkyl ethers, such as C_{tert}−O−C_{quat} (e.g., ^{t}Bu−O−^{i}Pr), require a correction to $\Delta_f H_m^\circ$ of 10 kJ·mol^{-1}. Then, the extremely strained structures of alkyl ethers, such as C_{tert}−O− C_{tert} (e.g., ^{t}Bu−O−^{t}Bu), have to be corrected with a contribution to $\Delta_f H_m^\circ$ of 22 kJ·mol^{-1} (C_{tert} denotes the C atom in the alkyl chain connected directly to the oxygen). *tert*-Octyl ethers (**55**−**64**) represent a special case of strain due to steric repulsions generally within a branched alkyl chain, which contribute 27 kJ·mol^{-1} to $\Delta_f H_m^\circ$.

Enthalpies of vaporization, $\Delta_l^g H_m^\circ$, of alkyl ethers can be accurately estimated, to within 0.8 kJ·mol^{-1}, by using the increments evaluated in this work (see Table 8). Surprisingly, the family of alkyl *tert*-octyl ethers (**55**−**64**) does not obey this additivity. A comparison of $\Delta_l^g H_m^\circ$ values for these compounds reveals that the extension of alkyl chain from methyl (**55**) to hexyl (**64**), as well as the branching of the alkyl chain (**61**−**63**), enhances the deviation from additivity monotonically to 10 kJ·mol^{-1}. It is important to note that experimental $\Delta_l^g H_m^\circ$ values were obtained for these (**55**−**64**) compounds using three different methods (02-Ver/Kra). In addition, these values demonstrate a

Table 4. Results for the Vapor Pressure p and Enthalpy of Vaporization $\Delta_l^g H_m^\circ$ Measured for Ortho Esters and Spiro[4,4]nonane by the Transpiration Method

T[a] K	m[b] mg	$V(N_2)$[c] dm^3	p[d] Pa	$p_{exp} - p_{calc}$ Pa	$\Delta_l^g H_m^\circ$ kJ·mol^{-1}
2-methoxy-1,3-dioxolane (19693-75-5), **157**; $\Delta_l^g H_m^\circ$(298.15 K) = (46.37 ± 0.80) kJ·mol^{-1} $\ln(p/\text{Pa}) = 290.473/R - 69\ 233.332/[R(T/\text{K})] - 76.70/R \ln[(T/\text{K})/298.15]$					
278.2	10.00	0.960	275.98	−6.48	47.90
283.3	7.85	0.500	403.97	−5.47	47.50
288.2	12.10	0.500	598.62	22.49	47.13
293.2	11.10	0.340	815.93	11.32	46.74
298.1	9.48	0.210	1111.91	10.57	46.37
303.2	10.80	0.180	1506.54	−0.11	45.98
308.2	10.40	0.130	1973.17	−49.76	45.59
phenyltrimethoxymethane (707-07-3), **170**; $\Delta_l^g H_m^\circ$(298.15 K) = (59.88 ± 0.38) kJ·mol^{-1} $\ln(p/\text{Pa}) = 301.743/R - 83\ 495.704/[R(T/\text{K})] - 79.20/R \ln[(T/\text{K})/298.15]$					
294.3	13.30	18.17	10.04	0.14	60.19
298.2	2.35	2.40	13.33	−0.32	59.88
303.2	2.77	1.85	20.40	0.10	59.48
308.2	2.20	1.01	29.60	−0.13	59.09
313.1	2.43	0.760	43.33	0.73	58.70
318.3	2.27	0.500	61.86	0.38	58.29
323.3	2.01	0.330	83.99	−2.34	57.89
328.2	1.78	0.200	120.79	1.84	57.50
333.2	1.65	0.140	162.65	−0.36	57.11
spiro[4,4]nonane (175-93-9); $\Delta_l^g H_m^\circ$(298.15 K) = (44.52 ± 0.59) kJ·mol^{-1} $\ln(p/\text{Pa}) = 256.938/R - 60\ 900.53/[R(T/\text{K})] - 54.95/R \ln[(T/\text{K})/298.15]$					
278.3	10.50	1.454	153.5	−0.75	45.61
281.4	6.95	0.792	184.7	−6.88	45.44
283.3	12.60	1.172	224.0	5.80	45.33
288.4	13.80	0.918	309.8	3.46	45.05
293.4	11.80	0.570	424.0	2.46	44.78
298.3	13.70	0.490	568.6	−0.77	44.51
303.4	14.40	0.365	799.2	30.08	44.23
308.6	11.00	0.222	995.5	−36.99	43.94
313.3	9.47	0.143	1331.0	−2.95	43.68

[a] Temperature of saturation. N_2 gas flow of 0.22−0.69 cm^3 s^{-1}. [b] Mass of transferred sample condensed at T = 243 K. [c] Volume of nitrogen used to transfer mass m of sample. [d] Vapor pressure at temperature T calculated from m and the residual vapor pressure at T = 243 K.

mutual consistency, because, within the chemical family of compounds **55**−**64**, the contribution from CH_2 increments remains about constant. Hence, it seems that such a phenomenon could account for the counterplay of intermolecular attractive and repulsive forces in the liquid phase. On one side, the highly branched *tert*-octyl substituent enhances repulsive interactions and reduces the vaporization enthalpy, while at the same time, the linear alkyl chain contributes to more regular packing of the molecules in the liquid phase and enhances the contribution to the vaporization enthalpy.

Benzyl Ethers. To estimate the thermochemical properties of the benzyl ethers (**65**−**80**), the following additional increments are required: C−(O)(H)$_2$(Cb), C−(O)(H)(Cb)-(C), and C−(O)(Cb)(C)$_2$. The data for their estimation are listed in Table 6, and the results for the GAVs are presented in Table 8. The average standard deviation for all 15 species considered was about 1.5 kJ·mol^{-1} for all three correlated properties. It is worth mentioning that the enthalpy of formation of gaseous (1-cyclohexyl oxyethyl)-benzene (**76**) exhibit a 5.3 kJ·mol^{-1} deviation from additivity; however, this amount of strain definitely could be ascribed to the six-membered ring correction similar to that used for cyclohexanol (02-Ver/Hei).

Acetals and Ketals. Thermochemical results for acetals and ketals (Table 7) are divided into two types: straight-chained and cyclic compounds. According to Benson, the following increments are defined for the estimation of the thermochemical properties of acetals and ketals: C−(O)$_2$-(H)$_2$, C−(O)$_2$(H)(C), and C−(O)$_2$(C)$_2$. We decided to evaluate these GAVs using only the experimental data on straight-chained species. We included in the correlation a set of 14 experimental data (**81**−**83**, **94**−**100**, **110**−**113**) for $\Delta_f H_m^\circ$(l), a set of 7 experimental data (**81**, **82**, **94**, **95**, **100**, **110**, **111**) for $\Delta_f H_m^\circ$(g), and a set of 8 experimental data (**81**−**83**, **94**, **96**, **97**, **110**, **111**) for $\Delta_l^g H_m^\circ$. The average standard deviation for all compounds included was at the level of 1.8 kJ·mol^{-1} for enthalpies of formation and 0.8 kJ·mol^{-1} for enthalpies of vaporization. The enthalpy of formation in the liquid state and the enthalpy of vaporization of dibutoxymethane (**83**) fit the additivity rules well, but the deviation of 6.5 kJ·mol^{-1} for the value of $\Delta_f H_m^\circ$(g) suggests strain in this molecule apparently due to nonbonded repulsions of the alkyl chains.

For the estimation of the thermochemical properties of aromatic acetals and ketals (**127**−**137**), the additional increments C−(O)$_2$(H)(Cb), C−(O)$_2$(Cb)(C), and C−(O)$_2$(Cb)$_2$ (Table 8) were evaluated using experimental data on **127**, **128**, **131**, and **132**.

GAVs derived for the prediction thermochemical properties of acetals and ketals are presented in Table 8. These values provide now the possibility of deriving ring-strain corrections of the cyclic species presented in Table 7 as the difference between the experimental enthalpy of formation and the sum of the GAVs for a molecule (see Table 7).

The ring-strain corrections for $\Delta_f H_m^\circ$(g) of the five-membered cyclic acetals and ketals 1,3-dioxolane (30.0 kJ·mol^{-1} from **84**), 2-alkyl-substituted 1,3-dioxolane (28.0 kJ·mol^{-1} from **102** and **103**), and 2,2-dialkyl-substituted 1,3-dioxolane (21.7 kJ·mol^{-1} from **116**−**119**) are very close to those of cyclopentane (29.7 kJ·mol^{-1} from 96-Coh).

The ring-strain corrections for $\Delta_f H_m^\circ$(g) of the six-membered cyclic acetals 1,3-dioxane (14.1 kJ·mol^{-1} from **85** and

Table 5. Experimental Results[a] Available for Linear and Branched Ethers at 298.15 K in kJ·mol^{-1}

		$\Delta_f H^\circ_m$(l)			$\Delta_l^g H^\circ_m$			$\Delta_f H^\circ_m$(g)[b]		
		exp	calc	Δ	exp	calc	Δ	exp	calc	Δ
1	Me−O−Me	−202.6[b]	−202.9	0.3	18.5 (76-Amb/Ell)	19.19	−0.7	−184.1 ± 0.5 (64-Pil)	−183.7	−0.4
2	Et−O−Me	−240.3[b]	−240.0	−0.3	23.9 (76-Amb/Ell)	22.39	1.5	−216.4 ± 0.7 (64-Pil)	−217.3	0.9
3	Pr−O−Me	−266.0 ± 0.7 (75-Fen/Har)	−265.5	−0.5	**27.64 ± 0.16** (75-Fen/Har) 27.57 ± 0.20 (80-Maj/Wag) 27.5 (76-Amb/Ell)	27.38	0.3	−238.4	−238.2	−0.2
4	Bu−O−Me	−290.6 ± 1.2 (75-Fen/Har)	−291.0	0.4	**32.30** (75-Fen/Har) 32.4 ± 0.2 (80-Maj/Wag) 32.4 (76-Amb/Ell)	32.36	−0.6	−258.3	−259.1	0.8
5	^{i}Bu−O−Me		−297.7		30.31 (85-Maj/Svo)	31.06	−0.7		−269.1	
6	Am−O−Me		−316.5		36.91 (85-Maj/Svo)	37.34	−0.4		−280.0	
7	^{i}Am−O−Me		−323.2		35.75 (85-Maj/Svo)	36.04	−0.3		−290.0	
8	Hex−O−Me		−342.0		42.40 (85-Maj/Svo)	42.32	0.1		−300.9	
9	Dec−O−Me	−443.4 ± 2.1 (75-Fen/Har)	−444.0	0.6	62.6 (76-Amb/Ell) **62.30** (75-Fen/Har)	62.24	0.1	−381.1	−384.5	3.4
10	Et−O−Et	−276.9 ± 1.8 (68-Pih/Hei)	−277.2	0.3	**27.2** (76-Amb/Ell) 27.09 (71-Cou/Lee) 27.2 ± 0.2 (80-Maj/Wag)	25.60	1.6	−252.1 ± 0.8 (63-Pil)	−250.9	−1.2
11	Pr−O−Et	−303.6 ± 1.1 (75-Fen/Har)	−302.7	−0.9	**31.24 ± 0.10** (75-Fen/Har) 31.4 ± 0.2 (80-Maj/Wag) 31.4 (76-Amb/Ell)	30.58	0.7	−272.4	−271.8	−0.6
12	Bu−O−Et		−328.2		36.8 (76-Amb/Ell)	35.56	1.2		−292.7	
13	^{i}Bu−O−Et		−334.8		34.14 (85-Maj/Svo)	34.26	−0.1		−302.7	
14	Am−O−Et		−353.6		41.06 (85-Maj/Svo)	40.54	0.5		−313.6	
15	Pr−O−Pr	**−328.8 ± 0.9** (65-Col/Pel) −333.1 ± 2.1 (57-Mur)	−328.2	−0.6	**35.7 ± 0.2** (80-Maj/Wag) 35.7 (76-Amb/Ell) 36.5 ± 1.3 (65-Col/Pel)	35.56	0.1	−293.1	−292.7	−0.4
16	Bu−O−Pr		−353.6		40.26 (85-Maj/Svo)	40.54	−0.3		−313.6	
17	^{i}Bu−O−Pr		−360.3		38.25 (85-Maj/Svo)	39.24	−1.0		−323.6	
18	Am−O−Pr		−379.2		42.81 (85-Maj/Svo)	45.52	−2.7		−334.5	
19	Bu−O−Bu	−377.1 ± 3.4 (57-Sku/Str) −377.6 ± 2.8 (57-Mur) **−377.9 ± 1.0** (65-Col/Pel)	−379.2	1.3	44.68 (80-Fuc/Pea) 44.4 (76-Amb/Ell) **45.0 ± 0.2** (80-Maj/Wag)	45.52	−0.5	−332.9	−334.5	1.4
20	^{i}Bu−O−^{i}Bu		−392.5		40.85 (85-Maj/Svo) **43.1** (76-Amb/Ell)	42.92	0.2		−354.5	
21	Am−O−Am	−435.2 ± 3.0 (57-Mur)	−430.2	−5.0	57.82[c] (49-Dre) 45.2 (57-Mur) **54.8** (76-Amb/Ell)	55.48	−0.7	−380.4	−376.3	−4.1

