

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 $\Delta_f^g H_m^\circ$ 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, 298.15 K) of alkyl ethers, acetals, ketals, and ortho esters were derived using the data for the $\Delta_f H_m^\circ$ (l or cr, 298.15 K) 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 interrelationships 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 to 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 ($\geq 99.9\%$).

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

$$p = mRT_a/V(N_2)M \quad (1)$$

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 $\pm 0.001\ dm^3$.

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

$$\frac{dp}{dT} = \frac{\Delta_l^g H_m}{T\Delta_l^g V_m} \quad (2)$$

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 in the 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

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

Under the assumption that

$$\begin{cases} \Delta_l^g H_m \approx \Delta_l^g H_m^0 + \Delta_l^g C_{p,m}^0 (T - T_0) \\ \Delta_l^g V_m \approx \frac{RT}{p} \end{cases} \quad (4)$$

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

$$R \ln p = a + \frac{b}{T} + \Delta_l^g C_{p,m}^0 \ln\left(\frac{T}{T_0}\right) \quad (5)$$

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

$$\Delta_l^g H_m(T) = -b + T\Delta_l^g C_{p,m}^0 \quad (6)$$

where $\Delta_l^g C_{p,m}^0 = \Delta_l C_{p,m}^0 - \Delta_g C_{p,m}^0$ is the difference between the molar heat capacities of the liquid and the gaseous phase. Values of $\Delta_l^g C_{p,m}^0$ based on the molar heat capacities $\Delta_l C_{p,m}^0$ and $\Delta_g C_{p,m}^0$ calculated according to 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 $\Delta_l^g H_m^0$ have been calculated as a function of temperature using eq 6 and are listed in Tables 1–4. To assess the uncertainty of the $\Delta_l^g H_m^0(298.15\ K)$ 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 $\Delta_l^g H_m^0$ at 298.15 K derived in this manner were used to calculate the gaseous enthalpies of formation $\Delta_f H_m^0(g)$, as well as to evaluate the group-additivity contributions for predicting $\Delta_l^g H_m^0$.

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 $\Delta_1^g H_m^\circ$ Measured for Acetals and Ketals by the Transpiration Method

| T^a K | m^b mg | $V(N_2)^c$ dm ³ | p^d Pa | $p_{\text{exp}} - p_{\text{calc}}$ Pa | $\Delta_1^g H_m^\circ$ kJ·mol ⁻¹ |
|--|-------------|-------------------------------|-------------|--|--|
| 4-methyl-1,3-dioxane (1120-97-4), 86 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (43.46 \pm 0.30) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 266.415/R - 60\,360.47/[R(T/\text{K})] - 56.7/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (39.12 \pm 0.33) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 270.097/R - 59\,901.257/[R(T/\text{K})] - 69.7/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (42.78 \pm 0.61) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 260.616/R - 55\,031.034/[R(T/\text{K})] - 41.1/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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- <i>n</i> -propyl-1,3-dioxolane (3390-13-4), 103 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (45.21 \pm 0.34) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 266.754/R - 61\,938/[R(T/\text{K})] - 56.10/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (44.86 \pm 0.60) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 258.923/R - 58\,278.857/[R(T/\text{K})] - 45.00/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (37.63 \pm 0.42) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 262.556/R - 55\,066.835/[R(T/\text{K})] - 58.50/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (43.17 \pm 0.39) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 295.905/R - 68\,544.434/[R(T/\text{K})] - 85.10/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 | $p_{\text{exp}} - p_{\text{calc}}$ | $\Delta_f^g H_m^\circ$ |
|---|-------|-----------------|--------|------------------------------------|------------------------|
| K | mg | dm ³ | Pa | Pa | kJ·mol ⁻¹ |
| 2,2-dimethyl-1,3-dioxolane (2916-31-6), 116 ; $\Delta_f^g H_m^\circ(298.15 \text{ K}) = (41.08 \pm 0.16) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 267.854/R - 57\,925.274/[R(T/\text{K})] - 56.50/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_f^g H_m^\circ(298.15 \text{ K}) = (42.82 \pm 0.29) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 271.808/R - 61\,905.414/[R(T/\text{K})] - 64.00/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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- <i>n</i> -propyl-1,3-dioxolane (4352-98-1), 118 ; $\Delta_f^g H_m^\circ(298.15 \text{ K}) = (46.16 \pm 0.34) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 282.336/R - 67\,480.549/[R(T/\text{K})] - 71.50/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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- <i>n</i> -pentyl-1,3-dioxolane (4352-95-8), 119 ; $\Delta_f^g H_m^\circ(298.15 \text{ K}) = (53.99 \pm 0.28) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 305.337/R - 79\,809.604/[R(T/\text{K})] - 86.60/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_f^g H_m^\circ(298.15 \text{ K}) = (43.90 \pm 0.24) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 268.180/R - 64\,327.624/[R(T/\text{K})] - 68.50/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_f^g H_m^\circ(298.15 \text{ K}) = (49.93 \pm 0.30) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 292.479/R - 73\,934.389/[R(T/\text{K})] - 80.50/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 cm³ s⁻¹. ^b Mass of transferred sample condensed at $T = 243 \text{ K}$. ^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 $T = 243 \text{ K}$.

