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# Thermochemical Properties of Diphenylalkanes

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The standard ($p° = 0.1$ MPa) molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ at the temperature $T = 298.15$ K for diphenylmethane, (4-methylphenyl)phenylmethane, 1,1-diphenylethane, 1,1-bis(4-methylphenyl)ethane, 2-methyl-1,1-diphenylpropane, 1,1-diphenylpropane, and 1,1-diphenylbutane were obtained from the temperature dependence function of vapor pressure measured in a flow system. Standard molar enthalpies of formation $\Delta_f H_m^\circ$(l) at the temperature $T = 298.15$ K were measured using combustion calorimetry for 1,1-diphenylethane and 2-methyl-1,1-diphenylpropane. These experimental results together with the data available from the literature were used for the calculation of strain enthalpies of diphenylalkanes using the group-contribution procedure. The estimated strain enthalpies of the compounds studied were negligible within the boundaries of experimental uncertainties of about 1−2 kJ·mol$^{-1}$. Thus no new strain corrections are needed for the prediction of the $\Delta_f H_m^\circ$(g) of similarly shaped molecules by using group-additivity procedures.

## Introduction

The concept of strain in organic molecules, although inexact, is conceptually useful. The strain enthalpy is defined as the difference between the experimental value of the standard enthalpy of formation $\Delta_f H_m^\circ$(g) and the sum of strain-free increments for alkanes (Schleyer et al., 1970). The strain enthalpies of monophenyl substituted alkanes derived in this way (Beckhaus, 1983) for ethylbenzene (1.3 kJ·mol$^{-1}$), isopropylbenzene (5.0 kJ·mol$^{-1}$), and *tert*-butylbenzene (12.7 kJ·mol$^{-1}$) indicated an increase of strain due to steric repulsions resulting from branching of the alkane chain attached to the phenyl ring. What is the interaction energy among two geminal phenyl groups placed on the alkane chain?

A few reliable thermochemical quantities of diphenyl substituted alkanes are known from the literature (Pedley et al., 1986). For the methyl substituted diphenylmethanes (Good and Lee, 1976) and some diphenylalkanes (Coops et al., 1953a,b; Serijan and Wise, 1951), values of the standard molar enthalpy of formation are reported for the condensed state. Only for diphenylmethane has $\Delta_f H_m^\circ$(g) been measured in the gas phase (Steele et al., 1995). This limited set of thermochemical information fails to provide a reliable concept of strain for the diphenylalkanes. We report here a systematic study of the thermochemical properties of a series of diphenyl substituted methanes A to B, ethanes C to D, propanes E to F, and butane G (see Figure 1). We have obtained $\Delta_f H_m^\circ$(g) at the temperature $T = 298.15$ K by combining enthalpy of formation results obtained by combustion calorimetry with vaporization enthalpies measured by transpiration. Strain enthalpies $H_S$ of geminal diphenylalkanes were derived from their standard molar enthalpies of formation in the gaseous phase. The energies of the intramolecular interactions between the phenyl and alkyl substituents are discussed in terms of how much enthalpies of formation depart from those estimated using group additivity. These experimental results together with the data available from the literature provide a quantitative understanding of the relation between the structure and properties of diphenylalkanes.

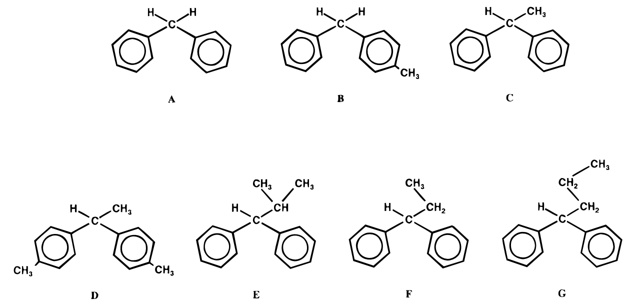

**Figure 1.** Structures of diphenylmethane (A), (4-methylphenyl)phenylmethane (B), 1,1-diphenylethane (C), 1,1-bis-(4-methylphenyl)-ethane (D), 2-methyl1,1-diphenyl-propane (E), 1,1-diphenylpropane (F), and 1,1-diphenylbutane (G).

## Experimental Procedure

***Materials***. Samples of diphenyl substituted alkanes B−G were synthesized via reduction of an appropriate olefin (Serijan and Wise, 1951) and were purified by repeated distillation under vacuum. The structures of the compounds A−G were proved by NMR spectroscopy. Purities of the samples were determined by GLC. No impurities (≥0.01 mass %) could be detected in all of the samples used for the thermochemical measurements.

