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Enthalpies of Combustion of 1,1,4,4-Tetramethylcyclodecane and of 1,1,5,5-Tetramethylcyclodecane in the Liquid State

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Enthalpies of combustion of 1,1,4,4-tetramethylcyclodecane and of 1,1,5,5-tetramethylcyclodecane in the liquid state have been determined. For the 1,1,4,4 compound $-\Delta H_c^\circ(l, 298.15 \text{ K})/\text{kJ mol}^{-1} = 9172.7 \pm 1.2$ and for the 1,1,5,5 compound $-\Delta H_c^\circ(l, 298.15 \text{ K})/\text{kJ mol}^{-1} = 9182.2 \pm 1.7$. The difference between the enthalpies of combustion is $9.5 \pm 1.4 \text{ kJ mol}^{-1}$. A possible correction of about $+0.02\%$ to be applied to $-\Delta H_c^\circ$, connected with the presence of dissolved air in the samples, is discussed. The densities, required for buoyancy corrections, were determined.

Introduction

In this article is described the combustion-calorimetric part of the study by Bixon, Dekker, Dunitz, Eser, Lifson, Mosselman, Sicher, and Svoboda (4) about structural and strain-energy consequences of "intraannular" substitution in the cyclodecane ring. The samples of 1,1,4,4-tetramethylcyclodecane and of 1,1,5,5-tetramethylcyclodecane were provided by Svoboda, Yudin, and Sicher. The syntheses, purification, and purity control have been described (16).

Experimental Section

Apparatus. The temperature of the isoperibol combustion bomb calorimeter (6-8, 13) was measured with the platinum resistance thermometer and the Smith method No. 3 bridge described in ref 13.

The calorimeter was calibrated with benzoic acid, National Bureau of Standards sample 39i, certified to have a specific internal energy of combustion of 26434 J g^{-1} under so-called certification conditions (12).

The method of enclosing the volatile sample was the version of the covered crucible method (14) that has been indicated in footnote a of that reference.

For particulars concerning the balance for weighing the sample and concerning ancillary equipment for the resistance measurements, see ref 13. To ensure the constancy of the amount of water in the calorimeter can (apart from a buoyancy correction, ref 13) within a series of combustions, a balance was used having a reproducibility of 50 mg at a maximum load of 5 kg per pan.

Materials. The oxygen used in the combustion bomb was first passed through a purifier (1), designed for the removal of oxidizable impurities, as a matter of routine.

The organic impurity content of the samples to be burned was less than 0.05% (16).

Procedure. This was essentially as described in ref 13. The sample was ignited when the calorimeter temperature had reached 25.00°C . The amount of sample was chosen so that a final temperature of 27°C was obtained. The jacket temperature was about 26.0°C , with a stability of about $\pm 0.001^\circ\text{C}$. Variations were accounted for (12). The initial and the final rating period were 4 and 8 min, respectively. In the least-squares method, both periods were approximated as straight lines (12). The reaction period was taken as only 11.5 min in order to speed up the experiment. This duration is somewhat too short for the thermal equilibration to be complete, but the error arising from this fact, in the order of 0.01%, is the same in a calibration with benzoic acid, and, therefore, cancels.

Units and Auxiliary Quantities. Throughout this section, 1 bar = 10^5 N m^{-2} . In the bomb was placed 1 cm^3 of water and the bomb was flushed with oxygen in order to remove the air from its interior (9). The bomb was charged with oxygen to a pressure of 30.9 bar at 25.00°C . The volume of the bomb available to the reactants and the water was 0.3360 dm^3 .

For the combustible auxiliary substances we measured and used the following values valid at 25.00°C : Vaseline, $-\Delta u_c^\circ/\text{J g}^{-1} = 45997.8 \pm 2.8$; cotton thread used as the fuse, $-\Delta u_c^\circ/\text{J g}^{-1} = 16470$. Δu_c° is the change in internal energy upon combustion, with the reactants and the products in their standard states. The uncertainty interval represents twice the standard deviation of the mean of the series of combustions. The elemental composition of the Vaseline was $\text{C}_{17}\text{H}_{34}$ and its density 0.854 g cm^{-3} .

The water content of the samples was determined by means of the Karl Fischer dead-stop method (2). The 1,1,4,4 compound and the 1,1,5,5 compound were found to have a water content of $0.008 \pm 0.002\%$ and of $0.011 \pm 0.004\%$, respectively. The uncertainties given are estimated maximum uncertainties.

The samples as weighed were saturated with air. Because of uncertainty as regards the exact value of the correction, for this aspect, to be applied to the weighed masses, enthalpies of combustion are given at this stage as calculated from the uncorrected mass. The correction to $\Delta H_c^\circ(l)$ should be about 0.02-0.03%; see for instance ref 3.

The vapor pressure of the substances was low enough to allow one to neglect, in the buoyancy correction of weighed masses, the presence of vapor in the gas space of the closed crucible.