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 $\Delta_1^g H_m^\circ$ Measured for Phenyl-Substituted Acetals and Ketals by the Transpiration Method

| T^a | m^b | $V(N_2)^c$ | p^d | $p_{\text{exp}} - p_{\text{calc}}$ | $\Delta_1^g H_m^\circ$ |
|---|-------|-----------------|--------|------------------------------------|------------------------|
| K | mg | dm ³ | Pa | Pa | kJ·mol ⁻¹ |
| phenyldimethoxymethane (1125-88-8), 127 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (60.91 \pm 0.49) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 314.565/R - 84\,163.453/[R(T/\text{K})] - 78.00/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (62.76 \pm 0.59) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 337.746/R - 93\,980.475/[R(T/\text{K})] - 104.7/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (62.64 \pm 0.68) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 298.913/R - 85\,300.69/[R(T/\text{K})] - 76.00/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (69.18 \pm 0.82) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 321.786/R - 94\,580.961/[R(T/\text{K})] - 85.20/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (54.01 \pm 0.82) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 305.821/R - 81\,852.912/[R(T/\text{K})] - 93.40/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 | $p_{\text{exp}} - p_{\text{calc}}$ | $\Delta_1^g H_m^\circ$ |
|--|-------|-----------------|----------|------------------------------------|------------------------|
| K | mg | dm ³ | Pa | Pa | kJ·mol ⁻¹ |
| 1-phenyl-1,1-dimethoxypropane (25310-92-3), 132 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (58.92 \pm 0.28) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 325.455/R - 89\,006.156/[R(T/\text{K})] - 100.90/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (82.89 \pm 0.89) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 386.407/R - 110\,142.041/[R(T/\text{K})] - 91.40/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (66.39 \pm 0.80) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 341.610/R - 96\,385.581/[R(T/\text{K})] - 100.60/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (106.7 \pm 1.2) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 410.202/R - 131\,790.187/[R(T/\text{K})] - 84.30/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (97.2 \pm 1.1) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 424.619/R - 137\,029.997/[R(T/\text{K})] - 133.70/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (99.7 \pm 1.1) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 325.250/R - 109\,110.521/[R(T/\text{K})] - 31.60/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 | m^b | $V(N_2)^c$ | p^d | $p_{\text{exp}} - p_{\text{calc}}$ | $\Delta_f^g H_m^\circ$ |
|--|-------|-----------------|-------|------------------------------------|------------------------|
| K | mg | dm ³ | Pa | Pa | kJ·mol ⁻¹ |
| 2,2-diphenyl-1,3-dioxolane (4359-34-6), 137 ; $\Delta_f^g H_m^\circ(298.15 \text{ K}) = (84.44 \pm 0.64) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 314.038/R - 102\,387.753/[R(T/\text{K})] - 60.20/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 cm³ s⁻¹. ^b Mass of transferred sample condensed at $T = 243 \text{ K}$. ^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 $T = 243 \text{ K}$.