We used the following equipment: GLC, Carlo Erba Fraktometer Vega Series GC 6000, Hewlett-Packard Integrator 3390A, $N_2$ flow 0.333 cm$^3$·s$^{-1}$, SE-30 capillary column of length 25 m. The standard temperature program of the GLC was $T = 313$ K for 60 s, followed by a heating rate of 0.167 K·s$^{-1}$ to $T = 523$ K. Specific heat capacities were determined with a Perkin-Elmer DSC-2C.

***Combustion Calorimetry.*** For the measurement of the enthalpies of combustion of 1,1-diphenylethane (C), an isoperibol macrocalorimeter fitted with a stirred water bath was used. Combustion experiments of 2-methyl-1,1-diphenylpropane (E) were performed in an isoperibolic aneroid microcalorimeter. The substances were placed in polyethylene or Mylar bags, which were burned in oxygen at a pressure of 3.04 MPa. The detailed procedure has been described previously (Beckhaus et al., 1980; Verevkin et al., 1992). The combustion products were examined for

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**Table 1. Density $\rho$ (293 K), Specific Heat Capacity $c_p$ (298.15 K), and Expansion Coefficients $(\delta V_m/\delta T)_p$ of the Materials Used in the Present Study**

| | $\rho$(293 K)$^a$/(g·cm$^{-3}$) | $c_p$(298.15 K)$^b$/(J·K$^{-1}$ g$^{-1}$) | $10^{-6}(\delta V_m/\delta T)_p{}^c$/(dm$^{-3}$·K$^{-1}$) |
|---|---|---|---|
| 1,1-diphenylmethane | 1.01 | 1.08 | 1.0 |
| 2-methyl-1,1-diphenylpropane | 1.01 | 2.00 | 1.0 |
| cotton$^d$ | 1.50 | 1.67 | 0.1 |
| polyethylene$^e$ | 0.92 | 2.53 | 0.1 |
| Mylar $^f$ | 1.38 | 1.32 | 0.1 |

[a] Measured with the pycnometer. [b] From DSC measurements. [c] Estimated. [d] From 10 combustion experiments $\Delta_c u°(CH_{1.774}O_{0.887}) = -(16945.2 \pm 4.2)$ J·g$^{-1}$. [e] From eleven combustion experiments $\Delta_c u°(CH_{1.930}) = -(46361.0 \pm 3.1)$ J·g$^{-1}$. [f] From eleven combustion experiments $\Delta_c u°(C_{10}H_8O_4) = -(22838.8 \pm 4.8)$ J·g$^{-1}$ correction of weight $m_{(Mylar)} = m_{moist}\,[1-4.64 \times 10^{-5}$ (relative moisture of air in percent)].

carbon monoxide (Dräger tube) and unburnt carbon (visual inspection), but neither was detected. The energy of ignition was determined to be 1.46 J. The energy equivalent of the calorimeters $\epsilon_{calor}$ were determined (macro, 25 089.5 ± 1.5 J·K$^{-1}$; micro, 1474.48 ± 0.10 J·K$^{-1}$) with a standard reference sample of benzoic acid (sample SRM 39i, NIST). For reduction of the data to standard conditions conventional procedures (Hubbard et al., 1956) were used. The atomic weights used were those recommended by the IUPAC Comission (CODATA, 1989). The densities of C and E were determined in a calibrated 10 cm$^3$ pycnometer. The specific heat capacities were measured by differential scanning calorimetry (DSC). A summary of auxiliary quantities for the combustion experiments and information necessary for reducing apparent mass to mass in a vacuum is given in Table 1.

***Transpiration Method***. The enthalpies of vaporization of compounds A−G and enthalpy of sublimation of A were determined using the transpiration method in a saturated $N_2$ stream (Cox and Pilcher, 1970; Beckhaus et al., 1980; Chickos et al., 1995). 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. A nitrogen flow of 0.28−0.56 cm$^3$·s$^{-1}$ was optimal in order to achieve saturation of the transporting gas at each temperature of the investigation. The amount of condensed product was determined by GLC analysis using an internal standard (hydrocarbons $n$-$C_{11}H_{24}$ or $n$-$C_{13}H_{28}$). The vapor pressure $p$ at each saturation temperature was calculated from the amount of product collected within a definite time period, and the small value of the residual vapor pressure at the temperature of condensation was added. The latter was calculated from a linear correlation between ln($p$) and $T^{-1}$ obtained by iteration. With the assumption that Dalton's law of partial pressures applied to the saturated nitrogen stream, values of $p$ from the ideal gas law were calculated. The molar enthalpies of vaporization or sublimation were calculated from the slope of the linear correlation: $\Delta_l^g H_m^\circ = -R\,[d(\ln(p))/dT^{-1}]$. The observed enthalpies of vaporization $\Delta_l^g H_m^\circ(T)$ at the temperature $T$ obtained by this procedure are listed in Table 2.