Table 5. (Continued)

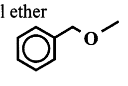
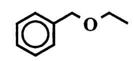
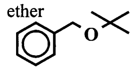
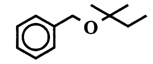
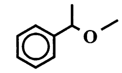
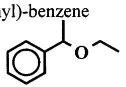
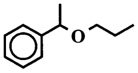
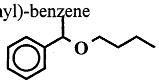
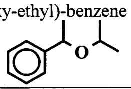
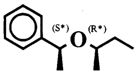
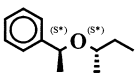
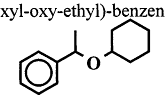
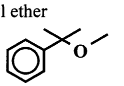
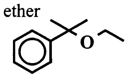
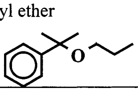
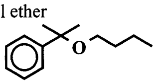
		$\Delta_f H^\circ_m$(l)			$\Delta_l^g H^\circ_m$			$\Delta_f H^\circ_m$(g)[b]		
		exp	calc	Δ	exp	calc	Δ	exp	calc	Δ
22	^{i}Am−O−^{i}Am		−443.5		49.94 (85-Maj/Svo) **51.6** (76-Amb/Ell)	52.88	−1.3		−396.3	
23	Hex−O−Hex		−481.1		64.1 (85-Maj/Svo)	65.44	−1.3		−418.1	
24	^{i}Pr−O−Me	−278.4[b]	−277.1	−1.3	**26.4** (76-Amb/Ell) 26.4 ± 0.2 (80-Maj/Wag)	25.46	0.9	252.0 ± 1.0 (64-Pil)	−251.6	−0.4
25	^{i}Pr−O−Et		−314.2		**30.04** (80-Maj/Wag) 30.32 (85-Maj/Svo)	28.66	1.4		−285.2	
26	^{i}Pr−O−Pr		−339.7		33.95 (85-Maj/Svo)	33.65	0.3		−306.1	
27	^{i}Pr−O−^{i}Pr	−351.5 ± 1.4 (65-Col/Pel)	−351.3	−0.2	**32.0** (76-Amb/Ell) 32.1 ± 0.2 (80-Maj/Wag)	31.73	0.3	−319.4	−319.5	0.1
28	^{i}Pr−O−Bu		−365.2		38.80 (85-Maj/Svo)	38.63	0.2		−327.0	
29	^{i}Pr−O−Am		−390.7		42.69 (85-Maj/Svo)	43.61	−0.9		−347.9	
30	^{s}Bu−O−Me		−302.6		30.41 (85-Maj/Svo)	30.44	−0.1		−272.5	
31	^{s}Bu−O−Et		−339.7		34.20 (85-Maj/Svo)	33.65	0.6		−306.1	
32	^{s}Bu−O−^{s}Bu	−401.5 ± 1.1 (65-Col/Pel)	−402.3	0.8	40.2 (76-Amb/Ell)	41.69	−1.5	−361.3	−361.3	0.0
33	^{t}Bu−O−Me	−322.8 ± 5.0 (61-Smu/Bon) **−313.6 ± 1.1** (75-Fen/Har) −315.4 ± 1.1 (85-Arn/Got)	−314.4	0.8	29.6 (76-Amb/Ell) **30.17 ± 0.10** (75-Fen/Har) 29.8 ± 0.2 (80-Maj/Wag) 30.0 ± 2.1 (61-Smu/Bon)	30.19	−0.1	−283.4	−283.7	0.3
34	^{t}Bu−O−Et	−350.8 ± 2.6 (95-Sha/Roz) −346.5 (95-Sol/Per) **−350.5 ± 2.2** (97-Gom/Cun) −349.3 ± 1.6 (94-Izq/Cun)	−351.6	1.1	32.6 (76-Amb/Ell) 33.78[c] (94-Kra/Gme) **33.69**[c] (99-Rar/Hor)	33.40	0.3	−313.9 ± 2.0 (89-Ibo/Izq) **−316.8**	−317.3	0.5
35	^{t}Bu−O−Pr	−377.6 ± 2.2[e]	−377.0	−0.6	38.34 (02-Ver/Kra)	38.38	0.1	−339.3 ± 2.1[d] (00-Chu)	−338.2	−1.1
36	^{t}Bu−O−Bu	**−403.3 ± 1.9** (91-Sha/Mis) −403.7 ± 4.9[e]	−402.6	−0.7	42.33 ± 0.25 (91-Sha/Mis) **43.18** (02-Ver/Kra)	43.36	−0.2	−360.5 ± 4.9[d] (00-Chu) **−360.1**	−359.1	−1.0
37	^{t}Bu−O−^{i}Bu	−409.1 ± 1.6 (91-Sha/Mis) **−409.1 ± 2.0** (96-Ver/Bec) −411.6 ± 4.9[e]	−409.3	0.2	40.12 ± 0.13 (91-Sha/Mis) **41.19 ± 0.31** (02-Ver/Kra)	42.06	−0.9	−370.4 ± 4.9[d] (00-Chu) **−367.9**	−369.1	1.2
38	^{t}Bu−O−^{i}Pr	−393.0 ± 3.0 (61-Smu/Bon) **−378.5 ± 1.7** (97-Cal/Tej) −377.3 ± 1.9 (97-Sol/Per) −396.3 ± 2.5[e]	−378.6[f]	0.1	35.1 (61-Smu/Bon) 34.67 (85-Maj/Svo) 35.92 (99-Rar/Hor) **36.18** (02-Ver/Kra)	36.46	−0.3	−360.1 ± 2.4[d] (00-Chu) **−342.3**	−341.6[f]	−0.7
39	^{t}Bu−O−^{s}Bu	−420.3 ± 1.8 (91-Sha/Mis)	−404.1[f]	−16.2	40.34 ± 0.18 (91-Sha/Mis) **41.31** (02-Ver/Kra)	41.44	−0.1	−379.0	−362.5[f]	−16.5
40	^{t}Bu−O−^{t}Bu	−402.2 ± 1.3 (61-Smu/Bon) −399.6 ± 1.2 (75-Fen/Har) **−398.5 ± 0.7** (96-Ste/Chi)	−425.9	27.4	37.7 ± 0.8 (61-Smu/Bon) 37.6 ± 0.1 (75-Fen/Har) 37.2 (76-Amb/Ell) **37.27 ± 0.23** (96-Ste/Chi)	41.20	−3.9	−361.2	−383.7	22.5

Table 5. (Continued)

		$\Delta_f H^\circ_m$(l)			$\Delta_l^g H^\circ_m$			$\Delta_f H^\circ_m$(g)[b]		
		exp	calc	Δ	exp	calc	Δ	exp	calc	Δ
41	^{t}Bu−O−Am	−428.8[b]	−428.1	−0.7	46.89 ± 0.99 (90-Roz/Bar) **48.25** (02-Ver/Kra)	48.34	−0.9	**−380.6 ± 6.8** (90-Roz/Bar)	−380.0	−0.6
42	^{t}Bu−O−Hex		−453.5		53.22 (02-Ver/Kra)	53.32	−0.1		−400.9	
43	^{t}Bu−O−Hep		−479.0		56.60 (02-Ver/Kra)	58.30	−1.7		−421.8	
44	^{t}Bu−O−Oct		−504.5		61.41 (02-Ver/Kra)	63.28	−1.9		−442.7	
45	^{t}Am−O−Me	**−336.8 ± 1.7**[h] (this work) −334.7 ± 2.7 (97-Sol/Per) −340.1 ± 0.8 (91-Roz/Saf)	−335.9[g]	−0.5	**35.27 ± 0.39** (02-Ver/Kra) 35.30[c] (94-Kra/Gme)	35.17	0.1	−301.1	−300.6[g]	−0.5
46	^{t}Am−O−Et	−379.8 ± 1.4 (95-Sha/Roz) −383.4 ± 2.6[e] **−372.7** (95-Kyt/Dat)	−373.0[g]	0.3	38.78[c] (94-Kra/Gme) 37.79[c] (99-Hei/Fis) **39.22 ± 0.39** (02-Ver/Kra)	38.38	0.8	−333.5 −344.4 ± 2.6[d] (00-Chu)	−334.2[g]	0.7
47	^{t}Am−O−Pr		−398.5[g]		43.76 ± 0.65 (02-Ver/Kra)	43.36	0.4		−355.1[g]	
48	^{t}Am−O−^{i}Pr		−400.1[f,g]		41.57 (02-Ver/Kra)	41.44	0.1		−358.5[f,g]	
49	^{t}Am−O−^{i}Bu		−430.7[g]		46.25 (02-Ver/Kra)	47.04	−0.8		−386.0[g]	
50	^{t}Am−O−^{s}Bu		−425.6[f,g]		46.75 (02-Ver/Kra)	46.42	0.3		−379.4[f,g]	
51	^{t}Am−O−Bu	−424.0 ± 2.4[h] (this work)	−424.1[g]	0.1	48.30 ± 0.56 (02-Ver/Kra)	48.34	−0.1	−375.7	−376.0[g]	0.3
52	^{t}Am−O−Am		−449.5[g]		53.53 (02-Ver/Kra)	53.32	0.2		−396.9[g]	
53	^{t}Am−O−cHex				54.24 ± 0.19 (02-Ver/Kra)	55.04	−0.8			
54	^{t}Am−O−Hex		−475.0[g]		58.57 (02-Ver/Kra)	58.30	0.3		−417.8[g]	
55	^{t}Oct−O−Me	−406.7 ± 1.5 (96-Ver/Bec)	−406.6[i]	−0.1	45.32[c] (01-Uus/Pok) 45.28 ± 0.33 (02-Ver/Kra)	46.49	−1.2		−361.6[i]	0.2
56	^{t}Oct−O−Et		−348.2[j]		46.98 ± 0.41 (02-Ver/Kra)	49.69	−2.7		−395.2[i]	
57	^{t}Oct−O−Pr		−466.2[j]		50.10 ± 0.33 (02-Ver/Kra)	54.67	−4.6		−416.1[i]	
58	^{t}Oct−O−^{i}Bu		−498.6[j]		51.55 (02-Ver/Kra)	58.35	−6.8		−447.0[i]	
59	^{t}Oct−O−Bu		−489.9[j]		52.87 ± 0.35 (02-Ver/Kra)	59.65	−6.9		−437.0[i]	
60	^{t}Oct−O−Am		−513.8[j]		55.86 ± 0.28 (02-Ver/Kra)	64.63	−8.8		−457.9[i]	
61	^{t}Oct−O−(4-MePe)[k]		−546.3[j]		57.50 (02-Ver/Kra)	68.31	−10.8		−488.8[i]	
62	^{t}Oct−O−(3-MePe)[l]		−546.8[j]		57.96 (02-Ver/Kra)	68.31	−10.4		−488.8[i]	
63	^{t}Oct−O−(3,3-diMeBu)[m]		−556.5[j]		56.43 (02-Ver/Kra)	65.98	−9.6		−500.1[i]	
64	^{t}Oct−O−Hex		−538.0[j]		59.18 (02-Ver/Kra)	69.61	−10.4		−478.8[i]	

[a] Values selected for the calculation of the group-additivity contributions are in bold. [b] Calculated as the difference between selected values of $\Delta_f H^\circ_m$ and $\Delta_l^g H^\circ_m$. [c] Calculated in this work using original experimental $p-T$ data available from the literature. [d] Value of $\Delta_f H^\circ_m$(g) calculated from the experimental reaction enthalpy in the gaseous phase reported by Chu (00-Chu) (see text). [e] Value of $\Delta_f H^\circ_m$(l) calculated from the experimental $\Delta_f H^\circ_m$(g) value reported by Chu (00-Chu) (see footnote d) and selected value of $\Delta_l^g H^\circ_m$. [f] $C_{tert}-O-C_{quat}$ correction of 10.0 kJ·mol^{-1} was added (see text). [g] ^{t}Am is $CH_3-CH_2-C(CH_3)_2-$. Ether gauche correction of 4.0 kJ·mol^{-1} was added (see text). [h] Experimental value reported by Verevkin et al. (96-Ver/Bec) was corrected for water traces (see text). [i] ^{t}Oct is $C(CH_3)_3-CH_2-C(CH_3)_2-$. Correction for strain in *tert*-octyl substituent of 27.0 kJ·mol^{-1} was added (see text). [j] Value of $\Delta_f H^\circ_m$(l) obtained from the calculated $\Delta_f H^\circ_m$(g) value (see footnote i) and the experimental value of $\Delta_l^g H^\circ_m$. [k] Product of the reaction of 2,4,4-trimethyl-2-pentene with 2-methyl-1-pentanol. Product of the reaction of 2,4,4-trimethyl-2-pentene with 3-methyl-1-pentanol. [m] Product of the reaction of 2,4,4-trimethyl-2-pentene with 3,3-dimethyl-1-butanol.