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, $\Delta_c H_m^\circ = -(4025.1 \pm 0.7) \text{ kJ·mol}^{-1}$ instead of $-(4020.1 \pm 0.7) \text{ kJ·mol}^{-1}$ (91-Roz/Saf) measured with 0.082 mass % of water. For *tert*-amyl butyl ether, $\Delta_c H_m^\circ = -(5975.9 \pm 2.1) \text{ kJ·mol}^{-1}$ instead of $-(5971.51 \pm 2.1) \text{ kJ·mol}^{-1}$ (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



T range = 298–383 K

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

calorimetrically at 298 K

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



T range = 314–353 K

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

T range = 313–353 K

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

calorimetrically at 298 K

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



calorimetrically at 298 K

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

The following reactions have been investigated (00-Chu)

Table 3. Results for the Vapor Pressure p and Enthalpy of Vaporization $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}$ Measured for Ketals Attached to the Small Rings by the Transpiration Method

| T^a | m^b | $V(\text{N}_2)^c$ | p^d | $p_{\text{exp}} - p_{\text{calc}}$ | $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}$ |
|--|-------|-------------------|--------|------------------------------------|--|
| K | mg | dm ³ | Pa | Pa | kJ·mol ⁻¹ |
| 1,1-dimethoxy-2-phenylcyclopropane (18523-34-7), 138 ; $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (63.65 \pm 0.60) \text{ kJ}\cdot\text{mol}^{-1}$ $\ln(p/\text{Pa}) = 306.372/R - 86\,222.319/[R(T/\text{K})] - 75.70/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (91.70 \pm 0.81) \text{ kJ}\cdot\text{mol}^{-1}$ $\ln(p/\text{Pa}) = 314.322/R - 93\,278.636/[R(T/\text{K})] - 73.70/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (71.30 \pm 0.71) \text{ kJ}\cdot\text{mol}^{-1}$ $\ln(p/\text{Pa}) = 314.322/R - 93\,278.636/[R(T/\text{K})] - 73.70/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (98.04 \pm 0.34) \text{ kJ}\cdot\text{mol}^{-1}$ $\ln(p/\text{Pa}) = 333.845/R - 104\,898.303/[R(T/\text{K})] - 23.00/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (41.97 \pm 0.29) \text{ kJ}\cdot\text{mol}^{-1}$ $\ln(p/\text{Pa}) = 270.965/R - 61\,113.565/[R(T/\text{K})] - 64.20/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 |
| cyclopentanone dimethylacetal (53355-43-4), 142 ; $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (44.52 \pm 0.35) \text{ kJ}\cdot\text{mol}^{-1}$ $\ln(p/\text{Pa}) = 277.130/R - 65\,866.985/[R(T/\text{K})] - 71.60/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 | m^b | $V(N_2)^c$ | p^d | $p_{\text{exp}} - p_{\text{calc}}$ | $\Delta_1^g H_m^\circ$ |
|--|-------|-----------------|--------|------------------------------------|------------------------|
| K | mg | dm ³ | Pa | Pa | kJ·mol ⁻¹ |
| cyclopetanone ethylene acetal (176-32-9), 143 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (47.47 \pm 0.48) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 263.220/R - 63\,719.038/[R(T/\text{K})] - 54.50/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (53.77 \pm 0.51) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 277.509/R - 72\,764.691/[R(T/\text{K})] - 63.70/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (48.64 \pm 0.21) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 289.565/R - 72\,313.335/[R(T/\text{K})] - 79.40/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (50.36 \pm 0.56) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 273.332/R - 68\,902.478/[R(T/\text{K})] - 62.20/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (59.27 \pm 0.63) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 294.582/R - 80\,589.561/[R(T/\text{K})] - 71.50/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (50.39 \pm 0.22) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 299.905/R - 77\,133.244/[R(T/\text{K})] - 89.70/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_1^g H_m^\circ(298.15 \text{ K}) = (54.00 \pm 0.40) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 302.978/R - 80\,151.966/[R(T/\text{K})] - 87.70/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 | m^b | $V(N_2)^c$ | p^d | $p_{\text{exp}} - p_{\text{calc}}$ | $\Delta_f^g H_m^\circ$ |
|---|-------|-----------------|-------|------------------------------------|------------------------|
| K | mg | dm ³ | Pa | Pa | kJ·mol ⁻¹ |
| bicyclo[2,2,1]heptane-7-one 2,2-dimethylpropylene acetal, 150 ; $\Delta_f^g H_m^\circ(298.15 \text{ K}) = (84.34 \pm 0.87) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 320.476/R - 92\,848.884/[R(T/\text{K})] - 28.50/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 cm³ s⁻¹. ^b Mass of transferred sample condensed at $T = 243 \text{ K}$. ^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 $T = 243 \text{ K}$.