## Results and Discussion

*Combustion Calorimetry*. Results for a typical combustion experiment on each compound are given in Table 3. The individual values of the standard massic energy of combustion ($\Delta_c u°$), enthalpies of combustion (the given standard deviations of the mean include the uncertainties from calibration and the uncertainties from the combustion energies of the auxiliary materials), and enthalpies of formation of compounds C and E are given in Table 4. To derive $\Delta_f H_m^\circ$(l) from $\Delta_c H_m^\circ$ the following molar enthalpies of formation were used (CODATA, 1989): for $H_2O$(l), −(285.83 ± 0.04) kJ·mol$^{-1}$; and for $CO_2$(g), −(393.51 ± 0.13) kJ·mol$^{-1}$. Table 5 lists the derived standard molar enthalpies of formation in the liquid and the gaseous states.

The standard enthalpy of formation $\Delta_f H_m^\circ$(l) of diphenylmethane (A) has been redeterminated by Steele et al. (1995) using combustion calorimetry. They circumvented the ambiguities of which state (solid or liquid) achieved their sample in the bomb under the pressure of oxygen at 296 or 297 K (the melting point of the diphenylmethane is within these boundaries). Their value $\Delta_f H_m^\circ$(l) = −(97.1 ± 1.4) kJ·mol$^{-1}$ is substantially more reliable than earlier measurements (see the discussion by Steele et al. (1995) and was taken into account here for the calculation of the standard enthalpy of formation $\Delta_f H_m^\circ$(g) of diphenylmethane (Table 5).

The determination of the standard enthalpy of formation, $\Delta_f H_m^\circ$(l), of (4-methylphenyl)phenylmethane (B) has been made by Good and Lee (1976), using combustion calorimetry. Their value (61.5 ± 1.1) kJ·mol$^{-1}$ was taken into account here for the calculation of the standard enthalpy of formation $\Delta_f H_m^\circ$(g) of (4-methylphenyl)phenylmethane (Table 5).

The only previous determination of the standard enthalpy of formation $\Delta_f H_m^\circ$(l) of 1,1-diphenylethane (C) has been made by Coops et al. (1953a), using combustion calorimetry. Their value (48.7 ± 2.1) kJ·mol$^{-1}$ is in very poor agreement with our value (65.61 ± 0.96) kJ·mol$^{-1}$. The sample of 1,1-diphenylethane (C) used for combustion by Coops et al. (1953a) was fractionally distilled, but they do not mention the degree of purity of their specimen. A second possible reason for the observed deviation could be that samples of C were weighed and burned in an open crucible with addition of paraffin oil in order to decrease the volatility of C. The standard enthalpy of formation $\Delta_f H_m^\circ$(l) of 1,1-bis(4-methylphenyl)ethane (D) has been measured (Coops et al., 1953b) in a similar manner. Therefore their value $\Delta_f H_m^\circ$(l) = −(33.2 ± 2.1) kJ·mol$^{-1}$ also seems to be doubtful.

Measurements of thermochemical properties of 2-methyl-1,1-diphenylpropane (E) are reported for the first time.

Values for the enthalpy of formation of 1,1-diphenylpropane (F), $\Delta_f H_m^\circ$(l) = 49.4 kJ·mol$^{-1}$, and of 1,1-diphenylbutane (G), $\Delta_f H_m^\circ$(l) = 41.8 kJ·mol$^{-1}$, have been calculated by Stull et al. (1969) from the enthalpies of combustion measured by Serijan and Wise (1951, 1952). The purities of samples from these investigations were generally claimed to be 99 mass %, but no other details for each individual compound of interest were given. Serijan and Wise measured energies of combustion using ASTM method D240-39. That method is used in industry to obtain “balk-park“ values for the energy of combustion of fuels and hence is not very precise. That is why their results for 1,1-diphenylpropane and of 1,1-diphenylbutane are not abstracted in