Table 6. Experimental Results[a,b] for Benzyl Ethers at 298.15 K in kJ·mol^{-1}

		$\Delta_f H^\circ_m$ (liq) exp	$\Delta_f H^\circ_m$ calc	Δ	$\Delta_l^g H^\circ_m$ exp	$\Delta_l^g H^\circ_m$ calc	Δ	$\Delta_f H^\circ_m$ (g) exp	$\Delta_f H^\circ_m$ (g) calc	Δ
65	Methyl Benzyl ether 	-133.5±1.5	-131.2	-2.3	51.40±0.29	48.59	2.8	-82.1±1.5	-82.8	0.7
66	Ethyl Benzyl ether 	-167.8±1.9	-168.3	0.5	53.49±0.43	51.8	1.7	-114.3±1.9	-116.4	2.1
67	tButyl Benzyl ether 	-241.3±2.2	-242.7	1.4	57.86±0.29	59.59	-1.7	-183.4±2.2	-182.8	-0.5
68	tAmyl Benzyl ether 	-263.8±3.0	-264.2[a]	0.4	61.81±0.23	64.57	-2.8	-202.0±3.0	-199.8[a]	-2.2
69	(1-Methoxy-ethyl)-benzene 	-161.5±2.2	-159.8	-1.7	49.08±0.43	48.50	0.6	-112.4±2.2	-111.5	-0.9
70	(1-Ethoxy-ethyl)-benzene 	-196.2±1.1	-196.9	0.7	52.63±0.20	51.71	0.9	-143.6±1.1	-145.1	1.5
71	(1-Propoxy-ethyl)-benzene 	-222.3±2.7	-222.5	0.2	56.71±0.24	56.69	0.1	-165.6±2.7	-166.0	0.4
72	(1-Butoxy-ethyl)-benzene 	-249.8±3.0	-248.0	-1.8	59.80±0.34	61.67	-1.9	-190.0±3.0	-186.9	-3.1
73	(1-iso-Propoxy-ethyl)-benzene 	-233.3±1.0	-234.0	0.7	55.41±0.27	54.77	0.6	-177.9±1.0	-179.4	1.5
74	S*R*-(1-sec-Butoxy-ethyl)-benzene 	-259.8±2.9	-259.5	-0.3	58.70±0.46	59.75	-1.1	-201.1±2.9	-200.3	-0.7
75	S*S*-(1-sec-Butoxy-ethyl)-benzene 	-258.1±2.9	-259.5	1.4	59.13±0.48	59.75	-0.6	-199.0±2.9	-200.3	1.3
76	(1-cyclo-Hexyl-oxy-ethyl)-benzene 	-263.8±2.2	-264.5	0.7	69.75±0.45	68.37	1.4	-194.1±2.3	-200.3	6.2
77	Methyl Cumyl ether 	-193.4±2.5	-193.8	0.4	52.85±0.16	51.53	1.3	-140.5±2.5	-142.3	1.8
78	Ethyl Cumyl ether 	-230.2±2.7	-231.0	0.8	54.70±0.52	54.74	-0.1	-175.5±2.7	-175.8	0.4
79	Propyl Cumyl ether 	-257.4±2.4	-256.5	-0.9	59.31±0.20	59.72	-0.4	-198.1±2.4	196.8	-1.3
80	Butyl Cumyl ether 	-282.3±3.1	-282.0	-0.3	63.84±0.50	64.70	-0.9	-218.5±3.1	-217.7	-0.8

[a] Data are from 02-Ver/Kra, 02-Kra/Vas 02-Ver/Hei, 01-Ver/Hei, and 01-Vere/Hei. [b] Ether gauche correction of 4.0 kJ·mol^{-1} was added (see text).

86) and 2-alkyl-substituted 1,3-dioxane (0.0 kJ·mol^{-1} from **106** and **107**) are different from those of cyclohexane (2.9 kJ·mol^{-1} from 96-Coh).

The enthalpies of formation $\Delta_f H^\circ_m$(l) of a large set of five- and six-membered cyclic acetals and ketals (**84**, **86**–**93**, **100**–**102**, **104**–**109**, and **122**–**126**) were measured by Pihlaja et al. (70-Pih/Tuo, 69-Pih/Hei, 69-Pih/Lau, 68-Pih/Hei, and 68-Pih/Luo). They calculated values for enthalpies of vaporization using coarse empirical correlation. The GAVs derived for the prediction of enthalpies of vaporization of acetals and ketals in this work were evaluated from experimental data only on straight-chained species. Hence,

Table 7. Database for Acetals, Ketals, Ortho Esters, and Ortho Carbonates at 298.15 K in kJ·mol^{-1} [e]

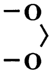
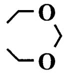
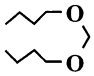
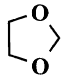
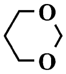
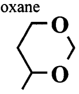
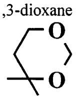
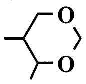
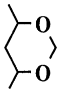
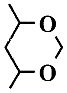
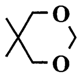
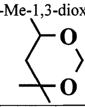
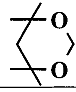
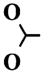
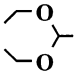
			$\Delta_f H^\circ_m$ (liq) exp	$\Delta_f H^\circ_m$ calc	Δ	$\Delta_l^g H^\circ_m$ exp	$\Delta_l^g H^\circ_m$ calc	Δ	$\Delta_f H^\circ_m$ (g)^a exp	$\Delta_f H^\circ_m$ (g) calc	Δ
81	di-Methoxy-methane 	liq	-377.1^a	-375.4	-1.7	29.57^b 49-Nic/Laf **28.86±0.21** 64-McE/Kil 30.44^b 01-Alb/Hah	29.65	-0.8	-348.2±0.8 69-Pil	-347.9	-0.3
82	di-Ethoxy-methane 	liq	**-450.4±0.8** 69-Man -448.7±0.4 80-Gut/Leb	-449.7	-0.7	**35.65±0.17** 69-Man 37.0±2.0 77-Leb/Rya 35.98^b 49-Nic/Laf	36.07	-0.4	-414.8	-415.1	0,3
83	di-Butoxy-methane 	liq	-549.4±1.7 57-Sku/Str	-551.7	2.3	57.20^b 00-Pal	56.00	1.2	-492.2	-498.7	6.5
84	1,3-dioxolane 	liq	-333.0±0.5 57-Sku/Str -337.6±4.1 59-Fle/Mor **-337.2±1.4** 69-Pih/Hei	-352.7	15.5	34.02^b 68-Che **35.6±0.4** 59-Fle/Mor	24.77	10.8	-301.6	331.6	30.0
85	1,3-dioxane 	liq	**-377.5±1.1** 82-Bys/Man -384.6±1.8 68-Pih/Luo -376.66±0.8 61-Sne/Ski -395.2±5.9 59-Fle/Mor -388.9±0.9 57-Sku/Str	-378.2	0.7	**39.08±0.04** 82-Bys/Man 35.30±0.13 71-Cab/Con 35.56±0.84 59-Fle/Mor	29.75	9.3	-338.4	-352.5	14.1
86	4-Me-1,3-dioxane 	liq	**-416.1±2.9** 68-Pih/Luo -425.9±0.8 57-Sku/Koz	-416.1	-0.8	43.46±0.30 this work	32.81	10.7	-372.6	-386.8	14.2
87	4,4-di-Me-1,3-dioxane 	liq		-452.6		**43.74**^{b} 68-Kac/Nem 43.59^b 69-Les	37.54	6.2		-418.9	
88	4,5-di-Me-1,3-dioxane 	liq	-451.7±2.0 68-Pih/Luo	-447.5	-4.2		36.49			-417.7	
89	cis-4,6-di-Me-1,3-dioxane 	liq	-474.8±2.4 68-Pih/Luo	-452.4	-22.4		35.87			-421.1	
90	trans-4,6-di-Me-1,3-dioxane 	liq	-462.6±1.8 68-Pih/Luo	-452.4	-10.2		35.87			-421.1	
91	5,5-di-Me-1,3-dioxane 	liq	-461.3±2.2 68-Pih/Luo	-446.4	-14.9		36.08			-415.6	
92	4,4,6-tri-Me-1,3-dioxane 	liq	-500.6±3.5 68-Pih/Luo	-489.7	-10.9		40.60			-453.2	
93	4,4,6,6-tetra-Me-1,3-dioxane 	liq	-518.0±2.6 87-Pih	-527.0	9.0		45.33		-470.6	-485.3	
94	di-Methoxy-ethane 	liq	**-420.0±0.8** 70-Bir/Ski -420.3±0.8 80-Wib	-419.1	-09	32.56^b 49-Nic/Laf	32.33	0.2	-389.7±0.8 69-Pil	-388.9	-0.8
95	di-Ethoxy-ethane 	liq	**-493.07±0.39** 9Ver/Pen -491.4±2.3 68-Pih/Hei	-493.4	0.3	**39.12±0.33** this work 38.91^b 49-Nic/Laf 41.63^b 47-Stu	38.75	0.4	-454.0	-456.1	2.1

Table 7. (Continued)