in the gaseous phase using Al_2O_3 as the catalyst



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

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

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



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

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

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



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

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

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



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

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

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



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

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

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

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 $T = 298.15 \text{ K}$. 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 $\Delta_f^g H_m^\circ$ 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 $C_{\text{quat}}-O-C_{\text{second}}$ (e.g., ${}^s\text{Bu-O-Et}$) and $C_{\text{quat}}-O-C_{\text{quat}}$ (e.g., ${}^s\text{Bu-O-}{}^s\text{Bu}$), 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 $C_{\text{tert}}-O-C_{\text{quat}}$ (e.g., ${}^t\text{Bu-O-}{}^i\text{Pr}$), require a correction to $\Delta_f H_m^\circ$ of 10 kJ·mol⁻¹. Then, the extremely strained structures of alkyl ethers, such as $C_{\text{tert}}-O-C_{\text{tert}}$ (e.g., ${}^t\text{Bu-O-}{}^t\text{Bu}$), 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, $\Delta_f^g H_m^\circ$, 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 $\Delta_f^g H_m^\circ$ 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 $\Delta_f^g H_m^\circ$ 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 $\Delta_f^g H_m^\circ$ 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 | $p_{\text{exp}} - p_{\text{calc}}$ Pa | $\Delta_f^g H_m^\circ$ kJ·mol ⁻¹ |
|---|-------------|-------------------------------|-------------|--|--|
| 2-methoxy-1,3-dioxolane (19693-75-5), 157 ; $\Delta_f^g H_m^\circ(298.15 \text{ K}) = (46.37 \pm 0.80) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 290.473/R - 69\,233.332/[R(T/\text{K})] - 76.70/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 ; $\Delta_f^g H_m^\circ(298.15 \text{ K}) = (59.88 \pm 0.38) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 301.743/R - 83\,495.704/[R(T/\text{K})] - 79.20/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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); $\Delta_f^g H_m^\circ(298.15 \text{ K}) = (44.52 \pm 0.59) \text{ kJ·mol}^{-1}$ $\ln(p/\text{Pa}) = 256.938/R - 60\,900.53/[R(T/\text{K})] - 54.95/R \ln[(T/\text{K})/298.15]$ | | | | | |
| 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 cm³ s⁻¹. ^b Mass of transferred sample condensed at $T = 243 \text{ K}$. ^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 $T = 243 \text{ K}$.

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: $\text{C}-(\text{O})(\text{H})_2(\text{Cb})$, $\text{C}-(\text{O})(\text{H})(\text{Cb})-(\text{C})$, and $\text{C}-(\text{O})(\text{Cb})(\text{C})_2$. 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: $\text{C}-(\text{O})_2-(\text{H})_2$, $\text{C}-(\text{O})_2(\text{H})(\text{C})$, and $\text{C}-(\text{O})_2(\text{C})_2$. 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 $\Delta_f H_m^\circ(\text{l})$, a set of 7 experimental data (**81**, **82**, **94**, **95**, **100**, **110**, **111**) for $\Delta_f H_m^\circ(\text{g})$, and a set of 8 experimental data (**81–83**, **94**, **96**, **97**, **110**, **111**) for $\Delta_f^g H_m^\circ$. 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 $\Delta_f H_m^\circ(\text{g})$ 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 $\text{C}-(\text{O})_2(\text{H})(\text{Cb})$, $\text{C}-(\text{O})_2(\text{Cb})(\text{C})$, and $\text{C}-(\text{O})_2(\text{Cb})_2$ (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 $\Delta_f H_m^\circ(\text{g})$ 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 $\Delta_f H_m^\circ(\text{g})$ 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

