Enthalpies of Combustion, Formation, and Vaporization of Spiro[4.5]decane, Spiro[5.5]undecane, and 7-*n*-Hexadecylspiro[4.5]decane

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The enthalpy of combustion of 7-*n*-hexadecylspiro[4.5]decane was measured by precision oxygen-bomb combustion calorimetry. The standard enthalpy of combustion, $\Delta H_c°(298.15)$, of this compound in the liquid state was −(4012.08 ± 0.53) kcal mol^{-1}. The derived standard enthalpy of formation at 298.15K in the liquid state was −(141.12 ± 0.57) kcal mol^{-1}. The enthalpies of vaporization of spiro[4.5]decane and spiro[5.5]undecane at 298.15K were measured using a vaporization calorimeter. The reported standard enthalpies of vaporization were 13.127 ± 0.021 and 13.417 ± 0.030 kcal mol^{-1}, respectively.

This laboratory is involved in thermochemical investigations dealing with the energy-structural relations in certain representative classes of polyatomic organic substances, such as the spiroalkanes. As part of this continuing effort, precision oxygen-bomb calorimetry has been employed to determine the enthalpy of combustion and subsequently the derived standard enthalpy of formation of 7-*n*-hexadecylspiro[4.5]decane in the liquid state at 298.15K. Furthermore, this substance with a 16-member normal size chain will serve as a key compound for testing the incremental homologous series correlation procedure. The enthalpy of vaporization data is necessary to derive the standard enthalpy of formation in the ideal gaseous state. These data are basic for developing a precise and reliable correlation procedure for estimating the gas-phase enthalpies of the spiroalkanes and for providing information on the nature of the central spiro-carbon atom in structural organic chemistry.

Materials. The spiroalkanes used in this study were American Petroleum Institute-Pennsylvania State University samples (*1*). The purity and characterization of the samples were established using mass spectroscopy, infrared spectroscopy, NMR spectroscopy, and gas chromatography. Based on information concerning the synthesis of these compounds (*15*), it was possible to selectively analyze for possible specific contaminants and to employ routine screening methods for the determination of unexpected impurities.

Infrared spectra obtained on the Beckmann IR-12 and NMR data obtained from the Varian-100 indicated that the API-PSU samples were of very good purity. Mass spectroscopy data indicated a purity of better than 99.9 mol % which was further supported by the gas chromatographic data in Table I.

Flame ionization was employed to obtain a quantitative gas chromatographic analysis. Columns used were a 150-ft × 0.02-in. 3% SE, a 6-ft × 0.25-in. 5% Carbowax 200M on Haloport 500 and a 6-ft × 0.25-in. QF-1. All columns were stainless steel. Half-scale deflection was achieved with 0.1 μl of a mixture of isooctane, *n*-decane, *n*-dodecane, and *n*-tetradecane. This was equivalent to 220 ppm for one-half scale deflection for *n*-decane. The analysis was performed isothermally and by programming from 110° to 310°C at 20°C/min. Sensitivity was less than 2.0 μg. No extraneous peaks appeared on the Carbowax or the QF-1 columns. The SE-30 column showed a small additional peak for the [4.5] and [5.5] spiranes. The R_f value for this extraneous peak ranged between 2.5 and 3.5 cm but did not differ in peak height. Water content was analyzed using gas chromatography and a thermal conductivity detector and a Porapak Q column 6 ft × 0.25 in. Less than 0.02 mg of water was found. From the analytical characterization, it was concluded that the amount of water present would not significantly affect the heat of combustion determinations, and all samples were of 99.97 mol % purity or better. Matheson Coleman & Bell spectrograde carbon tetrachloride and cyclohexane were employed as vaporization test substances and were used without further purification.

Enthalpy of Combustion

Auxiliary quantities. National Bureau of Standards benzoic acid sample 39i was used for the calibration of the precision static combustion bomb calorimeter. Its specific energy of combustion is −(26.434 ± 0.003) kJ g^{-1} under certificate conditions. Conversion to standard conditions (*9*) gives −(6313.02 ± 0.72) cal g^{-1} for $\Delta E_c°/M$, the specific energy of the idealized combustion reaction. The auxiliary oil, USBM-P3a, had the empirical formula $CH_{1.894}$ (*7*). This material had $\Delta E_c°/M$ of −(10984.30) cal g^{-1}. The cotton thread fuse, $CH_{1.774}O_{0.887}$, had $\Delta E_c°/M$ of 3950 cal g^{-1} (*2*).