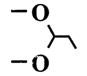
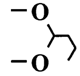
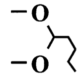
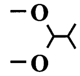
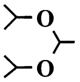
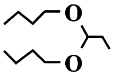
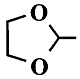
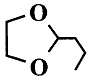
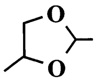
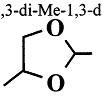
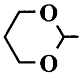
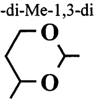
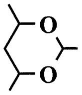
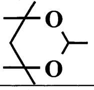
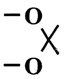
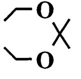
			$\Delta_f H^\circ_m$ (liq) exp	$\Delta_f H^\circ_m$ calc	Δ	$\Delta_l^g H^\circ_m$ exp	$\Delta_l^g H^\circ_m$ calc	Δ	$\Delta_f H^\circ_m$ (g)^a exp	$\Delta_f H^\circ_m$ (g) calc	Δ
96	1,1-di-Methoxy-propane 	liq	-443.3±1.1 79-Wib/Sq	-444.6	1.3					-409.9	
97	1,1-di-Methoxy-butane 	liq	-468.2±1.5 79-Wib/Sq **-467.4±0.8** 94-Wib/Mor	-466.8	-0.6	41.7 94-Wib/Mor	42.29	-0.6	-425.7	-430.7	5.0
98	1,1-di-Methoxy-pentane 	liq	-494.6±2.4 79-Wib/Sq	-495.6	1.0		47.27			-451.7	
99	1,1-di-Methoxy-2-Me-propane 	liq	-476.2±1.7 79-Wib/Sq	-476.8	0.6		41.00			-440.8	
100	di-iPropoxy-ethane 	liq	-569.2±3.5 69-Pih/Lau	-567.5	-1.7		44.87			-524.8	
101	1,1-di-Butoxy-propane 	liq	-608.6±3.3 69-Pih/Lau	-620.9	12.3		63.65			-560.6	
102	2-Me-1,3-dioxolane 	liq	-385.1±2.2 72-Pih/Hei	-396.3	11.2	42.78±0.61 this work	27.45	15.3	-344.1	-372.6	28.5
103	2-nPr-1,3-dioxolane 	liq	-431.98±0.71 98-Ver/Pen	-447.3	15.3	45.21±0.34 this work	37.41	7.8	-386.8	-414.4	27.6
104	cis-2,3-di-Me-1,3-dioxolane 	liq	-421.3±2.3 69-Pih/Hei	-444.8	23.5		33.10			-414.4	
105	trans-2,3-di-Me-1,3-dioxolane 	liq	-419.8±2.4 69-Pih/Hei	-444.8	25.0		33.10			-414.4	
106	2-Me-1,3-dioxane 	liq	-436.5±2.6 68-Pih/Luo	-421.8	-14.7		32.43			-393.5	
107	cis-2,4-di-Me-1,3-dioxane 	liq	**-470.98±0.54** this work -465.2±4.2 68-Pih/Luo	-458.9	-14.7	44.86±0.60 this work	35.49	9.37	-426.1	-427.8	1.7
108	2,4,6-tri-Me-1,3-dioxane 	liq	-488.3±2.8 68-Pih/Luo	-496.0	7.7		38.55			-462.1	
109	2,4,4,6,6-penta-Me1,3-dioxane 	liq	-559.9±3.1 87-Pih	-570.6	10.7		48.01	-0.9		-526.3	
110	2,2-di-Methoxy-propane 	liq	**-460.7±0.8** 94-Wib/Mor -457.1±1.0 62-Ster/Dor -459.5±0.6 79-Wib/Squ	-460.7	0.0	**37.63±0.**42 this work 35.27±0.75 79-Wib/Squ	37.19	0.4	-423.1	-425.7	2.6
111	2,2-di-Ethoxy-propane 	liq	-538.5±1.1 62-Ster/Dor	-535.0	-3.5	43.17±0.39 this work	43.61	-0.4	-495.3	-492.9	-2.4

Table 7. (Continued)

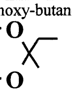
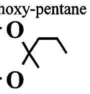
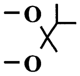
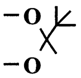
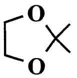
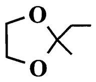
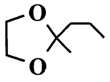
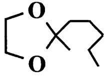
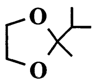
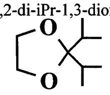
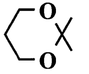
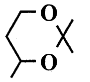
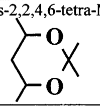
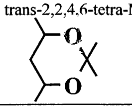
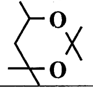
			$\Delta_f H^\circ_m$ (liq) exp	$\Delta_f H^\circ_m$ calc	Δ	$\Delta_l^g H^\circ_m$ exp	$\Delta_l^g H^\circ_m$ calc	Δ	$\Delta_f H^\circ_m$ (g)^a exp	$\Delta_f H^\circ_m$ (g) calc	Δ
112	2,2-di-Methoxy-butane 	liq	-485.1±1.1 79-Wib/Sq	-486.2	1.1		42.17			-446.7	
113	2,2-di-Methoxy-pentane 	liq	-509.2±1.2 79-Wib/Sq	-511.7	2.5		47.15			-467.6	
114	2,2-di-Methoxy3-Me-butane 	liq	-512.2±1.1 79-Wib/Sq	-518.4	6.2		45.85			-477.6	
115	2,2-di-Methoxy3,3-di-Me-butane 	liq	-524.4±1.1 79-Wib/Sq	-554.4	30.0		48.50			-509.8	
116	2,2-di-Me-1,3-dioxolane 	liq	**-430.49±0.32** 98-Ver/Pen -423.1±2.9 42-Jun/Dah	-437.9	7.4	41.08±0.16 this work	32.31	8.8	-389.4	-409.4	20.0
117	2-Me-2-Et-1,3-dioxolane 	liq	-452.56±0.42 98-Ver/Pen	-463.4	10.8	42.82±0.29 this work	37.29	5.5	-409.7	-430.3	20.6
118	2-Me-2-nPr-1,3-dioxolane 	liq	-475.4±1.3 98-Ver/Pen	-488.9	13.5	46.16±0.34 this work	42.27	3.9	-429.2	-451.2	22.0
119	2-Me-2-nPe-1,3-dioxolane 	liq	-522.8±1.1 98-Ver/Pen	-539.9	17.1	53.99±0.28 this work	52.23	1.7	-468.8	-493.0	24.2
120	2-Me-2-iPr-1,3-dioxolane 	liq	-465.8±1.4 98-Ver/Pen	-495.6	29.8	43.90±0.24 this work	40.97	2.9	-421.9	-461.2	39.3
121	2,2-di-iPr-1,3-dioxolane 	liq	-505.9±1.3 98-Ver/Pen	-553.3	47.4	49.93±0.30 this work	49.63	0.3	-456.0	-513.0	57.0
122	2,2-di-Me1,3-dioxane 	liq	-468.9±2.1 68-Pih/Luo	-463.4	-5.5		37.29			-430.3	
123	2,2,4-tri-Me1,3-dioxane 	liq	-500.9±2.6 68-Pih/Luo	-500.5	-0.4		40.35			-464.6	
124	cis-2,2,4,6-tetra-Me-1,3-dioxane 	liq	-539.4±3.4 68-Pih/Luo	-537.6	-1.8		43.41			-498.9	
125	trans-2,2,4,6-tetra-Me-1,3-dioxane 	liq	-526.3±4.7 68-Pih/Luo	-537.6	11.3		43.41			-498.9	
126	2,2,4,4,6-penta-Me-1,3-dioxane 	liq	-567.1±3.6 87-Pih	-574.9	7.8		48.14			-531.0	

Table 7. (Continued)

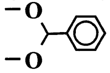
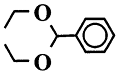
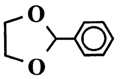
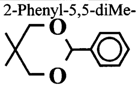
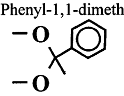
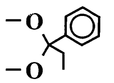
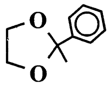
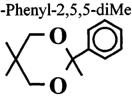
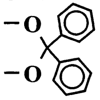
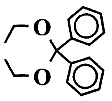
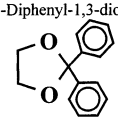
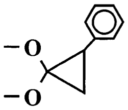
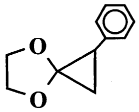
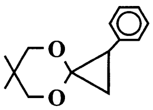
			$\Delta_f H_m^\circ$ (liq) exp	$\Delta_f H_m^\circ$ calc	Δ	$\Delta_l^g H_m^\circ$ exp	$\Delta_l^g H_m^\circ$ calc	Δ	$\Delta_f H_m^\circ$ (g)[a] exp	$\Delta_f H_m^\circ$ (g) calc	Δ
127	Phenyl-di-Methoxymethane 	liq	-308.4±0.5 95-Ver/Dog	-303.5	-4.9	60.91±0.49 this work	58.62	2.3	-247.5	-245.2	-2.3
128	Phenyl-di-Ethoxymethane 	liq	-372.8±1.3 98-Ver/Pen	-377.7	4.9	62.76±0.59 this work	65.04	-2.3	-310.0	-312.3	2.3
129	2-Phenyl-1,3-dioxolane 	liq	-267.4±1.3 95-Ver/Dog	-280.7	13.3	62.64±0.68 this work	53.74	8.9	-204.8	-228.8	24.0
130	2-Phenyl-5,5-diMe-1,3-dioxane 	cr	-397.0±0.9 95-Ver/Dog	-		69.18±0.82 this work 87.78±0.84 (sub) this work $\Delta_{cr}^{l}H_m^\circ$ = 18.60 (307.6 K)	65.05	4.1	-309.2	-307.3[c]	-1.9
131	1-Phenyl-1,1-dimethoxyethane 	liq	-343.5±0.7 95-Ver/Dog	-341.8	-1.7	54.01±0.82 this work	53.97	0.1	-289.5	-287.6	-1.9
132	1-Phenyl-1,1-dimethoxypropane 	liq	-365.5±1.5 98-Ver/Pen	-367.3	1.7	58.92±0.28 this work	58.96	-0.1	-306.6	-308.5	1.9
133	2-Phenyl-2-Me-1,3-dioxolane 	cr	-343.8±2.1 95-Ver/Dog	-		82.89±0.89(sub) this work			-260.9	-271.2	10.3
134	2-Phenyl-2,5,5-diMe-1,3-dioxane 	liq	-414.5±0.8 95-Ver/Dog	-407.4[c]	-7.1	66.39±0.80 this work	60.40	6.0	-348.1	-349.7[c]	1.6
135	2,2-Diphenyl-dimethoxymethane 	cr	-270.6±3.4 98-Ver/Pen	-		106.7±1.2(sub) this work			-163.9	-163.9	0.0
136	2,2-Diphenyl-diethoxymethane 	cr	-328.41±0.84 98-Ver/Pen	-		97.2±1.1(sub) this work			-231.2	-231.1	-0.1
137	2,2-Diphenyl-1,3-dioxolane 	cr	-208.0±1.3 98-Ver/Pen	-		84.44±0.64 this work 99.7±1.1(sub) this work			-108.3	-147.5	39.2
138	1,1-Dimethoxy-2-phenylcyclopropane 	l	-229.7±1.6 98-Ver/Pen	-323.3	102.6	63.65±0.60 this work	64.68	-1.1	-166.1	-275.3	109.2
139	1-Phenyl-4,7-dioxaspiro[2,4]heptane 	cr	-182.6±1.1 98-Ver/Pen	-309.5	126.9	71.30±0.71 this work 91.70±0.81(sub) this work	59.80	11.5	-90.9	-258.9	168.0
140	1-Phenyl-6,6-dimethyl-4,8-dioxaspiro[2,5]octane 	cr	-302.4±1.2 98-Ver/Pen	-	95.2	70.84±0.40[d] $\Delta_{cr}^{l}H_m^\circ$ = 27.20 (351.2 K) 98.04±0.34 (sub) this work	71.11	-0.3	-204.4	-342.9	138.5

Table 7. (Continued)