| | | $\Delta_f H_m^o(l)$ | | | $\Delta_f H_m^o(g)$ | | | $\Delta_f H_m^o(g)^b$ | | |
|----|----------------------------|---|--------|----------|---|-------|----------|--------------------------|--------|----------|
| | | 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>i</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>i</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>i</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>i</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>i</i> Bu-O- <i>i</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)

| | | $\Delta_f H_m^\circ(l)$ | | | $\Delta_f H_m^\circ(g)$ | | | $\Delta_f H_m^\circ(g)^b$ | | |
|----|------------------------------------|--|---------------------|----------|---|-------|----------|--|---------------------|----------|
| | | exp | calc | Δ | exp | calc | Δ | exp | calc | Δ |
| 22 | $^i\text{Am}-\text{O}-^i\text{Am}$ | | -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 | $^i\text{Pr}-\text{O}-\text{Me}$ | -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 | $^i\text{Pr}-\text{O}-\text{Et}$ | | -314.2 | | 30.04 (80-Maj/Wag) 30.32 (85-Maj/Svo) | 28.66 | 1.4 | | -285.2 | |
| 26 | $^i\text{Pr}-\text{O}-\text{Pr}$ | | -339.7 | | 33.95 (85-Maj/Svo) | 33.65 | 0.3 | | -306.1 | |
| 27 | $^i\text{Pr}-\text{O}-^i\text{Pr}$ | -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 | $^i\text{Pr}-\text{O}-\text{Bu}$ | | -365.2 | | 38.80 (85-Maj/Svo) | 38.63 | 0.2 | | -327.0 | |
| 29 | $^i\text{Pr}-\text{O}-\text{Am}$ | | -390.7 | | 42.69 (85-Maj/Svo) | 43.61 | -0.9 | | -347.9 | |
| 30 | $^s\text{Bu}-\text{O}-\text{Me}$ | | -302.6 | | 30.41 (85-Maj/Svo) | 30.44 | -0.1 | | -272.5 | |
| 31 | $^s\text{Bu}-\text{O}-\text{Et}$ | | -339.7 | | 34.20 (85-Maj/Svo) | 33.65 | 0.6 | | -306.1 | |
| 32 | $^s\text{Bu}-\text{O}-^s\text{Bu}$ | -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 | $^t\text{Bu}-\text{O}-\text{Me}$ | -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 | $^t\text{Bu}-\text{O}-\text{Et}$ | -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 | $^t\text{Bu}-\text{O}-\text{Pr}$ | -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 | $^t\text{Bu}-\text{O}-\text{Bu}$ | -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 | $^t\text{Bu}-\text{O}-^i\text{Bu}$ | -409.1 ± 1.6 (91-Sha/Mis) -409.1 ± 2.0 (96-Ver/Bec) -411.6 ± 4.9 ^e -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 | -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 | $^t\text{Bu}-\text{O}-^i\text{Pr}$ | -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 | $^t\text{Bu}-\text{O}-^s\text{Bu}$ | -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 | $^t\text{Bu}-\text{O}-^t\text{Bu}$ | -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)