Apparatus and procedure. The calorimeter used was a static bomb system previously described by Joshi and Zwolinski (*12*). The procedures followed are those recommended by Rossini (*19*). The temperature was maintained within a few ten thousandths of an ohm of 28.2675 ohms in the water jacket of the calorimeter by using a Tronac PTC-1000a precision temperature controller. Each experiment was started at approximately 296.15K, and the final temperatures were very nearly 298.15K. Jacket temperature was controlled to ±0.003°C. A Parr Bomb (1106) with a Teflon seal was used in the inverted position. The bomb, with an internal volume of 387 ml, had 1 ml of water added and was filled with purified oxygen to a pressure of 30 atm at 25°C.

The thermometric system included the flat calorimetric-type platinum resistance thermometer (Leeds and Northrup type 816B) and a G-2 Mueller bridge (Leeds and Northrup). The sensitivity of the apparatus was 0.250 μV/10^{-4} at 4 mA thermometer current.

The measurements of the calorimetric system were taken as a function of time for greater accuracy. Corrections for time-dependent heat leaks could thus be made. A Gaertner B370A type chronograph was used during the fast period as

Table I. Gas Chromatographic Purity Analysis

Formula	Substance	Mol % purity
$C_{10}H_{18}$	Spiro[4.5]decane	99.974 ± 0.003
$C_{11}H_{20}$	Spiro[5.5]undecane	99.977 ± 0.002
$C_{26}H_{50}$	7-*n*-Hexadecylspiro[4.5]decane	99.970 ± 0.006

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a supplement to the synchronous electric clock, and two Precision Scientific Time-It timers were used during the slow temperature rise periods of the experiment.

The sample was ignited by means of a 1.5-mg piece of cotton thread fuse tied to a 3-cm piece of 0.004-in. platinum wire which was connected between the ignition leads of the bomb. A Parr ignition unit was used to supply the electrical energy. The ignition energy was approximately 0.5 cal.

The oxygen used in the combustion experiments was commercial grade which had been passed over copper oxide at 600°C to remove impurities and then passed through a tube containing Ascarite to remove the carbon dioxide (*11, 13*).

The combustion products were examined in a recovery train similar to that of Prosen and Rossini (*18*) and described in detail by Browne and Rossini (*3*). Prosen and Rossini (*17*) have described the absorption tubes used in these experiments. The method used in handling the tubes has been outlined by Rossini (*20*) so that the only weight gain in the tubes was due to carbon dioxide. No indication of incomplete combustion was detected. The carbon dioxide recovery for 7-*n*-hexadecylspiro[4.5]decane is 99.990 ± 0.006% recovery, representing the mean and standard deviation for five determinations.

The standard procedure utilizing fragile flexible ampuls of borasilicate glass to confine the liquid samples was employed (*6, 8*).

Since some nitric acid was formed during the bomb process owing to nitrogen present in the purified oxygen, the bomb was rinsed with distilled water after the carbon dioxide recovery. The amount of nitric acid formed was determined by titrating CO_2-free nitric acid solution with 0.01*N* sodium hydroxide to the phenolphthalein endpoint.

A standard system is defined in thermochemical investigations so that variations in reaction conditions and environment can be treated as deviations from the standard system. The standard system for these experiments was the combustion bomb previously described with all the internal fittings except the crucible, metal rods, platinum wire from the electrode, platinum fuse wire, 1 ml of distilled water, and 30 atm of oxygen.

The calculations involving reductions to a standard state were done on the IBM 360/65 computer using the program written by Wilhoit (*28*). The method used in this program follows the outline of Hubbard et al. (*10*).

The basic unit of energy used in these investigations was the absolute joule as transferred to this laboratory by means of National Bureau of Standards standard sample 39i benzoic acid (*14*). The energy values can be converted to the customary thermochemical unit by use of the following definition (*21*):

$$1\ \text{cal}_{th} = 4.184\ \text{(exactly) abs J}$$

The energy equivalent of the bomb calorimetric system was determined by measuring the temperature rise produced by the combustion of a weighted quantity of National Bureau of Standards sample 39i benzoic acid for which the heat of combustion is very accurately known.

The experimental results reported are based on 1961 atomic weights (*4*), and the ice point was taken as 273.15K.

Calorimetric results. A minimum of five successful determinations was made.