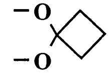
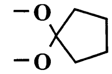
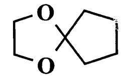
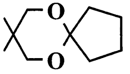
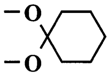
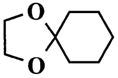
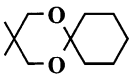
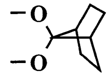
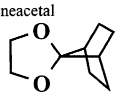
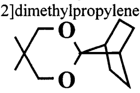
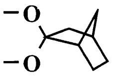
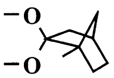
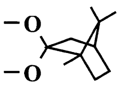
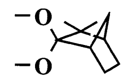
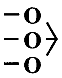
			$\Delta_f H_m^\circ$ (liq) exp	$\Delta_f H_m^\circ$ calc	Δ	$\Delta_l^g H_m^\circ$ exp	$\Delta_l^g H_m^\circ$ calc	Δ	$\Delta_f H_m^\circ$ (g)^a exp	$\Delta_f H_m^\circ$ (g) calc	Δ
141	Cyclobutanonedimetylacetal 	liq	-345.05±0.90 98-Ver/Pen	-440.2	95.2	41.97±0.29 this work	40.83	1.1	-303.1	-404.9	101.8
142	Cyclopetanonedimethylacetal 	liq	**-445.7±1.2** 98-Ver/Pen -444.0±1.0 94-Wib/Mor	-465.7	20.0	**44.52±0.35** this work 46.07 94-Wib/Mor	45.81	-1.3	-401.2	-425.8	24.6
143	Cyclopetanoneethyleneacetal 	liq	-417.56±0.91 98-Ver/Pen	-442.9	25.3	47.47±0.48 this work	40.93	6.5	-370.1	-409.4	39.3
144	Cyclopetanone-(2,2-dimethylpropylene)acetal 	liq	-517.4±1.1 98-Ver/Pen	-536.6	19.2	53.77±0.51 this work	52.24	1.5	-463.6	-493.4	29.8
145	Cyclohexanonedimethylacetal 	liq	-505.5±1.2 98-Ver/Pen **-492.0±0.8** 94-Wib/Mor	-491.2	-0.8	48.64±0.21 this work	51.79	-2.2	-443.4	-446.7	3.3
146	Cyclohexanoneethylenacetal 	liq	-466.9±1.4 98-Ver/Pen	-468.4	1.5	50.36±0.56 this work	45.91	4.4	-416.5	-430.3	13.8
147	Cyclohexanone-(2,2-dimethylpropylene)acetal 	liq	-561.3±3.0 98-Ver/Pen	-562.1	0.8	59.27±0.63 this work	57.22	2.0	-502.0	-514.3	12.3
148	7,7-Dimethoxybicyclo[2,2,1]heptane 	liq	**-423.8±1.2** 98-Ver/Pen -418.0±4.0 90-Wib/Cun	-484.1	60.3	50.39±0.22 this work	51.83	-1.5	-373.4	-445.8	72.4
149	Bicyclo[2,2,1]heptane-7-on-ethyleneacetal 	liq	-395.1±1.0 98-Ver7Pen	-461.3	66.2	54.00±0.40 this work	46.95	7.0	-341.1	-429.4	88.3
150	Bicyclo[2,2,1]heptane-7-on[2,2]dimethylpropylene]-acetal 	cr	-516.1±1.4 98-Ver/Pen			60.49±0.89 ^{d} $\Delta_{cr}^l H_m^\circ$ = 23.85 (346.7 K) 84.34±0.87(sub) this work	58.26	2.2	-431.8	-513.4	81.6
151	2-Norbornanone dimethyl ketal 	liq	-431.2±3.8 90-Wib/Cun	-484.1	52.9	53.01±0.08 90-Wib/Cun	51.83	1.1	-378.2	-445.8	67.8
152	1-Methyl-2-norbornanone dimethyl ketal 	liq		-520.1		54.64 ± 0.08 90-Wib/Cun	54.48	0.1		-478.0	
153	1,7,7-Trimethyl-2-norbornanone dimethyl ketal 	liq	-459.8 90-Wib/Cun	-588.3	128.5	61.30 90-Wib/Cun	60.86	0.4	-398.5	-541.1	142.6
154	3,3-Dimethyl-2-norbornanone dimethyl ketal 	liq		-543.1		58.32 90-Wib/Cun	55.15	3.1		-498.9	
155	tri-Methoxy-methane 	liq	**-568.9±0.9** 74-Hin/Klu -567.8 77-Gut -575.3±2.0 71-Pih/Tuo	-567.9	-1.0	**38.2±2.1** 74-Hin/Klu 37.1±1.5 95-Rak/Ver	38.14	-0.1	-530.8	-530.3	-0.5

Table 7. (Continued)

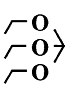
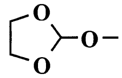
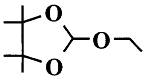
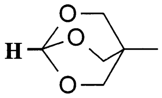
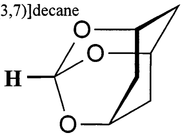
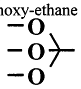
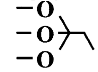
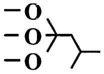
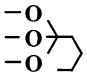
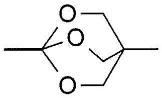
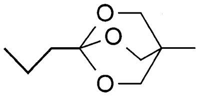
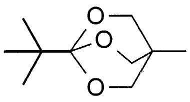
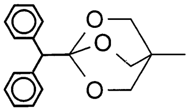
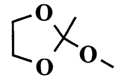
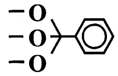
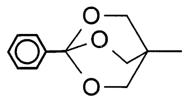
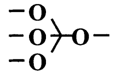
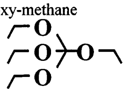
			$\Delta_f H_m^\circ$ (liq) exp	$\Delta_f H_m^\circ$ calc	Δ	$\Delta_l^g H_m^\circ$ exp	$\Delta_l^g H_m^\circ$ calc	Δ	$\Delta_f H_m^\circ$ (g)[a] exp	$\Delta_f H_m^\circ$ (g) calc	Δ
156	tri-Ethoxy-methane 	liq	-687.0±0.9 74-Hin/Klu -675.9±0.8 80-Gut/Leb -681.3±3.1 71-Pih/Tuo **-678.4±1.5** 85-Mar/Man	-679.4	1.0	45.23 74-Hin/Klu 49.0±2.0 80-Gut/Leb 46.02±0.84 71-Pih/Tuo **47.81±0.10** 85-Mar/Man	47.77	0.1	-630.6	-631.1	0.5
157	2-Methoxy-1,3 dioxolane 	liq	**-530.0±0.7** 95-Rak/Ver -523.2±3.3 77-Gut	-545.2	15.2	46.37±0.80 this work	33.26	13.1	-483.6	-483.6	30.4
158	2-Ethoxy-4,4,5,5-tetra-methyl-1,3-dioxolane 	liq	-727.5±8.7 77-Gut	-731.1	3.6	67.4±1.5 95-Rak/Ver	52.05	15.4	-660.1	-680.4	20.3
159	4-Methyl-2,6,7-trioxabicyclo[2,2,2]octane 	cr	-574.2±1.2 95-Rak/Ver	-		67.58±0.13 [b] 95-Rak/Ver	-		-506.6	-548.0	41.4
160	2,2,4,10-Trioxatricyclo-[3.3.1.1(3,7)]decane 	cr	-573.6±1.9 74-Man	-		74.39±0.38 74-Man	-		-499.2	-546.0	46.8
161	1,1,1-tri-Methoxy-ethane 	liq	-612.0±1.1 74-Hin/Klu **-610.0±0.5** 79-Wib/Squ	-609.3	-0.7	**39.20** 74-Hin/Klu 39.20±0.75 79-Wib/Squ 40.8±1.5 95-Rak/Ver	39.26	-0.1	-570.8	-569.9	-0.9
162	1,1,1-tri-Methoxy-propane 	liq	-634.2±1.1 80-Gut/Cul	-634.9	0.7	44.3±1.5 95-Rak/Ver	44.24	0.1	-589.9	-590.8	0.9
163	3-Me-1,1,1-tri-Methoxy-butane 	liq	-683.4 80-Gut/Cul	-629.6	9.2		52.90			-642.7	
164	1,1,1-tri-Methoxy-pentane 	liq	-681.8 80-Gut/Cul	-685.9	4.1		54.20			-642.7	
165	1,4-Dimethyl-2,6,7-trioxabicyclo[2,2,2]octane 	cr	-634.1±0.6 95-Rak/Ver	-		74.43±0.13 [b] 95-Rak/Ver			-559.7	-587.6	27.9
166	4-Methyl-1-propyl-2,6,7-trioxabicyclo[2,2,2]octane 	cr	-670.4±1.4 95-Rak/Ver	-		77.5±1.1 [b] 95-Rak/Ver			-592.9	-629.4	36.5
167	4-Methyl-1-t-butyl-2,6,7-trioxabicyclo[2,2,2]octane 	cr	-719.6±1.6 95-Rak/Ver	-		77.03±0.67 [b] 95-Rak/Ver			-642.6	-671.6	29.0
168	1-(Diphenylmethyl)-4-methyl-2,6,7-trioxabicyclo[2,2,2]octane 	cr	-438.0±1.4 95-Rak/Ver	-		127.2±2.0 [b] 95-Rak/Ver			-310.8	-367.6	56.8

Table 7. (Continued)

			$\Delta_f H^\circ_m$ (liq) exp	$\Delta_f H^\circ_m$ calc	Δ	$\Delta_l^g H^\circ_m$ exp	$\Delta_l^g H^\circ_m$ calc	Δ	$\Delta_f H^\circ_m$ (g)[a] exp	$\Delta_f H^\circ_m$ (g) calc	Δ
169	2-Me-2-Methoxy-1,3-dioxolane 	liq	-572.8±2.5 77-Gut	-586.6	13.8	50.6±1.5 95-Rak/Ver	34.38	16.2	-522.2	-553.6	31.4
170	Phenyl-tri-Methoxy-methane 	liq	**-491.9±1.2** 95-Rak/Ver -485.8±3.1 80-Gut/Cul			59.88±0.38 this work			-432.0		
171	1-Phenyl-4-methyl-2,6,7-trioxabicyclo[2,2,2]octane 	cr	-493.4±0.6 95-Rak/Ver			97.1±1.0[b] 95-Rak/Ver			-396.3	-449.6	53.3
172	tetra-Methoxy-methane 		**-767.1±1.3** 79-Wib/Squ -767.3 74-Hin/Klu	-766.6	-0.5	**39.99±0.75** 79-Wib/Squ 40.0 74-Hin/Klu	40.00	0.0	-727.1	-727.3	0.2
173	tetra-Ethoxy-methane 		**-914.6±2.1** 85-Mar/Man -919.0±1.0 77-Leb/Rya	-915.2	0.4	**52.85±0.15** 85-Mar/Man 41.0±3.0 77-Leb/Rya	52.84	0.0	-861.8	-861.6	-0.2

[a] Calculated as the difference between selected values of $\Delta_f H^\circ_m$ and $\Delta_l^g H^\circ_m$. [b] Calculated in this work using original experimental $p-T$ data available from the literature. [c] Correction for strain in 1,1-dimethylcyclohexene of 5.5 kJ·mol^{-1} was added. [d] Value of $\Delta_l^g H^\circ_m$ calculated as the difference $\Delta_{cr}^g H^\circ_m - \Delta_{cr}^l H^\circ_m$. [e] Values selected for the calculation of the group-additivity contributions are in bold.

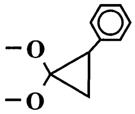
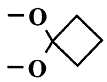
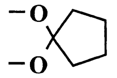
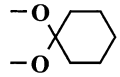
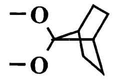
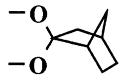
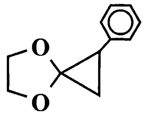
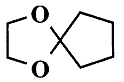
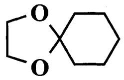
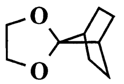
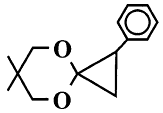
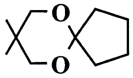
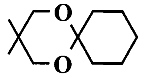
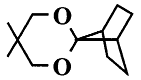
Table 8. Group-Additivity Values for Calculation of Enthalpies of Formation and Enthalpies of Vaporization of Acetals, Ketals, and Ortho Esters at 298.15 K in kJ·mol^{-1}

	$\Delta_f H^\circ_m$(l)		$\Delta_l^g H^\circ_m$	$\Delta_f H^\circ$	
	this work	Cohen[a]	this work	this work	Cohen[a]
C−(C)(H)$_3$		−48.5	5.65[b]		−41.8
C−(C)$_2$(H)$_2$		−25.5	4.98[b]		−20.9
C−(C)$_3$(H)		−9.2	3.01[b]		−10.0
C−(C)$_4$		3.3	0.01[b]		−0.4
Cb−(H)		8.2	5.65[b]		13.8
Cb−(C)		20.1	4.10[b]		23.0
C−(C)$_2$(Cb)(H)		−4.2	1.46[b]		−4.2
C−(O)(H)$_3$		−48.5	5.65[b]		−41.8
O−(C)$_2$	−105.9 ± 0.5	−105.0	7.89 ± 0.37	−100.1 ± 0.6	−99.6
C−(O)(H)$_2$(C)	−37.1 ± 0.3	−38.1	3.21 ± 0.22	−33.6 ± 0.4	−33.9
C−(O)(H)(C)$_2$	−25.7 ± 0.4	−29.3	0.62 ± 0.26	−26.1 ± 0.4	−30.1
C−(O)(C)$_3$	−14.5 ± 0.4	−23.4	−0.30 ± 0.25	−16.4 ± 0.5	−27.6
C−(O)(H)$_2$(Cb)	−37.9 ± 0.6	−	2.70 ± 0.79	−32.9 ± 0.8	−
C−(O)(H)(Cb)(C)	−18.0 ± 0.4	−	3.04 ± 0.56	−19.8 ± 0.6	−
C−(O)(Cb)(C)$_2$	−3.5 ± 0.6	−	−5.66 ± 0.80	−8.8 ± 0.8	−
C−(O)$_2$(H)$_2$	−66.7 ± 1.5	−69.5	2.57 ± 0.46	−64.2 ± 1.7	−69.0
C−(O)$_2$(H)(C)	−61.8 ± 1.0	−66.9	−0.84 ± 0.47	−63.4 ± 1.4	−66.1
C−(O)$_2$(C)$_2$	−54.9 ± 1.3	−66.1	−1.19 ± 0.57	−58.4 ± 1.7	−67.8
C−(O)$_2$(H)(Cb)	−55.8 ± 1.9	−	−0.81 ± 0.99	−53.4 ± 1.7	−
C−(O)$_2$(Cb)(C)	−45.6 ± 1.8	−	−11.11 ± 1.00	−54.0 ± 1.7	−
C−(O)$_2$(Cb)$_2$	−	−	−	−64.1 ± 0.1	−
C−(O)$_3$(H)	−104.8 ± 0.7	−105.9	−2.48 ± 0.42	−104.7 ± 0.6	−112.1
C−(O)$_3$(C)	−97.7 ± 0.7	−103.3	−7.01 ± 0.50	−102.5 ± 0.7	−106.7
C−(O)$_3$(Cb)	−89.8	−	−13.1	−98.3	−
C−(O)$_4$	−149.0 ± 0.8	−153.6	−14.16 ± 0.42	−159.7 ± 0.6	−161.5
gauche correction (ether)	4.0 ± 0.5		0.0	4.0 ± 0.5	
C_{tert}−O−C_{quat}	10.0		0.0	10.0	
C_{tert}−O−C_{tert}	27.0		−4.0	22.0	
C(CH$_3$)$_3$−CH$_2$−C(CH$_3$)$_2$−	27.0			27.0	
1,1-dimethylcyclohexane	5.5		0.0	5.5	

[a] Values are from 96-Coh. [b] Values are from 80-Duc/Gru.