| | | $\Delta_f H_m^\circ(l)$ | | | $\Delta_f^\circ H_m^\circ$ | | | $\Delta_f H_m^\circ(g)^b$ | | |
|----|--|---|-----------------------|----------|---|-------|----------|---|-----------------------|----------|
| | | 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 $\Delta_f H_m^\circ$ and $\Delta_f^\circ H_m^\circ$. ^c Calculated in this work using original experimental p – T data available from the literature. ^d Value of $\Delta_f H_m^\circ(g)$ calculated from the experimental reaction enthalpy in the gaseous phase reported by Chu (00-Chu) (see text). ^e Value of $\Delta_f H_m^\circ(l)$ calculated from the experimental $\Delta_f H_m^\circ(g)$ value reported by Chu (00-Chu) (see footnote d) and selected value of $\Delta_f^\circ H_m^\circ$. ^f C_{tert}–O–C_{quat} correction of 10.0 kJ·mol^{–1} was added (see text). ^g ^tAm is CH₃–CH₂–C(CH₃)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 ^tOct is C(CH₃)₃–CH₂–C(CH₃)₂–. Correction for strain in *tert*-octyl substituent of 27.0 kJ·mol^{–1} was added (see text). ^j Value of $\Delta_f H_m^\circ(l)$ obtained from the calculated $\Delta_f H_m^\circ(g)$ value (see footnote i) and the experimental value of $\Delta_f^\circ H_m^\circ$. ^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

| | | $\Delta_f H_m^\circ$ (liq) exp | $\Delta_f H_m^\circ$ calc | Δ | $\Delta_f^\circ H_m^\circ$ exp | $\Delta_f^\circ H_m^\circ$ calc | Δ | $\Delta_f H_m^\circ$ (g) exp | $\Delta_f H_m^\circ$ (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 $\Delta_f H_m^\circ$ (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








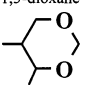


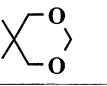

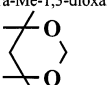

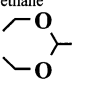
| | | | $\Delta_f H_m^\circ$ (liq) exp | $\Delta_f H_m^\circ$ calc | Δ | $\Delta_f H_m^\circ$ exp | $\Delta_f H_m^\circ$ calc | Δ | $\Delta_f H_m^\circ$ (g) ^a exp | $\Delta_f H_m^\circ$ (g) calc | Δ |
|----|---|-----|--|------------------------------|----------|---|------------------------------|----------|--|----------------------------------|----------|
| 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 | -0.9 | 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)

















| | | | $\Delta_f H_m^\circ$ (liq) exp | $\Delta_f H_m^\circ$ calc | Δ | $\Delta_f^\circ H_m^\circ$ exp | $\Delta_f^\circ H_m^\circ$ calc | Δ | $\Delta_f H_m^\circ$ (g) ^a exp | $\Delta_f H_m^\circ$ (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)



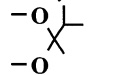
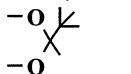
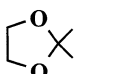
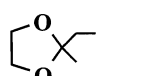
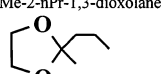
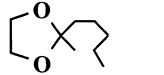
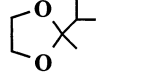
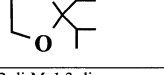
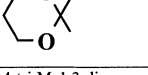
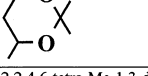
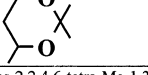
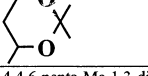
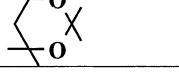
| | | | $\Delta_f H_m^\circ$ (liq) exp | $\Delta_f H_m^\circ$ calc | Δ | $\Delta_f^\circ H_m^\circ$ exp | $\Delta_f^\circ H_m^\circ$ calc | Δ | $\Delta_f H_m^\circ$ (g) ^a exp | $\Delta_f H_m^\circ$ (g) calc | Δ |
|-----|---|-----|--|------------------------------|----------|-----------------------------------|------------------------------------|----------|--|----------------------------------|----------|
| 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-Methoxy-3-Me-butane  | liq | -512.2±1.1 79-Wib/Sq | -518.4 | 6.2 | | 45.85 | | | -477.6 | |
| 115 | 2,2-di-Methoxy-3,3-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-Me-1,3-dioxane  | liq | -468.9±2.1 68-Pih/Luo | -463.4 | -5.5 | | 37.29 | | | -430.3 | |
| 123 | 2,2,4-tri-Me-1,3-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)