**Table 2. Results from Measurements of the Vapor Pressure $p$ with the Transpiration Method**

| $T^a$/K | $m^b$/mg | $V(N_2)^c$/ dm$^3$ | $p^d$/Pa | $T^a$/K | m$^b$/mg | $V(N_2)^c$/ dm$^3$ | $p^d$/Pa |
|---|---|---|---|---|---|---|---|
| Diphenylmethane; $\ln(p/\mathrm{Pa}) = 36.43 - 10639(T/\mathrm{K})^{-1}$ | | | | | | | |
| 273.2 | 0.260 | 48.62 | 0.07946 | 288.2 | 0.888 | 21.15 | 0.6196 |
| 278.3 | 0.260 | 24.33 | 0.1584 | 291.8 | 1.020 | 15.70 | 0.9556 |
| 283.3 | 0.730 | 33.06 | 0.3261 | 295.4 | 1.100 | 11.17 | 1.456 |
| $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(284.3\mathrm{K}) = (88.46 \pm 0.82)\ \mathrm{kJ{\cdot}mol^{-1}}$; | | | | | | | |
| $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(298.15\mathrm{K}) = (87.63 \pm 0.82)\ \mathrm{kJ{\cdot}mol^{-1}}$ | | | | | | | |
| Diphenylmethane; $\ln(p/\mathrm{Pa}) = 27.43 - 7981.2(T/\mathrm{K})^{-1}$ | | | | | | | |
| 303.4 | 1.57 | 7.46 | 3.099 | 328.2 | 1.53 | 1.040 | 21.63 |
| 308.2 | 1.80 | 5.72 | 4.653 | 333.2 | 1.30 | 0.610 | 30.55 |
| 313.2 | 1.41 | 2.97 | 7.019 | 338.3 | 1.56 | 0.490 | 47.05 |
| 318.1 | 1.61 | 2.33 | 10.19 | 343.3 | 1.97 | 0.430 | 67.41 |
| $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(323.3\mathrm{K}) = (66.36 \pm 0.54)\ \mathrm{kJ{\cdot}mol^{-1}}$; | | | | | | | |
| $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(298.15\mathrm{K}) = (67.87 \pm 0.54)\ \mathrm{kJ{\cdot}mol^{-1}}$ | | | | | | | |
| (4-Methylphenyl)phenylmethane; $\ln(p/\mathrm{Pa}) = 27.39 - 8250.6(T/\mathrm{K})^{-1}$ | | | | | | | |
| 293.2 | 1.43 | 40.56 | 0.4844 | 318.2 | 2.38 | 7.57 | 4.307 |
| 298.2 | 1.86 | 34.77 | 0.7332 | 323.2 | 1.85 | 3.92 | 6.456 |
| 303.2 | 1.73 | 20.03 | 1.183 | 328.2 | 1.86 | 2.69 | 9.445 |
| 308.2 | 1.90 | 14.20 | 1.833 | 333.2 | 2.04 | 2.01 | 13.88 |
| 313.2 | 1.68 | 8.05 | 2.854 | | | | |
| $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(313.2\mathrm{K}) = (68.60 \pm 0.34)\ \mathrm{kJ{\cdot}mol^{-1}}$; | | | | | | | |
| $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(298.15\mathrm{K}) = (69.50 \pm 0.34)\ \mathrm{kJ{\cdot}mol^{-1}}$ | | | | | | | |
| 1,1-Diphenylethane; $\ln(p/\mathrm{Pa}) = 27.02 - 8196.5(T/\mathrm{K})^{-1}$ | | | | | | | |
| 293.5 | 0.843 | 29.55 | 0.3893 | 313.2 | 0.478 | 2.720 | 2.394 |
| 298.2 | 0.576 | 12.63 | 0.6216 | 318.2 | 0.705 | 2.790 | 3.439 |
| 303.2 | 0.457 | 6.41 | 0.9721 | 323.1 | 0.380 | 0.990 | 5.226 |
| 308.3 | 0.580 | 5.10 | 1.549 | 328.2 | 0.328 | 0.600 | 7.442 |
| $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(313.2\mathrm{K}) = (68.15 \pm 0.57)\ \mathrm{kJ{\cdot}mol^{-1}}$; | | | | | | | |
| $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(298.15\mathrm{K}) = (68.91 \pm 0.57)\ \mathrm{kJ{\cdot}mol^{-1}}$ | | | | | | | |