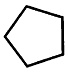
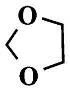
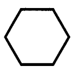
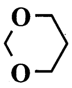
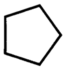
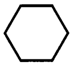
some additional terms should be necessary for calculations of the $\Delta_l^g H^\circ_m$ values of five- and six-membered cyclic acetals and ketals. However, a comparison of the experimental data on $\Delta_l^g H^\circ_m$ for alkyl-substituted 1,3-dioxolanes (**102**, **103**, **116**−**121**), measured in this work with those calculated using GAVs from Table 8 does not reveal any regularities; the differences span an interval of (1−15) kJ·mol^{-1}. Thus, hardly any additive scheme is able to

Table 9. Interpretation of Strain H_S (in kJ·mol^{-1}) in Cyclic Ketals

		$\Delta_f H^\circ_m$ (g)[a]	H_S[b]	Sum of strain corrections	Δ[c]
136		-166.1	109.2	115.9[d]	-6.7
139		-303.1	101.8	112.1[e]	-10.3
140		-401.2	24.6	29.7[f]	-5.1
143		-446.7	3.3	2.9[g]	0.4
146		-373.4	72.4	70.0[h]	2.4
149		-325.2	67.8	70.0[h]	-2.7
137		-90.9	168.0	21.7[i] + 115.9[d] = 137.6	30.4
141		-370.1	39.3	21.7[i] + 29.7[f] = 51.4	-12.1
144		-416.5	13.8	21.7[i] + 2.9[g] = 24.6	-10.8
147		-341.1	88.3	21.7[i] + 70.0[h] = 91.7	-3.4
138		-204.4	138.5	5.5[j] + 0.0[k] +115.9[d] = 121.4	17.1
142		-463.6	29.8	5.5[j] + 0.0[k] +29.7[f] = 35.2	-5.4
145		-502.0	12.3	5.5[j] + 0.0[k] +2.9[g] = 8.4	3.9
148		-431.8	81.6	5.5[j] + 0.0[k] + 70.0[h] = 75.5	6.1

[a] Data are from the Table 7. [b] Strain enthalpy calculated as $H_S = \Delta_f H^\circ_m$(g) (exp) $- \Sigma$ increments (Table 8). [c] Sum of the individual strain corrections; $\Delta = H_S - \Sigma$ strain corrections. [d] Ring strain correction for three-membered ring of 115.9 kJ·mol^{-1}. [e] Ring strain correction for four-membered ring of 112.1 kJ·mol^{-1}. [f] Ring strain correction for five-membered ring of 29.7 kJ·mol^{-1}. [g] Ring strain correction for six-membered ring of 2.9 kJ·mol^{-1}. [h] Ring strain correction for norbornane of 70.0 kJ·mol^{-1}. [i] Ring strain correction for 2,2-alkyl-substituted 1,3-dioxolane ring of 21.7 kJ·mol^{-1}. [j] Ring strain correction for 1,1-dimethyl-substituted six-membered ring of 5.5 kJ·mol^{-1}. [k] Ring strain correction for 2,2-alkyl-substituted 1,3-dioxane ring of 0.0 kJ·mol^{-1}.

Table 10. Calculation of the GAVs for Spiro-compounds (in kJ·mol^{-1})

					
 $\Delta_f H^\circ_m$ (g) *C*spiro[a]	Spiro[2,2]pentane 185.1±0.8 86-Ped/Nyl 268.7		Compound **139** -90.9 this work 109.6		Compound **140** -204.4 this work 74.6
 $\Delta_f H^\circ_m$ (g) *C*spiro[a]		Spiro[4,4]nonane -99.5±1.2 [b] this work 67.7	Compound **143** -370.1 this work -19.1	Spiro[4,5]decane -145.1±2.2 86-Ped/Nyl 43.0	Compound **144** -463.6 this work -34.1
 $\Delta_f H^\circ_m$ (g) *C*spiro[a]		Spiro[4,5]decane -145.1±2.2 86-Ped/Nyl 43.0	Compound **146** -416.5 this work -44.6	Spiro[5,5]undecane -188.3±3.1 86-Ped/Nyl 20.7	Compound **147** -502.0 this work -51.6
 $\Delta_f H^\circ_m$ (g) *C*spiro[a]			Compound **149** -341.1 this work 29.9		Compound **150** -431.8 this work 17.7

[a] Calculated as the difference $\Delta_f H^\circ_m$(g) (exp) − Σ increments (Table 8). [b] Value of $\Delta_f H^\circ_m$(l) = −(144.0 ± 1.0) kJ·mol^{-1} taken from 64-Koz/Mir. Value of $\Delta_l^g H^\circ_m$ = (44.52 ± 0.59) kJ·mol^{-1} was measured in this work (see Table 4).

predict $\Delta_l^g H^\circ_m$ of cyclic acetals and ketals accurately. Experimental measurements of $\Delta_l^g H^\circ_m$ must be available to convert the set of $\Delta_f H^\circ_m$(l) values of cyclic acetals and ketals measured by Pihlaja et al. to the gaseous state so that one can understand the interrelations of the structure and energetics of these species.

Strain in Cyclic and Spiro-Cyclic Ketals. Compounds **138**−**154** listed in Table 7 have an interesting structural peculiarity: the central C−(O)$_2$(C)$_2$ unit of these molecules is involved directly in the structure of the small ring. The geminal interaction of two alkoxy substituents attached to the same carbon atom is well-known as the stabilizing anomeric effect (98-Ver/Pen). This fact account for the relative abundance of one isomer over others in equilibrium mixtures in carbohydrate chemistry, for example. The strains (or ring-strain corrections) of the small (three-, four-, five-, and six-membered) hydrocarbon rings are well-established (96-Coh). In ketals **138**−**154**, one of the carbon atoms of the small ring is at the same time the geminal center connected to two alkoxy substituents. Does the anomeric effect in ketals impact the strain of the small ring? Experimental enthalpies of formation of compounds **138**−**154** elucidate this question. Let us consider ketals **138**, **141**, **142**, **145**, **148**, and **151**, in which two methoxy groups are bonded on cyclopropane, cyclobutane, cyclopentane, cyclohexane, and norbornane rings (see Table 9). The strains, H_S, of these compounds were calculated as the difference between the experimental $\Delta_f H^\circ_m$(g) values (see Table 7) and the sum of GAVs from Table 8. The strain of a molecule (cyclic ketal), H_S, is the energetic result of stabilizing and destabilizing interactions present in it. Hence, a comparison with the strain of the hydrocarbon ring reveals the effect of the alkoxy groups attached to the ring. Thus, according to Table 9, three-, four-, and five-membered rings (compounds **138**, **141**, and **142**) are stabilized by 6−10 kJ·mol^{-1} through the attachment of two alkoxy groups. Surprisingly, the cyclohexane and norbornane rings (compounds **145**, **148**, and **151** in Table 9) seem to be completely unaffected. Spiro-cyclic ketals (**139**, **143**, **146**, **149**, **140**, **144**, **147**, **150**) listed in Table 9 exhibit structures in which geminal oxygen atoms are involved in the spiro connection of two small rings. The strains H_S of these compounds were calculated in the same way as for cyclic ketals. As can be seen in Table 9, the magnitudes of H_S for spiro-ketals are very different. Only the spiro connection of the three-membered ring to the five- (**139**) or six-membered ring (**140**) indicates an appreciable destabilization effect. Other types of spiro connections provide rather stabilization of the structure through interactions of geminal oxygens. Taking into account the individual energetics of the spiro-ketals (see Table 10), the following special increments could be suggested for predictions of the enthalpies of formation of spiro-ketals Cspiro−(O)$_2$(C)$_2$, analogously to the increment Cspiro−(C)$_4$ for the spiro-hydrocarbons. Numbers of these increments for each spiro-compound are given in the Table 10.

Ortho Esters and Ortho Carbonates. A set of thermochemical results on ortho esters (**155**−**171**) and ortho carbonates (**172** and **173**) is listed in Table 7. According to Benson, the following increments are defined for the estimation of the thermochemical properties of these compounds: C−(O)$_3$(H), C−(O)$_3$(C), C−(O)$_3$(Cb), and C−(O)$_4$. We evaluate these GAVs (see Table 8) using only the experimental data on straight-chained species. We include in the correlation a set of 6 experimental data (**155**, **156**, **161**, **162**, **172**, **173**) for $\Delta_f H^\circ_m$(l), $\Delta_f H^\circ_m$(g), and $\Delta_l^g H^\circ_m$. The average standard deviation for the compounds considered was at the level of 1.0 kJ·mol^{-1} for enthalpies of formation and 0.6 kJ·mol^{-1} for enthalpies of vaporization.

Ortho esters (**159**, **165**−**168**, **171**) pose an interesting structural peculiarity: the central C atom, connected to three oxygens, is involved directly in the structure of the bicyclic ring [a hydrocarbon analogue is bicyclo[2,2,2]-octane, which has a ring strain of 46.4 kJ·mol^{-1} calculated from its $\Delta_f H^\circ_m$(g) = −99.04 ± 0.96 kJ·mol^{-1} from Pedley et al. (86-Ped/Nay)]. It is obviously from differences between experimental $\Delta_f H^\circ_m$(g) values and the sums of the GAVs (Table 8) that these bicyclic ortho esters are also significantly strained (about 30 kJ·mol^{-1}), but their strains are reduced in comparison with that of bicyclo[2,2,2]octane because of the stabilizing effect of the geminal unit containing three oxygen atoms.

A comparison of the group increments obtained in this work (Table 8) with those reported previously (96-Coh) shows that they are in most cases significantly (3−10 kJ·mol^{-1}) different because of the broader experimental database used in the evaluation of the GAVs.

4. Conclusion

The group-additivity method serves as a valuable tool for many scientists and engineers whose work involves the thermodynamic characterization of elementary and overall reaction processes. Improved group-additivity parameters and correction terms were systematically revised and evaluated in this work using an updated database. The derived values can be applied to the prediction of the thermochemical properties of a broad range the organic compounds containing the OR functional group.

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Literature Cited

02-Ver/Kra Verevkin S.P, Krasnykh, E.; Vasiltsova, T.; Heintz, A. Determination of vaporization enthalpies of the branched ethers from transpiration and correlation gas-chromatography methods. *J. Chem. Thermodyn.* 2002, manuscript submitted.

02-Kra/Vas Krasnykh, E.; Vasiltsova, T.; Verevkin, S. P.; Heintz, A. Vapor Pressures and Enthalpies of Vaporization of Benzyl Halides and Benzyl Ethers. *J. Chem. Eng. Data* **2002**, in press.

02-Ver/Hei Verevkin, S. P.; Heintz, A. Chemical equilibria study in the reacting system of the (1-alkoxyethyl)benzene synthesis from iso-alkanols and styrene. *J. Chem. Soc., Perkin Trans. 2* **2002**, 728−733.