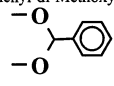
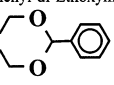
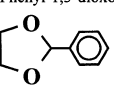
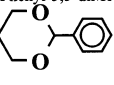
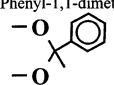
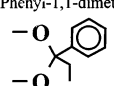
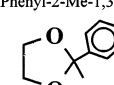
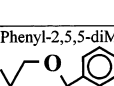
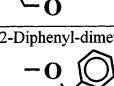
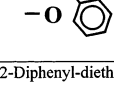
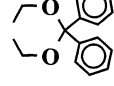
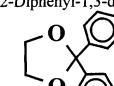
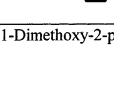
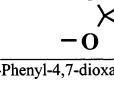
| | | | $\Delta_f H_m^\circ$ (liq) exp | $\Delta_f H_m^\circ$ calc | Δ | $\Delta_f^\circ H_m^\circ$ exp | $\Delta_f^\circ H_m^\circ$ calc | Δ | $\Delta_f H_m^\circ$ (g) ^a exp | $\Delta_f H_m^\circ$ (g) calc | Δ |
|-----|--|-----|-----------------------------------|------------------------------|----------|--|------------------------------------|----------|--|----------------------------------|----------|
| 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 $\Delta_{cr}^\circ H_m^\circ = 18.60$ (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 $\Delta_{cr}^\circ H_m^\circ = 27.20$ (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 | $\Delta_f^\circ H_m^\circ$ exp | $\Delta_f^\circ H_m^\circ$ calc | Δ | $\Delta_f H_m^\circ$ (g) ^a exp | $\Delta_f H_m^\circ$ (g) calc | Δ |
|-----|--|-----|---|------------------------------|----------|---|------------------------------------|----------|--|----------------------------------|----------|
| 141 | Cyclobutanonedimethylacetal  | 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 | Cyclopentanonedimethylacetal  | 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 | Cyclopentanoneethyleneacetal  | 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 | Cyclopentanone-(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 | Cyclohexanoneethyleneacetal  | 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-one-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-one-[2,2]dimethylpropylene-acetal  | cr | -516.1±1.4 98-Ver/Pen | | | 60.49±0.89 ^d $\Delta_{cr}^\circ H_m^\circ = 23.85$ (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)


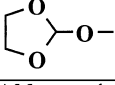
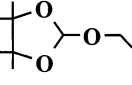
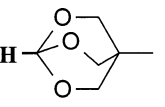
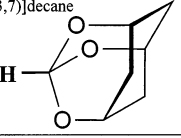




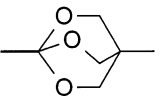
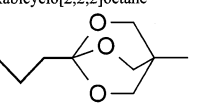
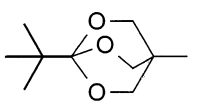
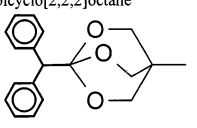
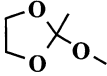
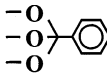
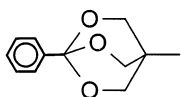
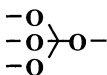
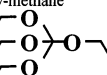
| | | | $\Delta_f H_m^\circ$ (liq) exp | $\Delta_f H_m^\circ$ calc | Δ | $\Delta_f^\circ H_m^\circ$ exp | $\Delta_f^\circ H_m^\circ$ calc | Δ | $\Delta_f H_m^\circ$ (g) ^a exp | $\Delta_f H_m^\circ$ (g) calc | Δ |
|-----|---|-----|--|------------------------------|----------|---|------------------------------------|----------|--|----------------------------------|----------|
| 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)

| | | | $\Delta_f H_m^\circ$ (liq) exp | $\Delta_f H_m^\circ$ calc | Δ | $\Delta_l^\circ H_m^\circ$ exp | $\Delta_l^\circ H_m^\circ$ calc | Δ | $\Delta_f H_m^\circ$ (g) ^a exp | $\Delta_f H_m^\circ$ (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 $\Delta_f H_m^\circ$ and $\Delta_l^\circ H_m^\circ$. ^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 $\Delta_l^\circ H_m^\circ$ calculated as the difference $\Delta_{cr}^\circ H_m^\circ - \Delta_{cr}^\circ H_m^\circ$. ^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