The values of the densities of the samples, used to calculate the buoyancy correction and reduction to standard states (10),

Table I

Expt no.	Mass/g		$\Delta R/\Omega^b$	$B/J \Omega^{-1} c$	$e_f(\text{cont})/J \Omega^{-1} d$	$\Sigma -\Delta u(i)/J^e$	RSS/J ^f	w_{ign}/J^g	$-\Delta u_c^\circ/J g^{-1}$
	Sample ^a	Vaseline							
				1,1,4,4					
1	0.396 752	0.022 255	0.139 577 9	-0.5	294.4	14.52	12.6	3.50	46 620.3
2	0.369 878	0.018 257	0.129 312 3	-0.7	291.9	14.01	12.4	3.50	46 620.3
3	0.336 902	0.041 250	0.125 898 8	-0.3	291.0	15.50	12.2	3.50	46 621.4
4	0.345 297	0.017 342	0.120 829 5	+0.2	290.5	13.11	12.2	3.50	46 624.8
								Mean	46 621.7
								Standard deviation	1.1
				1,1,5,5					
1	0.294 968	0.036 360	0.110 410 6	-1.9	282.8	10.89	11.9	3.36	46 674.7
2	0.299 894	0.018 746	0.106 247 8	-1.1	281.8	12.57	11.8	3.36	46 661.2
3	0.337 724	0.051 567	0.129 691 8	0.0	291.8	15.45	12.4	3.50	46 675.4
4	0.297 334	0.049 665	0.115 594 8	+0.3	288.3	16.67	12.1	3.50	46 668.3
								Mean	46 669.9
								Standard deviation	3.3

^a Mass corrected for water content and for buoyancy effects. ^b Increase in resistance of the thermometer, corrected for the effect of heat exchange between the calorimeter and its surroundings. ^c Buoyancy correction to be added to $\epsilon(\text{calor})$ owing to atmospheric conditions differing from normalized. ^d Energy equivalent of the contents of the bomb in their final state; $m(\text{Pt})/g = 12.2$ except in expt 1,1,5,5 no. 1 and 2, where it was 10.3; the mean temperature coefficient of the resistance of the thermometer (dR/dT)/ $\Omega K^{-1} = 0.061 819$ between 25 and 27 °C. ^e Sum of the energy of combustion of the fuse (7–10 J) and the energy change due to formation of nitric acid (4–7 J). ^f Reduction to standard states, calculated according to ref 10; the correction is to be applied so that it makes Δu_c° less negative than the internal energy change in the isothermal bomb process. ^g Electrical ignition energy.

Table II

	$-\Delta U_c^\circ(l)/kJ mol^{-1}$	$-\Delta H_c^\circ(l)/kJ mol^{-1}$	$-\Delta H_f^\circ(l)/kJ mol^{-1}$
1,1,4,4-Tetramethylcyclodecane	9155.35 ± 1.2	9172.70 ± 1.2	338.06 ± 1.2
1,1,5,5-Tetramethylcyclodecane	9164.81 ± 1.7	9182.16 ± 1.7	328.60 ± 1.7
Difference	9.5 ± 1.4		

were found to be, at 21 °C, 0.852 g cm⁻³ for the 1,1,4,4 compound and 0.846 g cm⁻³ for the 1,1,5,5 compound. An estimated value, 1.1 mm³ g⁻¹ K⁻¹, was used for $(1/m)(\partial V/\partial T)_p$ in the calculation of the sample compression term in the reduction to standard states.

The internal energy of solution of oxygen at a pressure of 31 bar in the sample was estimated, on the basis of solubility data for other compounds (see, e.g., ref 3), to be negligible.

The enthalpies of formation of CO₂(g) and H₂O(l), -393.51 and -285.830 kJ mol⁻¹, respectively, were taken from the CODATA report (5). The atomic weights used were those recommended by IUPAC in 1971, C = 12.011, H = 1.0079, which yields M = 196.3752.

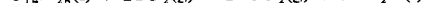
Results

For the energy equivalent of the empty calorimeter, $\epsilon(\text{calor})$ (12), 139.726 J Ω^{-1} was used. This figure pertains to the situation where the adjustment of the amount of water in the calorimeter, by weighing against fixed weights, would have been made under normalized atmospheric conditions, viz., the density of air is 1.200 g dm³.

A temperature rise of 2 °C required about 0.66 g of benzoic acid. For the auxiliary quantities concerning the calibration, see ref 12. For our bomb conditions, the energy of combustion calculated according to ref. 10 was 26 433.2 J g⁻¹.

The reduction of the isothermal bomb process, for the hydrocarbon combustions, to the process with all the compounds in their standard states was effected according to ref 10. The corresponding amount of energy is listed in Table I under the heading "RSS". A correction for energy of condensation of the part of the sample present in the closed crucible as a vapor was calculated to be negligible.

In Table II are listed the molar internal energy and enthalpy changes, $\Delta U_c^\circ(l)$ and $\Delta H_c^\circ(l)$, respectively, for the reaction



at 298.15 K with all the components in their standard states.