The value of $\Delta E_c°/M$ (Table II) refers to standard idealized combustion reactions for the spiroalkane at 298.15K. The combustion reaction of the compound is represented by Equation 1. The mean value and standard deviation of $\Delta E_c°/M$ are $-(11041.62 \pm 0.48)$ cal g^{-1}. Auxiliary data consisting of density, heat capacity, and $(\partial E/\partial p)_T$ are summarized in Table III. Values in parentheses are estimates. The density value was obtained from American Petroleum Institute Research Project 42, reporting on properties of hydrocarbons synthesized at Pennsylvania State University (*1*).

$$C_{26}H_{50}(l) + 38\tfrac{1}{2}\,O_2(g) \rightarrow 26\,CO_2(g) + 25\,H_2O(l) \quad (1)$$

Enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ were taken to be −94.051 and −68.315 kcal mol^{-1}, respectively (*23, 27*). Uncertainties assigned were 0.011 kcal mol^{-1} for $CO_2(g)$ (*21*) and 0.010 kcal mol^{-1} for $H_2O(l)$ (*22*).

Enthalpies of Vaporization

Apparatus and procedure. An LKB 8721-3 vaporization calorimeter was employed to make the experimental determinations at 25°C. The operation of this instrument has been described previously (*25, 26*). Temperature control was ±0.002°C. Sample size was about 80 mg. The spiroalkane samples were transferred to the calorimeter cell by syringe under a dry nitrogen atmosphere. The calorimeter cell ports were sealed, and the sample was weighed. Originally, four spiroalkanes were being investigated: spiro[4.5]decane, spiro[5.5]undecane, spiro[5.6]dodecane, and 7-*n*-hexadecylspiro[4.5]decane. The vapor pressures of these compounds have been estimated from the vapor-pressure data of Naro (*16*) and are shown in Table IV. The vapor-pressure range of the LKB calorimeter is 0.5–200 mm. Measurements on the [5.6] and the substituted spiro[4.5]decane were attempted, but an adequate rate of evaporization could not be achieved. Therefore, only the [4.5] and [5.5] spiranes were capable of being measured with the unmodified LKB unit. The operation of the instrument was continually monitored by determining the enthalpies of vaporization of two selected test substances, carbon tetrachloride and cyclohexane (Matheson

Table II. Observed Data for Typical Combustion Experiment for 7-*n*-Hexadecylspiro[4.5]decane

Characteristics	Value
Mass of sample, m_1, g	0.38484
Mass of oil, m_2, g	0.14108
Mass of ampul, m_3, g	0.08311
Mass of fuse, m_4, g	0.00101
Initial temp of calorimeter, t_i, Ω	0.0211607
Heat exchange correction, t_{corr}, Ω	0.0025450
Corrected final temp, $t_f - t_{corr}$, Ω_f	0.1390690
Correction for nitric acid, $\Delta E_{dec}(HNO_3)$, cal	0.07
Isothermal bomb energy, ΔE_B, cal	−5854.55
Correction to standard state, ΔE_Σ, cal	1.73
Energy for combustion at 25°C, $\Delta E_c°/M$, cal g^{-1}	−11042.33

Table III. Auxiliary Data for Combustion Study at 298.15K

Compound	Formula	ρ,[a] g cm^{-3}	C_p, cal g^{-1} deg^{-1}	$\left(\frac{\partial E}{\partial p}\right)_T \times 10^3$ cal g^{-1} atm^{-1}
7-*n*-Hexadecyl-spiro[4.5]-decane	$C_{26}H_{50}$	0.8596	(0.389)[b]	−(3.14)[b]

[a] See ref. *1*. [b] Values in parentheses are estimates.

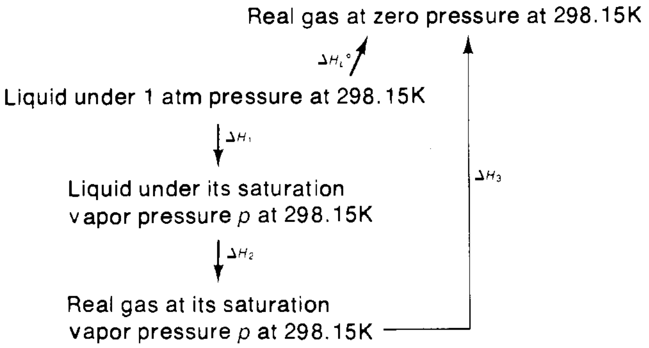
Table IV. Estimated Vapor Pressures of Spiroalkanes at 298.15K

Molecular formula	Substance	Vp, mm Hg
$C_{10}H_{18}$	Spiro[4.5]decane	1.72
$C_{11}H_{20}$	Spiro[5.5]undecane	0.38
$C_{12}H_{22}$	Spiro[5.6]dodecane	0.16
$C_{26}H_{50}$	7-*n*-Hexadecylspiro[4.5]decane	2.16×10^{-6}

Coleman & Bell spectrograde quality samples). The enthalpies of vaporization of these substances were determined earlier, and a comparison between the enthalpies of vaporization obtained in this study and those values determined by Wadso (*25*) is shown in Table V. All measurements were performed at 298.15K.