| | $\Delta_f H_m^\circ$ (l) | | $\Delta_l^\circ H_m^\circ$ | $\Delta_v H^\circ$ | |
|---|--------------------------|--------------------|----------------------------|--------------------|--------------------|
| | 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 $\Delta_l^\circ H_m^\circ$ values of five- and six-membered cyclic acetals and ketals. However, a comparison of the experimental data on $\Delta_l^\circ H_m^\circ$ 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 $\text{kJ}\cdot\text{mol}^{-1}$) in Cyclic Ketals

| | | $\Delta_f H_m^\circ (\text{g})^a$ | 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 $H_S = \Delta_f H_m^\circ (\text{g}) (\text{exp}) - \sum \text{increments (Table 8)}$. ^c Sum of the individual strain corrections; $\Delta = H_S - \sum \text{strain corrections}$. ^d Ring strain correction for three-membered ring of $115.9 \text{ kJ}\cdot\text{mol}^{-1}$. ^e Ring strain correction for four-membered ring of $112.1 \text{ kJ}\cdot\text{mol}^{-1}$. ^f Ring strain correction for five-membered ring of $29.7 \text{ kJ}\cdot\text{mol}^{-1}$. ^g Ring strain correction for six-membered ring of $2.9 \text{ kJ}\cdot\text{mol}^{-1}$. ^h Ring strain correction for norbornane of $70.0 \text{ kJ}\cdot\text{mol}^{-1}$. ⁱ Ring strain correction for 2,2-alkyl-substituted 1,3-dioxolane ring of $21.7 \text{ kJ}\cdot\text{mol}^{-1}$. ^j Ring strain correction for 1,1-dimethyl-substituted six-membered ring of $5.5 \text{ kJ}\cdot\text{mol}^{-1}$. ^k Ring strain correction for 2,2-alkyl-substituted 1,3-dioxane ring of $0.0 \text{ kJ}\cdot\text{mol}^{-1}$.

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

| |  |  |  |  |  |
|--|---|---|---|---|---|
|  $\Delta_f H_m^\circ$ (g) Cspiro ^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 |
|  $\Delta_f H_m^\circ$ (g) Cspiro ^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 |
|  $\Delta_f H_m^\circ$ (g) Cspiro ^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 |
|  $\Delta_f H_m^\circ$ (g) Cspiro ^a | | | Compound 149 -341.1 this work 29.9 | | Compound 150 -431.8 this work 17.7 |

^a Calculated as the difference $\Delta_f H_m^\circ$ (g) (exp) – \sum increments (Table 8). ^b Value of $\Delta_f H_m^\circ$ (l) = $-(144.0 \pm 1.0)$ kJ·mol⁻¹ taken from 64-Koz/Mir. Value of $\Delta_f^\circ H_m^\circ$ = (44.52 ± 0.59) kJ·mol⁻¹ was measured in this work (see Table 4).

predict $\Delta_f^\circ H_m^\circ$ of cyclic acetals and ketals accurately. Experimental measurements of $\Delta_f^\circ H_m^\circ$ must be available to convert the set of $\Delta_f H_m^\circ$ (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 $\Delta_f H_m^\circ$ (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 $\Delta_f H_m^\circ$ (l), $\Delta_f H_m^\circ$ (g), and $\Delta_f^\circ H_m^\circ$. 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 $\Delta_f H_m^\circ$ (g) = -99.04 ± 0.96 kJ·mol⁻¹ from Pedley et al. (86-Ped/Nay)]. It is obviously from differences between experimental $\Delta_f H_m^\circ$ (g) values and the sums of the GAVs (Table 8) that these bicyclic ortho esters are also signifi-

cantly 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 of the organic compounds containing the OR functional group.

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