| 1,1-Bis(4-methylphenyl)ethane; $\ln(p/\mathrm{Pa}) = 28.38 - 9057.7(T/\mathrm{K})^{-1}$ | | | | | | | |
| 298.2 | 0.528 | 48.01 | 0.1326 | 323.2 | 0.621 | 5.200 | 1.411 |
| 303.2 | 0.476 | 24.96 | 0.2278 | 328.2 | 0.567 | 3.120 | 2.148 |
| 308.1 | 0.444 | 14.24 | 0.3704 | 333.2 | 0.425 | 1.513 | 3.315 |
| 313.2 | 0.606 | 12.42 | 0.5783 | 338.3 | 0.368 | 0.860 | 5.053 |
| 318.2 | 1.100 | 15.01 | 0.8683 | | | | |
| $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(318.2\mathrm{K}) = (75.31 \pm 0.56)\ \mathrm{kJ{\cdot}mol^{-1}}$; | | | | | | | |
| $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(298.15\mathrm{K}) = (76.51 \pm 0.56)\ \mathrm{kJ{\cdot}mol^{-1}}$ | | | | | | | |
| 2-Methyl-1,1-Diphenylpropane; $\ln(p/\mathrm{Pa}) = 27.77 - 8663.2(T/\mathrm{K})^{-1}$ | | | | | | | |
| 298.2 | 0.797 | 34.50 | 0.2727 | 323.3 | 1.62 | 7.360 | 2.596 |
| 303.2 | 1.06 | 27.91 | 0.4468 | 328.0 | 1.63 | 4.750 | 4.038 |
| 308.3 | 1.19 | 19.49 | 0.7176 | 332.8 | 1.40 | 2.920 | 5.643 |
| 313.3 | 1.36 | 14.49 | 1.104 | 338.0 | 1.19 | 1.700 | 8.268 |
| 318.4 | 1.56 | 10.79 | 1.701 | | | | |
| $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(318.1\mathrm{K}) = (72.03 \pm 0.47)\ \mathrm{kJ{\cdot}mol^{-1}}$; | | | | | | | |
| $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(298.15\mathrm{K}) = (73.22 \pm 0.47)\ \mathrm{kJ{\cdot}mol^{-1}}$ | | | | | | | |
| 1,1-Diphenylpropane; $\ln(p/\mathrm{Pa}) = 28.20 - 8592.2{\cdot}(T/\mathrm{K})^{-1}$ | | | | | | | |
| 298.3 | 1.88 | 43.07 | 0.5534 | 323.2 | 1.72 | 4.310 | 5.030 |
| 303.3 | 2.87 | 42.43 | 0.8542 | 328.2 | 2.12 | 3.690 | 7.248 |
| 308.3 | 2.23 | 19.75 | 1.429 | 333.1 | 1.97 | 2.320 | 10.72 |
| 313.3 | 1.67 | 10.06 | 2.101 | 338.2 | 1.18 | 0.880 | 16.90 |
| 318.3 | 1.64 | 6.32 | 3.282 | 343.3 | 0.856 | 0.450 | 24.05 |
| $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(320.8\mathrm{K}) = (71.44 \pm 0.52)\ \mathrm{kJ{\cdot}mol^{-1}}$; | | | | | | | |
| $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(298.15\mathrm{K}) = (72.80 \pm 0.52)\ \mathrm{kJ{\cdot}mol^{-1}}$ | | | | | | | |
| 1,1-Diphenylbutane; $\ln(p/\mathrm{Pa}) = 29.15 - 9127.4{\cdot}(T/\mathrm{K})^{-1}$ | | | | | | | |
| 298.1 | 0.855 | 43.29 | 0.2331 | 322.7 | 0.773 | 3.800 | 2.399 |
| 303.0 | 1.360 | 42.44 | 0.3787 | 327.6 | 1.030 | 3.260 | 3.736 |
| 308.1 | 0.908 | 18.49 | 0.5794 | 332.5 | 0.943 | 2.050 | 5.423 |
| 312.8 | 0.747 | 8.92 | 0.9880 | 337.5 | 0.550 | 0.780 | 8.321 |
| 317.8 | 0.739 | 5.60 | 1.556 | 342.4 | 0.399 | 0.400 | 11.77 |
| $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(320.2\mathrm{K}) = (75.89 \pm 0.58)\ \mathrm{kJ{\cdot}mol^{-1}}$; | | | | | | | |
| $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(298.15\mathrm{K}) = (77.21 \pm 0.58)\ \mathrm{kJ{\cdot}mol^{-1}}$ | | | | | | | |