01-Ver/Hei Verevkin, S. P.; Heintz, A. Chemical equilibria study in the reacting system of the alkyl cumyl ether synthesis from *n*-alkanols and α-methylstyrene. *J. Chem. Eng. Data* **2001**, *46*, 41−46.

01-Ver/Hei Verevkin, S. P.; Heintz, A. Chemical equilibria study in the reacting system of the (1-alkoxyethyl)benzene synthesis from alkanols and styrene. *J. Chem. Eng. Data* **2001**, *46*, 984−990.

01-Alb/Hah Albert, M.; Hahnenstein, I.; Hasse, H.; Maurer, G. Vapor−Liquid and Liquid−Liquid Equilibria in Binary and Ternary Mixtures of Water, Methanol, and Methylal. *J. Chem. Eng. Data* **2001**, *46*, 897−903.

01-Uus/Pok Uusi-Kyyny, P.; Pokki, J.-P.; Aittamaa, J.; Liukkonen, S. Vapo− Liquid Equilibrium for the Binary Systems of 2-Methyl-2-propanol + 2,4,4-Trimethyl-1-pentene at 333 K and 348 K and 2-Butanol + 2,4,4-Trimethyl-1-pentene at 360 K. *J. Chem. Eng. Data* **2001**, *46*, 1244−1248.

00-Ver Verevkin, S. P. Measurement and Prediction of Monocarboxylic Acids Thermochemical Properties. *J. Chem. Eng. Data* **2000**, *45*, 946−952.

00-Chu Churkina, A. Ph.D. Thesis, Samara State Technical University, Samara, Russia, 2000.

00-Pal/Sza Palczewska-Tuliska, M.; Szafraski, A. M. Selected Physicochemical Properties of Dibutoxymethane. *J. Chem. Eng. Data* **2000**, *45*, 988−990.

99-Rar/Hor Rarey, J.; Horstmann, S.; Gmehling, J. Vapor−Liquid Equilibria and Vapor Pressure Data for the Systems Ethyl *tert*-Butyl Ether + Ethanol and Ethyl *tert*-Butyl Ether + Water. *J. Chem. Eng. Data* **1999**, *44*, 532−538.

99-Hei/Fis Heine, A.; Fischer, K.; Gmehling, J. Various Thermodynamic Properties for Binary Systems with Tertiary Ethers. *J. Chem. Eng. Data* **1999**, *44*, 373−378.

98-Ver Verevkin, S. P. Thermochemistry of Alcohols: Experimental Standard Molar Enthalpies of Formation and Strain of Some Alkyl and Phenyl Congested Alcohols. *Struct. Chem.* **1998**, *9*, 375−382.

98-Ver/Pen Verevkin, S.P.; Peng, W.-H.; Beckhaus, H.-D.; Rüchardt, C. Does the Anomeric Effect in Ketals Depend on the Hybridization of the Central Carbon Atom? *Eur. J. Org. Chem.* **1998**, *2323*, 3−2332.

97-Ver/Mor Verevkin, S. P.; Morgenthaler, J.; Rüchardt, C. Thermochemistry of imines. Experimental standard molar enthalpies of formation. *J. Chem. Thermodyn.* **1997**, *29*, 1175−83.

97-Ver Verevkin, S. P. Thermochemistry of amines. Experimental standard enthalpies of formation of some aliphatic and aromatic amines. *J. Chem. Thermodyn.* **1997**, *29*, 891−899.

97-Sol/Per Sola, L.; Pericas, M. A.; Cunill, F.; Izquierdo, J. F. A comparative thermodynamic and kinetic study of the reaction between olefins and light alcohols leading to branced ethers. Reaction calorimetry study of the formation of *tert*-amyl methyl ether (TAME) and *tert*-butyl isopropyl ether (IPTBE). *Ind. Eng. Chem. Res.* **1997**, *36*, 2012−2018.

97-Sch/Ver Schaffer, F.; Verevkin, S. P.; Rieger, H.-J.; Beckhaus, H.-D.; Rüchardt, C. Geminal Substituent Effects. 15. Enthalpies of Formation of a Series of Fluorinated Hydrocarbons and Strain-Free Group Increments to Assess Polar and Anomeric Stabilization and Strain. *Liebigs Ann.* **1997**, *1*, 1333−1344.

97-Gom/Cun Gomez, C.; Cunill, F.; Iborra, M.; Izuierdo, J. F.; Tejero, J. Experimental study of of the simultaneous synthesis of methyl *tert*-butyl ether and ethyl *tert*-butyl ether in liquid phase. *Ind. Eng. Chem. Res.* **1997**, *36*, 4756−4762.

97-Cal/Tej Calderon, A.; Tejero, J.; Izuierdo, J. F.; Iborra, M.; Cunill, F. Equilibrium Constants for the Liquid-Phase Synthesis of Isopropyl *tert*-Butyl Ether from 2-Propanol and Isobutene. *Ind. Eng. Chem. Res.* **1997**, *36*, 896−902.

96-Coh Cohen, N. Revised Group Additivity Values for Enthalpies of Formation (at 298 K) of Carbon−Hydrogen and Carbon−Hydrogen−Oxygen Compounds. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1411−1481.

96-Ste/Chi Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Smith, N. K. Thermodynamic properties and ideal-gas enthalpies of formation for butyl vinyl ether, 1,2-dimethoxyethane, methyl glycolate, bicyclo[2.2.1]hept-2-ene, 5-vinylbicyclo[2.2.1]hept-2-ene, *trans*-azobenzene, butyl acrylate, di-*tert*-butyl ether, and hexane-1,6-diol. *J. Chem. Eng. Data* **1996**, *41*, 1285−1302.

96-Ver/Bec Verevkin, S. P.; Beckhaus, H.-D.; Belen'kaja, R.S; Rakus, K.; Rüchardt, C. Geminal Substituent Effects. 9. Enthalpies of Formation and Strain-Free Increments of Branched Esters and Ethers. *Thermochim. Acta* **1996**, *279*, 47−64.

95-Nol/Ver Nölke, M.; Verevkin, S. P.; Beckhaus, H. D.; Rüchardt, C.Substituent Effects on the Strength of C−C Bonds. 16. Thermal Stability and Enthalpies of Formation of *β*-di-Carbonyl Compounds. Stabilization of α,α-Diketoalkyl Radikals. *Liebigs Ann.* **1995**, 41−51.

95-Sha/Roz Sharonov, K. G.; Rozhnov, A. M.; Korol'kov, A. V.; Karaseva, S. Y. Enthalpies of formation of 2-methyl-2-ethoxypropane and 2-ethyl-2-ethoxypropane from equilibrium measurements. *J. Chem. Thermodyn.* **1995**, *27*, 751−753.

95-Ver/Dog Verevkin, S. P.; Dogan, B.; Hädrich, J.; Beckhaus, H.-D.; Rüchardt, C. Geminal Substituent Effects. VIII. Enthalpies of Formation of Acetals. *J. Pract. Chem.* **1995**, *337*, 93−98.

95-Kit/Dat Kitchaiya, P.; Datta, R. Ethers from Ethanol. 2. Reaction equilibria of simultaneous *tert*-amyl ethyl ether synthesis and isoamylene isomerization. *Ind. Eng. Chem. Res.* **1995**, *34*, 1092−1101.

95-Sol/Per Sola, L.; Pericas, M. A.; Cunill, F.; Tejero, J. Thermodynamic and kinetic studies of the liquid-phase synthesis of *tert*-butyl ethyl ether using a reaction calorimeter. *Ind. Eng. Chem. Res.* **1995**, *34*, 3718−3725.

95-Rak/Ver Rakus, K.; Verevkin, S. P.; Peng, W.-H.; Beckhaus, H. D.; Rüchardt, C. Geminal Substituent Effects. 11. The Anomeric Effect in Ortho Esters. The Concept of Geminal Pairwise Interactions for the Interpretation of Enthalpies of Formation. *Liebigs Ann.* **1995**, *1*, 2059−2067.

94-Rak/Ver Rakus, K.; Verevkin, S. P.; Beckhaus, H.-D.; Rüchardt, C. Substituent Effects on the Strength of C−C Bonds. 15. Geminal Substituent Effects. VII. Thermochemistry and Thermal Decomposition of Alkyl-Substituted Tricyanomethyl Compounds. *Chem. Ber.* **1994**, *127*, 2225−2234.

94-Izq/Cun Izquierdo, J. F.; Cunill, F.; Vila, M.; Iborra, M.; Tejero, J. Equilibrium constants for methyl *tert*-butyl ether and ethyl *tert*-butyl ether synthesis using C_4 olefinic cut. *Ind. Eng. Chem. Res.* **1994**, *33*, 2830−2835.

94-Wib/Mor Wiberg, K. B.; Morgan, K. M.; Maltz, H. Thermochemistry of carbonyl reactions. 6. A study of hydration equilibria. *J. Am. Chem. Soc.* **1994**, *116*, 11067−11077.

94-Kra/Gme Krähenbühl, M. A.; Gmehling, J. Vapor pressures of methyl *tert*-butyl ether, ethyl *tert*-butyl ether, isopropyl *tert*-butyl ether, *tert*-amyl methyl ether, and *tert*-amyl ethyl ether. *J. Chem. Eng. Data* **1994**, *39*, 29−32.

93-Dom/Hea Domalski, E. S.; Hearing, E. D. Estimation of Thermodynamic Properties of C−H−N−O−Halogen Compounds at 298.15 K. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805−1159.

91-Wib/Hao Wiberg, K. B.; Hao, S. Enthalpies of hydration of alkenes. 4. Formation of acyclic *tert*-alcohols. *J. Org. Chem.* **1991**, *56*, 5108−5110.

91-Roz/Saf Rozhnov, A. M.; Safronov, V. V.; Verevkin, S. P.; Sharonov, K. G.; Alenin, V. I. Enthalpy of combustion and enthalpy of vaporization of 2-ethyl-2-methoxypropane and thermodynamics of its gas-phase synthesis from (methanol + α-2-methylbutene). *J. Chem. Thermodyn.* **1991**, *23*, 629−635.

91-Sha/Mis Sharonov, K. G.; Mishentseva, Y. B.; Rozhnov, A. M.; Miroshnichenko, E. A.; Korchatova, L. I. Molar enthalpies of formation and vaporization of *tert*-butoxybutanes and thermodynamics of their synthesis from butanol and 2-methylpropene. 2. Enthalpies of combustion and vaporization of *tert*-butoxybutanes. *J. Chem. Thermodyn.* **1991**, *23*, 637−642.

90-Roz/Bar Rozhnov, A. M.; Barkov, V. I.; Sharonov, K. G.; Tsvetkov, V. S. Investigation of the equilibria of the reaction: $CH_3(CH_2)_4OH + (CH_3)_2C{:}CH_2 = CH_3(CH_2)_4OC(CH_3)_3$. *J. Chem. Thermodyn.* **1990**, *22*, 327−333.

90-Wib/Cun Wiberg, K. B.; Cunningham, W. C., Jr. Thermochemical studies of carbonyl reactions. 4. Enthalpies of hydrolysis of norbornyl ketals. *J. Org. Chem.* **1990**, *55*, 679−684.

90-Bec/Dog Beckhaus, H.-D.; Dogan, B.; Verevkin, S. P.; Hädrich, J.; Rüchardt, C. Dependence of anomeric stabilization on structure in acetales. *Angew. Chem.* **1990**, *102*, 313−314; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 320.

89-Ibo/Izq Iborra, M.; Izquierdo, J. F.; Tejero, J.; Cunill, F. Equilibrium constant for ethyl *tert*-butyl ether vapor-phase synthesis. *J. Chem. Eng. Data* **1989**, *34*, 1−5.

87-Pih Pihlaja, K. iN *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers, Inc.: New York, 1987; Vol. 2, p 173.

86-Ped/Nay Pedley, J. P.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

85-Maj/Svo Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation*; Blackwell Scientific Publications: Oxford, 1985; p 300.

85-Arn/Got Arntz, H.; Gottlieb, K. High-pressure heat-flow calorimeter determination of the enthalpy of reaction for the synthesis of methyl *tert*-butyl ether from methanol and 2-methylpropene. *J. Chem. Thermodyn.* **1985**, *17*, 967−972.