The enthalpy change was calculated from the internal energy change according to $\Delta H_c^\circ(l) = \Delta U_c^\circ(l) + RT\Delta n(g)$ with $R/J K^{-1} mol^{-1} = 8.3143$ and the change in the number of moles of gas in the reaction equation, $\Delta n(g)/mol = -7$.

The uncertainty interval (15) in ΔU_c° was calculated as the root of the sum of the squares of the following noninterdependent quantities (ppm): (a) estimated uncertainty in the weight of the sample as a consequence of the systematic use of certain weights in the balance, 20; (b) uncertainty in the energy equivalent of the calorimeter, two times the standard deviation of the series of ten benzoic acid calibrations, 35; (c) uncertainty in the certification value of benzoic acid, 110; (d) one-tenth of the uncertainty of the energy of combustion of Vaseline, according to the ratio of the energy productions, 10; (e), uncertainty in the series of sample combustions, two times the standard deviation of the series, 45 for the 1,1,4,4 and 140 for the 1,1,5,5 isomer of tetramethylcyclodecane; (f) estimated maximum uncertainty in the determination of the water content of the samples, 20 and 40 for the 1,1,4,4 and the 1,1,5,5 isomers respectively. The uncertainties in the enthalpies of formation of CO₂ and H₂O were not, at present, incorporated in the uncertainty of ΔH_f° for the hydrocarbons since the situation with respect to the graphite sample used for the determination of $\Delta H_f^\circ(\text{CO}_2)$ is not sharply defined (5). Therefore, the uncertainties in ΔH_f° of the samples are given here as the same figures as those in their ΔH_c° .

In the calculation of the uncertainty of the entry "Difference" in Table II, only the items (e) and (f) enter, since the other items are common to both substances.

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Physical and Thermodynamic Properties of 1,1,2-Trifluorotrchloroethane (R-113)

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The critical temperature, vapor pressure, liquid densities, and $P-V-T$ relations for R-113 were measured from 0.1 to 1.2 times the critical density. The physical properties were correlated to appropriate equations and consistent thermodynamic tables and graphs generated.

Introduction

The compound 1,1,2-trifluorotrchloroethane (R-113) is a well-known solvent and refrigerant. In recent years, there has been an increasing use of R-113 in high-temperature and high-pressure applications. A review of the thermodynamic properties shows that there is a lack of data in this region of interest. To assist designers in these applications, it was felt that improved and extended thermodynamic data should be developed. Thus, physical properties were measured, and a comprehensive thermodynamic table was generated.

The physical properties measured were the critical temperature, vapor pressure (from the freezing point to the critical temperature), liquid densities, and $P-V-T$ relations from 0.1 to 1.2 times the critical density. The ideal heat capacities were obtained from the work of Higgens and Lielmezs (7). These values were corrected for the asymmetrical top contribution.

The thermodynamic properties were computed from the equations used to represent the physical properties of R-113 using thermodynamic relationships as described by Martin (13). The tables and graphs compiled are complete and thermodynamically consistent.

Experimental Work

(a) **Sample Preparation.** A sample of R-113 was distilled in a 5-ft vacuum-jacketed column with Podbielniak "Heli-Pak" packing. A heart cut, based on gas chromatography, was taken and a 1-kg sample obtained. The sample was dried, degassed

(15) and vacuum transferred to an evacuated cylinder. A purity of 99.99+ (area %) was obtained as measured by gas chromatography and this sample was used for all the physical property measurements. All transfers were performed on a vacuum line to ensure a dry and air-free sample.

(b) **Critical Temperature.** The critical temperature was determined by observation of the meniscus in a sealed glass tube. The technique has been previously described (15). All temperatures were measured with a calibrated platinum resistance thermometer (U.S. National Bureau of Standards °C. Int., 1968) using a L&N "Speedomax" G resistance recorder to ± 0.01 °C.

(c) **Saturated Liquid Densities.** The liquid densities were determined by a float technique which was found to be accurate to 0.1% over the range covered (15). The float density was corrected for the thermal expansion of glass from its calibration temperature at 23 °C.

(d) **Vapor Pressure.** The saturated vapor pressure was measured over the range from -22 °F to the critical temperature using three techniques. (1) At temperatures below room temperature and subatmospheric pressures, the vapor pressures were measured directly using a mercury manometer and a cathetometer. The accuracy of these measurements was better than 0.1%. (2) From temperatures just below room temperature to above room temperature and to about 25 psia, the vapor pressures were obtained by means of an isoteniscope and a mercury manometer. The accuracy of these measurements was better than 0.1%. (3) For high temperatures and pressures a calibrated null point pressure transmitter and balancing system was used (15, 17). The balancing pressure was read on calibrated 16-in. Heise gauges (0-100, 0-300, and 0-1000 psi). Periodically pressures were checked with a Harwood controlled clearance pressure gauge. These gauges were accurate to 0.1% of the full scale reading. All samples were thermostated in liquid baths using various fluids at different temperatures or in an air oven which were controlled to ± 0.02 and ± 0.05 °F, respectively. The bath temperatures cycled over a time span