[a] Temperature of saturation, $N_2$ gas flow (0.26 to 0.52) $\mathrm{cm^3{\cdot}s^{-1}}$. [b] Mass of transferred sample condensed at $T = 243$ K. [c] Volume of nitrogen used to transfer sample. [d] Vapor pressure at temperature $T$ of experiment; corrections for residual vapor pressure at $T = 243$ K were made.

**Table 3. Results for Typical Combustion Experiments at $T = 298.15$ K ($p^{\circ} = 0.1$ MPa)[a]**

| | 1,1-diphenylethane | 2-methyl-1,1-diphenylpropane |
|---|---|---|
| $m(\mathrm{substance})^b$/g | 0.345 153 | 0.037 110 |
| $m'(\mathrm{cotton})^b$/g | 0.001 018 | 0.000 521 |
| $\mathrm{m}''(\mathrm{polyethylene})^b$/g | 0.456 273 | |
| $\mathrm{m}'''(\mathrm{Mylar})^b$/g | | 0.011 511 |
| $\Delta T_c{}^c$/K | 1.414 61 | 1.245 58 |
| $(\epsilon_{\mathrm{calor}})(-\Delta T_c)$/J | −35491.86 | −1836.58 |
| $(\epsilon_{\mathrm{cont}})(-\Delta T_c)$/J | −20.14 | −3.43 |
| $\Delta U_{\mathrm{corr}}{}^d$/J | 15.11 | 0.98 |
| $-m'\Delta_c u'$/J | 17.24 | 8.83 |
| $-m''\Delta_c u''$/J | 21153.25 | |
| $-m'''\Delta_c u'''$/J | | 262.89 |
| $\Delta_c u^{\circ}(\mathrm{substance})/(\mathrm{J{\cdot}g^{-1}})$ | −41503.3 | −42193.0 |

[a] For the definition of the symbols Hubbard et al. (1956). Macrocalorimeter: $T_h = 298.15$ K; $V_{\mathrm{bomb}} = 0.2664\ \mathrm{dm^3}$; $p_{\mathrm{gas}}^{\mathrm{i}} = 3.04$ MPa; $m_{\mathrm{water}}^{\mathrm{i}} = 0.78$ g; $E_{\mathrm{ignition.}} = 1.46$ J; $m_{\mathrm{platin}} = 12.181$ g. Microcalorimeter: $T_h = 298.15$ K; $V_{\mathrm{bomb}} = 0.0460\ \mathrm{dm^3}$; $p_{\mathrm{gas}}^{\mathrm{i}} = 3.04$ MPa; $m_{\mathrm{water}}^{\mathrm{i}} = 0.23$ g; $E_{\mathrm{ignition}} = 1.46$ J; $m_{\mathrm{platin}} = 2.883$ g. [b] Masses obtained from apparent masses. [c] $\Delta T_c = T^{f} - T^{i} + \Delta T_{\mathrm{corr}}$; $(\epsilon_{\mathrm{cont}})(-\Delta T_c) = (\epsilon_{\mathrm{cont}}^{\mathrm{i}})(T^{i} - (298.15\ \mathrm{K})) + (\epsilon_{\mathrm{cont}}^{\mathrm{f}})((298.15\ \mathrm{K}) - T^{f} + \Delta T_{\mathrm{corr}})$. [d] $\Delta U_{\mathrm{corr}}$, the correction to standard state is the sum of items 81 to 85, 87 to 90, 93, and 94 in Hubbard et al. (1956).

**Table 4. Summary of Experimental Specific Energies of Combustion and Standard Molar Thermodynamic Functions at $T = 298.15$ K ($p^{\circ} = 0.1$ MPa)**

| | |
|---|---|
| 1,1-Diphenylethane (C); $[(\Delta_c u^{\circ})\{\text{1,1-Diphenylethane, l, 298.15 K}\}]/(\mathrm{J{\cdot}g^{-1}})$ | |
| −41 503.3 | −41 531.4 |
| −41 503.3 | −41 519.0 |
| −41 521.6 | −41 512.3 |
| $\langle -\Delta_c u^{\circ}\rangle/(\mathrm{J{\cdot}g^{-1}}) = -41\,515.2 \pm 4.5$ | |
| $\Delta_c H_{\mathrm{m}}^{\circ}(\mathrm{l})/(\mathrm{kJ{\cdot}mol^{-1}}) = -7575.55 \pm 0.96$ | |
| $\Delta_f H_{\mathrm{m}}^{\circ}(\mathrm{l})/(\mathrm{kJ{\cdot}mol^{-1}}) = 65.61 \pm 0.96$ | |
| 2-Methyl-1,1-diphenylpropane (E); $[(\Delta_c u^{\circ})\{\text{2-Methyl-1,1-diphenylpropane, l, 298.15 K}\}]/(\mathrm{J{\cdot}g^{-1}})$ | |
| −42 141.8 | −42 193.0 |
| −42 155.5 | −42 168.0 |
| −42 178.2 | |
| $\langle -\Delta_c u^{\circ}\rangle/(\mathrm{J{\cdot}g^{-1}}) = -42\,167.3 \pm 8.9$ | |
| $\Delta_c H_{\mathrm{m}}^{\circ}(\mathrm{l})/(\mathrm{kJ{\cdot}mol^{-1}}) = -8879.8 \pm 1.9$ | |
| $\Delta_f H_{\mathrm{m}}^{\circ}(\mathrm{l})/(\mathrm{kJ{\cdot}mol^{-1}}) = 11.2 \pm 1.9$ | |

contemporary thermochemical archives (Cox and Pilcher, 1970; Pedley et al., 1986).