85-Mar/Man Marsh, K. N.; Mansson, M. Standard molar enthalpies of formation of triethoxymethane and tetraethoxymethane by rotating bomb calorimetry. *J. Chem. Thermodyn.* **1985**, *17*, 995−1002.

82-Bys/Man Byström, K.; Mansson, M. Enthalpies of formation of some cyclic 1,3- and 1,4-di- and poly-ethers: Thermochemical strain in the −O−C−O and −O−C−C−O− groups. *J. Chem. Soc., Perkin Trans. 2* **1982**, 565.

80-Duc/Gru Ducros, M.; Gruson, J. F.; Sannier, H. Estimation des enthalpies de vaporisation des composes organiques liquides. Partie 1. Applications aux alcanes, cycloalcanes, alcenes, hydrocarbures benzeniques, alcools, alcanes thiols, chloro et bromoalcanes, nitriles, esters, acides et aldehydes, *Thermochim. Acta* **1980**, *36*, 39−65.

80-Wib Wiberg, K. B. *Energies of Organic Compounds*; Report DOE-E(11-1)4060; Prepared for U.S. Department of Energy by Yale University, New Haven, CT, 1980; pp 1−24. Avail. NTIS.

80-Gut/Leb Gutner, N. M.; Lebedeva, N. D.; Dobychin, S. L.; Kiseleva, N. N. Thermochemical study of aliphatic ethers. *J. Appl. Chem. USSR* **1980**, *53*, 1523−1525.

80-Gut/Cul Guthrie, J. P.; Cullimore, P. A. Effect of the acyl substituent on the equilibrium constant for hydration of esters. *Can. J. Chem.* **1980**, *58*, 1281−1294.

80-Fuc/Pea Fuchs, R.; Peacock, L. A. Heats of vaporization of esters by the gas chromatography−calorimetry method. *Can. J. Chem.* **1980**, *58*, 2796.

79-Wib/Squ Wiberg, K. B.; Squires, R. R. A microprocessor-controlled system for precise measurement of temperature changes. Determination of the enthalpies of hydrolysis of some polyoxygenated hydrocarbons. *J. Chem. Thermodyn.* **1979**, *11*, 773−786.

79-Wib/Squ Wiberg, K. B.; Squires, R. R. Thermodynamics of hydrolysis aliphatic ketals. An entropy component of steric effects. *J. Am. Chem. Soc.* **1979**, *101*, 5512−5515.

77-Gut Guthrie, J. P. Cyclization of glycol monoesters to give hemiortho esters: A test of the thermochemical method for determining free energies of tetrahedral intermediates. *Can. J. Chem.* **1977**, *55*, 3562−3574.

77-Leb/Rya Lebedeva, N. D.; Ryadnenko, V. L.; Gutner, N. M.; Nazarova, L. F.; Kiseleva, N. N.; Aizenshtadt, I. N.; Kirilenko, I. V. Possibility of using additive schemes for estimation of the enthalpies of formation of polyfunctional compounds. *J. Anal. Chem. USSR (Engl. Transl.)* **1977**, *50*, 726−729.

76-Ben Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

76-Amb/Ell Ambrose, D.; Ellender, J. H.; Sparke, C. H. S.; Townsend, R. Thermodynamic properties of organic ozygen compounds. XLIII. Vapor pressures of some ethers. *J. Chem. Thermodyn.* **1976**, *8*, 165−178.

75-Fen/Har Fenwick, J. O.; Harrop, D.; Head, A. J. Thermodynamic properties of organic oxygen

	compounds. 41. Enthalpies of formation of eight ethers. *J. Chem. Thermodyn.* **1975**, *7*, 943−954.
74-Hin/Klu	Hine, J.; Klueppet, A. W. Structural effects on rates and equilibria. XVIII. Thermodynamic stability of ortho esters. *J. Am. Chem. Soc.* **1974**, *96*, 2924−2929.
74-Man	Mansson, M. Nonbonded oxygen−oxygen interactions in 2,4,10-trioxa-adamantane and 1,3,5,7,9-pentoxecane. *Acta Chem. Scand., Ser. B* **1974**, *28*, 895−899.
72-Pih/Hei	Pihlaja, K.; Heikkila, J. Heats of formation of cyclic vinyl ethers. A correction. *Suom. Kemistil.* **1972**, *45*, 148.
71-Pih/Tuo	Pihlaja, K.; Tuomi, M. Bond−bond interactions in organic oxygen compounds. Part V. Enthalpies of formation of methyl and ethyl orthoformates and the contributory group increments. The magnitude of the so-called rabbit-ear effect in acyclic oxygen compounds. *Acta Chem. Scand.* **1971**, *25*, 465−469.
71-Cou/Lee	Counsell, J. F.; Lee, D. A.; Martin, J. F. Thermodynamic properties of organic oxygen compounds. Part XXVI. Diethyl ether. *J. Chem. Soc. A* **1971**, 313.
71-Cab/Con	Cabani, S.; Conti, G.; Lepori, L. Thermodynamic study on aqueous dilute solutions of organic compounds. Part 2. Cyclic ethers. *Trans. Faraday Soc.* **1971**, *67*, 1943−1950.
70-Bir/Ski	Birley, G. I.; Skinner, H. A. Enthalpies of hydrolysis of dimethoxymethane and 1,1-dimethoxyethane. *Trans. Faraday Soc.* **1970**, *66*, 791−793.
70-Pih/Tuo	Pihlaja, K.; Tuomi, M. Bond−Bond interactions in organic oxygen compounds. Part II. Anomalous stablization in *cis*-2,4,6-trimethyl-1,3,5-trioxane. *Suom. Kemistil.* **1970**, *43*, 224−226.
69-Pih/Hei	Pihlaja, K.; Heikklia, J. Enthalpies of formation of cyclic acetals. 1,3-Dioxolane, 2-methyl-1,3-dioxolane, and 2,4-dimethyl-1,3-dioxolanes. *Acta Chem. Scand.* **1969**, *23*, 1053−1055.
69-Pil	Pilcher, G.; Fletcher, R. A. Measurements of heats of combustion by flame calorimetry. Part 5. Dimethoxymethane, 1,1-Dimethoxyethane. *Trans. Faraday Soc.* **1969**, *65*, 2326−2330.
69-Man	Mansson, M. Non-bonded oxygen−oxygen interactions in straight-chain compounds. *J. Chem. Thermodyn.* **1969**, *1*, 141−151.
69-Pih/Lau	Pihlaja, K.; Launosalo, T. Heats of combustion of 2,4,6-trimethyl-3,5-dioxaheptane and 6-ethyl-5,7-dioxaundecane. *Acta Chem. Scand.* **1969**, *23*, 3264−3265.
68-Pih/Hei	Pihlaja, K.; Heikkil, J. Heats of combustion. Diethyl ether and 1,1-diethoxyethane. *Acta Chem. Scand.* **1968**, *22*, 2731−2732.
68-Pih/Luo	Pihlaja, K.; Luoma, S. Heats of formation and conformational energies of 1,3-dioxane and its methyl homologues. *Acta Chem. Scand.* **1968**, *22*, 2401−2414.
68-Che/Pet	Cherkaskaya, E. L.; Petrenkova, Z. E.; Tur, A. M.; Lubinova, V. I. Phase Equilibrium of Liquid−Steam in System of Dioxolane−Water. *Zh. Prikl. Khim. (Leningrad)* **1968**, *41*, 2553−2554.
67-Pih/Hei	Pihlaja, K.; Heikkila, J. The configurations of isomeric 2,2,4,6-tetramethyl-1,3-dioxanes. *Acta Chem. Scand.* **1967**, *21*, 2430−2434.
66-Wad	Wadso, I. A heat of vaporization calorimeter for work at 25 °C and for small amounts of substances. *Acta Chem. Scand.* **1966**, *20*, 544−550.
65-Cha/Ros	Chao, J.; Rossini, F. D. Heats of combustion, formation, and isomerization of nineteen alkanols. *J. Chem. Eng. Data* **1965**, *10*, 374−379.
65-Col/Pel	Colomina, M.; Pell, A. S.; Skinner, H. A.; Coleman, D. J. Heats of combustion of four dialkyl ethers. *Trans. Faraday Soc.* **1965**, *61*, 2641.
64-Koz/Mir	Kozina, M. P.; Mirzaeva, A. K.; Sosina, I. E.; Elagina, N. V.; Skuratov, S. M. The heats of formation of spiro hydrocarbons. *Dokl. Phys. Chem. (Engl. Transl.)* **1964**, *155*, 375−377.
64-Pil	Pilcher, G.; Pell, A. S.; Coleman, D. J. Measurements of heats of combustion by flame calorimetry. Part 2. Dimethyl ether, methyl ethyl ether, methyl *n*-propyl ether, methyl isopropyl ether. *Trans. Faraday Soc.* **1964**, *60*, 499−505.
64-McE/Kil	McEachern, D. M., Jr.; Kilpatrick, J. E. Entropy and related thermodynamic properties of dimethoxymethane. *J. Chem. Phys.* **1964**, *41*, 3127−3131.
63-Pil	Pilcher, G.; Skinner, H. A.; Pell, A. S.; Pope, A. E. Measurements of heats of combustion by flame calorimetry. Part 1. Diethyl ether, ethyl vinyl ether and divinyl ether. *Trans. Faraday Soc.* **1963**, *59*, 316−330.
62-Ste/Dor	Stern, J. H.; Dorer, F. H. Standard heats of formation of 2,2-Dimethoxypropane (1) and 2,2 -Diethoxypropane (1). Group additivity theory and calculated heats of formation and five ketals. *J. Phys. Chem.* **1962**, *66*, 97−99.
61-Smu/Bon	Smutny, E. J.; Bondi, A. Di-*tert*-butyl ether: Strain energy and physical properties. *J. Phys. Chem.* **1961**, *65*, 546−550.
61-Sne/Ski	Snelson, A.; Skinner, H. A. Heats of combustion: *sec*-propanol, 1,4-dioxan, 1,3-dioxan and tetrahydropyran. *Trans. Faraday Soc.* **1961**, *57*, 2125−2131.
59-Fle/Mor	Fletcher, S. E.; Mortimer, C. T.; Springall, H. D. Heats of combustion and molecular structure. Part VII. 1,3-dioxa- and 1,3,5-trioxa-cycloalkanes. *J. Chem. Soc.* **1959**, 580−584.
57-Mur	Murrin, J. W.; Goldhagen, S. *Determination of the C−O Bond Energy from the Heats of Combustion of Four Aliphatic Ethers*; NAVORD Report No. 5491; U.S. Naval Powder Factory Research and Development Department: Washington, DC, 1957; pp 1−14.
57-Sku/Str	Skuratov, S. M.; Strepikheev, A. A.; Shtekhter, S. M.; Volokhina, A. V. About the enthalpies of polymerization of cyclic formales. *Dokl. Akad. Nauk SSSR* **1957**, *117*, 263−265.
57-Sku/Str	Skuratov, S. M.; Strepikheev, A. A.; Kozina, M. P. About the reaction activity of five and six-membered heterocyclic compounds. *Dokl. Akad. Nauk SSSR* **1957**, *117*, 452−454.
57-Sku/Koz	Skuratov, S. M.; Kozina, M. P.; Shteher, S. M.; Varushyenko, R. M. The heats of combustion of several purified compounds. *Thermochem. Bull. (Moscow State Univ.)* **1957**, 36−37.
51-Pro/Mar	Prosen, E. J.; Maron, F. W.; Rossini, F. D. Heats of combustion, formation, and isomerization of ten C4 hydrocarbons. *J. Res. NBS* **1951**, *46*, 106−112.
49-Dre/Shr	Dreisbach, R. R.; Shrader, S. A. Vapor Pressure−Temperature Data on Some Organic Compounds. *Ind. Eng. Chem.* **1949**, *41*, 2879−2880.
49-Nic/Laf	Nicolini, E.; Laffitte, P. Tensions de Vapeur de Quelques Liquides Organiques Purs. *Compt. Rend.* **1949**, *229*, 757−759.
47-Stu	Stull, D. R. Vapor Pressure of Pure Substances Organic Compounds. *Ind. Eng. Chem.* **1947**, *39*, 517−540.
42-Jun/Dah	Jung, G.; Dahmlos, J. Thermochemische Untersuchungen zur Frage der Drehbarkeit um C−C-Bindunge. *Z. Phys. Chem.* **1942**, *190*, 230−240.

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