Results and discussion. The experimentally determined enthalpies of vaporization are shown in Table VI. Some difficulties were experienced in achieving an adequate rate of vaporization, since the vapor pressures of these spiroalkanes were rather low. This is reflected in the precision of the values given in Table VI.

Data refer to the isothermal process (25.00°C) when the real gas is formed under its saturation pressure. The standard enthalpy of vaporization at 298.15K can be related to the enthalpy of vaporization measured at the saturation vapor pressure of the liquid by the cycle (*5*):



From the first law: $\Delta H_v° = \Delta H_1 + \Delta H_2 + \Delta H_3$. The quantities ΔH_1 and ΔH_3 may both be evaluated from:

$$\Delta H_1 = \int_1^p \left[-T\left(\frac{\partial v}{\partial T}\right)_p + v \right] dp \qquad (2)$$

and

$$\Delta H_3 = \int_p^0 \left[-T\left(\frac{\partial v}{\partial T}\right)_p + v \right] dp \qquad (3)$$

For 1 mole of an organic liquid, the value of the integrand in the equation for ΔH_1 is likely to be less than 100 cm^3. The value for the enthalpy in this equation will be largest for $p = 0$ and will then approach 100 cm^3 atm which is approximately 2 cal. Since a typical value of ΔH_2 is 10 kcal, with an uncertainty range of 5–20 cal, ΔH_1 can be neglected in the evaluation of the standard enthalpy of vaporization from the first law. For 1 mole of many organic vapors, the value of ΔH_3 will be in the range of 10^3–10^4 cm^3. The value for ΔH_3 will depend on p. For p less than 0.1 atm, it is permissible to write $\Delta H_v° = \Delta H_2 = \Delta H_v$, since for spiro[4.5]decane with a p = 0.002 atm, the integrand in Equation 3 is approximately 0.2 cal which is well within the experimental uncertainty. Thus, the measured enthalpies of vaporization are the same within experimental uncertainties as the standard enthalpies of vaporization.

By combining the previously determined values of the standard enthalpies of formation in the liquid state (*24*) and the values determined for the standard enthalpies of vaporization, the standard enthalpies of formation in the ideal gaseous state have been derived and are reported in Table VII.

Since the development of an ideal gaseous state correlation procedure for the enthalpies of formation of the spiroalkanes is not possible based on the values available for only two key substances, suggestions for future work would include determinations of the enthalpies of vaporization of at least the remaining two spiroalkanes (*24*). From the experimental data, an appropriate correlation procedure for the gaseous state could then be developed. It is expected that the nonbonded interactions and eclipsed contributions in the liquid state would be reduced in magnitude owing to the enhanced flexibility of the strained spiroalkane in the gaseous state.

Table V. Comparison of Calorimetric Measurements at 298.15K

Substance	$\Delta H_v°$, cal mol^{-1} This work	$\Delta H_v°$, cal mol^{-1} Ref 25	No. determinations
Carbon tetrachloride	7732 ± 10[a]	7752 ± 6	6
Cyclohexane	7875 ± 9	7886 ± 5	6

[a] Each value reported is the mean value. Uncertainties refer to twice the standard deviation of the mean.

Table VI. Enthalpies of Vaporization of Spiroalkanes at 298.15K

Substance	$\Delta H_v°$, cal mol^{-1}	No. determinations
Spiro[4.5]decane	13127 ± 21[a]	8
Spiro[5.5]undecane	13417 ± 30	9

[a] Each value reported is the mean value. Uncertainties refer to twice the standard deviation of the mean.

Table VII. Enthalpies of Formation in Ideal Gaseous State at 248.15K

Substance	$\Delta H_f°$, kcal mol^{-1}
Spiro[4.5]decane	−34.68 ± 0.53[a]
Spiro[5.5]undecane	−44.81 ± 0.75

[a] Uncertainties refer to twice the standard deviation of the mean.

The study represents the second in a series of thermochemical investigations dealing with the tabulation of experimental data which will ultimately lead to an empirical understanding of the contribution that the central spiro-carbon atom makes to the overall energetics of the spiroalkane molecule and possibly to an adequate correlation procedure which will allow quantitative predictions of the enthalpies of formation of parent spiroalkane compounds and their alkyl derivatives.