***Enthalpies of Vaporization or Sublimation.*** The resulting enthalpies of vaporization, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}$, or sublimation, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}$, at $T = 298.15$ K are recorded in Table 2. Because of the deviations from $T = 298.15$ K, the observed values of the enthalpies of vaporization or sublimation of diphenylalkanes measured by transpiration had to be ajusted to the reference temperature. The values of corrections were estimated via the "Sidgwick correction":

$$\{\Delta_{\mathrm{l}}^{\mathrm{g}}\,H_{\mathrm{m}}^{\circ}(\langle T\rangle) - \Delta_{\mathrm{l}}^{\mathrm{g}}\,H_{\mathrm{m}}^{\circ}(298.15\mathrm{K})\}/(\mathrm{kJ{\cdot}mol^{-1}}) = -6 \times 10^{-2}((\langle T\rangle/\mathrm{K}) - 298.15)$$

following the recommendation of Chickos et al. (1992). With these corrections and the measured values of $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(T)$ and $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(T)$, the standard molar enthalpies of vaporization and sublimation at $T = 298.15$ K were calculated (Tables 2 and 5).

Determinations of the enthalpies of sublimation and vaporization of diphenylmethane have been made by a number of groups in recent years (see Table 6). The observed values $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\mathrm{T})$ and $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\mathrm{T})$ given in the literature were extrapolated to $T = 298.15$ K in the same manner as our results, using Sidgwick's correction (Chickos

**Table 5. Thermochemical Results at $T = 298.15$ K ($p^\circ = 0.1$ MPa)**

| | $\Delta_l^g H_m^{\circ\,a}$ / (kJ·mol$^{-1}$) | $\Delta_f H_m^\circ(l)^b$ / (kJ·mol$^{-1}$) | $\Delta_f H_m^\circ(g)$/ (kJ·mol$^{-1}$) | Σ increments$^f$ / (kJ·mol$^{-1}$) | $H_s{}^g$ / (kJ·mol$^{-1}$) |
|---|---|---|---|---|---|
| diphenylmethane | 67.87 ± 0.54$^c$ | 97.1 ± 1.4$^d$ | 165.0 ± 1.5 | 162.8 | 2.2 ± 1.5 |
| (4-methylphenyl)phenylmethane | 68.60 ± 0.34 | 61.5 ± 1.1$^e$ | 130.1 ± 1.2 | 130.5 | −0.4 ± 1.2 |
| 1,1-diphenylethane | 68.91 ± 0.57 | 65.61 ± 0.96 | 134.5 ± 1.1 | 133.1 | 1.4 ± 1.1 |
| 2-methyl-1,1-diphenylpropane | 73.22 ± 0.47 | 11.2 ± 1.9 | 84.4 ± 2.0 | 82.0 | 2.4 ± 2.0 |

[a] From the measurements of vapor pressures at different temperatures (Table 2) using the Clausius−Clapeyron equation. [b] Calculated from the specific energies of combustion in Table 4. [c] Measured above the melting temperature. [d] Taken from Steele et al. (1995). [e] Taken from Good and Lee (1976). [f] Calculated as the sum of strain-free increments (see text). [g] Strain enthalpy of diphenylalkanes $H_s = \Delta_f H_m^\circ(g)$ (expt) − Σ increments. The uncertainties of $H_S$ were suggested to be only equal to those of the experimental $\Delta_f H_m^\circ(g)$ of diphenylalkanes.

**Table 6. Comparison with Earlier Values of Enthalpy of Vaporization or Sublimation of Diphenylmethane**

| | technique | $T_{av}$/K | obsd at $T_{av}$ | extrapolated$^a$ to $T = 298.15$ K | ref |
|---|---|---|---|---|---|
| $\Delta_{cr}^g H_m^\circ$/(kJ·mol$^{-1}$) | quarz thread | 297.2 | 71.96 ± 0.84 | 72.0 ± 0.8 | Wolf and Weghofer, 1938 |
| | viscosity gage | | | 82.4 ± 0.8 | Aihara, 1959 |
| | head space | | | 83.3 | Chickos and Annuziata, 1986 |
| | static manometer | 286.07 | 71.55 ± 0.95 | 70.8 ± 1.0 | Sasse et al., 1989 |
| | transpiration | 284.3 | 88.46 ± 0.82 | 87.6 ± 0.8 | this work |
| $\Delta_l^g H_m^\circ$/(kJ·mol$^{-1}$) | calorimetric | | | 67.5 ± 0.3 | Morawetz, 1972 |
| | static manometer | 353.15 | 63.7 ± 2.2 | 67.0 ± 2.2 | Sasse et al., 1989 |
| | transpiration | 393.15 | 67.3 ± 2.5 | 73.0 ± 2.5 | Sohda et al., 1990 |
| | non defined | | | 67.7 ± 0.6 | Steele et al., 1995 |
| | transpiration | 323.3 | 66.36 ± 0.54 | 67.9 ± 0.5 | this work |

[a] The observed value at $T_{av}$ was extrapolated to 298.15 K using the "Sidgwick correction" (see text), if it was not done in the original reference.

et al., 1992). The values of $\Delta_{cr}^g H_m^\circ$ are very inconsistent with this research, as can be seen by reference to Table 6. On the other hand, all known values of $\Delta_l^g H_m^\circ$ (excepting the value from Sohda et al. (1990)) measured by different techniques are very consistent with each other. The measured value of $\Delta_{cr}^g H_m^\circ$ for diphenylmethane, (87.63 ± 0.82) kJ·mol$^{-1}$, is in very good agreement with the sum of $\Delta_l^g H_m^\circ$, (67.87 ± 0.54) kJ·mol$^{-1}$, and the experimental enthalpies of fusion $\Delta_{cr}^g H_m^\circ$: (19.01 ± 0.01) kJ·mol$^{-1}$ (Steele et al., 1995), 19.25 kJ·mol$^{-1}$ (Chickos and Annuziata, 1986), and (18.20 ± 1.00) kJ·mol$^{-1}$ (Parks and Mosely, 1950).

Measurements of enthalpies of vaporization of diphenylalkanes B−G have been reported for the first time.

***Calculation of Strain Enthalpy $H_S$.*** Strain enthalpy reflects a nonadditive component of the enthalpy of a molecule. The nature of such deviations from additivity appears unique for each molecule. We define the strain of a molecule as the difference between the experimental standard enthalpy of formation $\Delta_f H_m^\circ(g)$ and the calculated sum of the Benson type (Benson, 1976) strain-free increments (Schleyer et al., 1970) of a molecule. The system of strain-free increments is based on the standard enthalpies of formation $\Delta_f H_m^\circ(g)$ of simple homologous ("strainless") molecules. Strain-free group additivity increments for hydrocarbons (Schleyer et al., 1970) and arenes (Beckhaus, 1983) are well-defined. Their advantage with respect to the classic Benson increments is the possibility of determining strain enthalpies. All the increments necessary in this work are as follows: $CH_3[C] = -42.05$ kJ·mol$^{-1}$; $CH_2[2C] = -21.46$ kJ·mol$^{-1}$; $CH[3C] = -9.04$ kJ·mol$^{-1}$; $C[4C] = -1.26$ kJ·mol$^{-1}$; $C_BH[2C_B] = 13.72$ kJ·mol$^{-1}$ ($C_B$ represents the aromatic C atoms); $C_B[C,2C_B] = 23.51$ kJ·mol$^{-1}$. Using these group-additivity parameters and the values of $\Delta_f H_m^\circ(g)$ of diphenylalkanes (Table 5) derived in this research, the values of strain enthalpies $H_S = \{\Delta_f H_m^\circ(g) - \Sigma \text{ increments}\}$ of the diphenylalkanes have been estimated (Table 5). The values of the strain enthalpies, $H_S$, of diphenylmethane (+2.2 kJ·mol$^{-1}$), (4-methylphenyl)phenylmethane (−0.4 kJ·mol$^{-1}$), 1,1-diphenylethane (+1.4 kJ·mol$^{-1}$), and 2-methyl-1,1-diphenyl-propane (+1.2 kJ·mol$^{-1}$) were calculated as the difference between the experimental value of the standard enthalpy of formation, $\Delta_f H_m^\circ(g)$ (Table 5), and the sum of strain-free increments. No considerable strain (within the boundaries of the experimental uncertainities, about ± 2.0 kJ·mol$^{-1}$) was observed for the diphenyl substituted alkanes studied. Thus no new strain corrections are needed for the prediction of the $\Delta_f H_m^\circ(g)$ of similar shaped molecules using group additivity.

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