Initial theoretical calculations indicate that destabilizing effects such as ring strains and nonbonded interactions make significant contributions to the enthalpy of formation of the spiroalkane compounds.

Acknowledgment

The authors gratefully acknowledge the assistance of members of the Thermodynamics Research Center staff for aid and cooperation in preparing the manuscript. The helpful discussions and suggestions of R. C. Wilhoit and G. R. Somayajulu were particularly encouraging. The API-PSU samples were provided by J. A. Dixon of Pennsylvania State University.

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Received for review October 21, 1974. Accepted April 16, 1975. This study partially supported by the API Research Project 44 of the Thermodynamics Research Center.

Permeation of Sulfur Dioxide Through Polymers

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Permeabilities, diffusivities, solubilities, and activation energies for permeation and diffusion are reported for the permeation of SO_2 through various polymers. Effects of gas pressure and humidity and membrane plasticization on SO_2 permeabilities are summarized.

The permeability of a polymer to a gas or vapor is the ratio $J/(\Delta p/h)$, where J is the flux of the gas through a flat membrane of thickness h, and Δp is the partial pressure difference across the membrane. If the equilibrium sorption of the gas in the polymer varies linearly with the partial pressure in the gas phase and diffusion of the gas through the polymer is Fickian with a constant diffusivity, then

$$P = DS \tag{1}$$

where P is permeability, $cm^3(STP)/sec \cdot cm \cdot cm\ Hg$; D is diffusivity, cm^2/sec; and S is solubility, $cm^3(STP)/cm^3 \cdot cm\ Hg$.

The temperature dependence of gas permeabilities frequently follows an Arrhenius relationship

$$P = P_0 \exp\left(-E_p/RT\right) \tag{2}$$

where E_p is the activation energy for permeation. Techniques for the measurement of P, D, and S are reviewed by Crank and Park (*6*), and factors which affect the values of these parameters are discussed by Stannett (*34*).

SO_2 permeabilities of a number of materials have been measured at temperatures from 25° to 232°C, and activation energies for permeation have been calculated. This paper reports the results of these experiments. In the course of this study, a literature search on the permeation of SO_2 through polymers was carried out, covering references through April 1974. Relatively few reported permeabilities were found, but a number of papers presented permeation rate data from which permeabilities could be calculated. These calculations have been performed, and the results are also reported in this paper.

Experimental

Span gas mixtures of SO_2 in air with SO_2 concentrations in the range 1,000–10,000 ppm were passed on one side of a flat polymer membrane or on the outside of a hollow tube in a thermostatically controlled oven. SO_2 permeated through the polymer into a carrier gas stream of pure air, which passed to an SO_2 analyzer. The SO_2 permeation rate was calculated as the product of the carrier gas flow rate and the SO_2 concentration in this gas at steady state; the permeability of the polymer to SO_2 was then calculated from the permeation rate, the SO_2 partial pressures in the span gas and the carrier gas, and the dimensions of the membrane or tube.

The experimental and calculational procedures for determining permeabilities and the permeation chamber used for hollow tubes are described in detail by Rodes et al. (*23*). A two-piece hollow stainless-steel cylinder with o.d. = 7.62 cm, i.d. = 5.08 cm, and outside height = 7.0 cm was used as a permeation chamber for flat membranes. The membranes were clamped between the two halves of the chamber, and the span gas and carrier gas were fed into the chamber on opposite sides of the membrane. The entrance and exit ports were situated so that the gases entered tangentially and swept across the entire membrane surface before exiting.

Span gas SO_2 concentrations were determined by passing a measured volume of the gas through a 3% H_2O_2 solution to absorb the SO_2, and then titrating with a 0.01N barium perchlorate solution in the presence of Thorin indicator (*9*). Carrier gas SO_2 concentrations were measured with a Meloy Laboratories Model SA-160 total sulfur analyzer or an Envirometrics Model NS-300M SO_2 analyzer.

Permeabilities, Diffusivities, and Solubilities

Materials for which SO_2 permeabilities, diffusivities, and/or solubilities have been found include TFE Teflon, FEP Teflon, several silicone and fluorosilicone rubbers, polyvinyl fluoride (Tedlar), polyvinylidene fluoride (Kynar), polycarbonate (Lexan), polyethylene, polypropylene, polyvinyl chloride, copolymers of polyvinyl chloride and polyvinylidene chloride, several natural rubbers, polyisobutene, polymethyl methacrylate, polyethylterephthalate (Mylar), several cellulosic films, a

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