Heat of Formation of Tetranitromethane by Combustion Calorimetry

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Energy of combustion of liquid tetranitromethane with gaseous carbon monoxide was determined, and the data was used to calculate the enthalpy of combustion at 25° C. and the standard heat of formation of tetranitromethane: −508.7 and +8.8 kcal. per mole, respectively, with an estimated over-all uncertainty of ±0.7 kcal. per mole.

VALUES REPORTED for the heat of decomposition of tetranitromethane are in poor agreement and use of these data to calculate the heat of formation give the values −4.5 (*1*), +25 (*5*), and +8.9 (*4*) kcal. per mole. Since tetranitromethane is an attractive liquid oxidizer it was considered important to measure the heat of combustion and to determine the heat of formation with some certainty. The method selected was combustion with carbon monoxide since, according to Equation 1, the products are simple gases and appreciable heat is evolved in the reaction per gram of tetranitromethane

$$C(NO_2)_4(\text{liq}) + 6CO(g) \rightarrow 7CO_2(g) + 2N_2(g) \qquad (1)$$

EXPERIMENTAL

Material. The tetranitromethane was used as received from the Hummel Chemical Co. Vapor-liquid chromatographic and infrared analyses indicated a purity better than 99.9%.

The carbon monoxide (Matheson Co., C.P. grade) had a minimum purity of 99.5% and contained no contaminants detectable by infrared analysis.

Apparatus. The combustion experiments were carried out using a Parr No. 1101 double-valve bomb in a Series 1300 isothermal jacket calorimeter. Temperature increments were measured with a calibrated mercury thermometer accurate to ±.002° C. The calorimeter was calibrated with standard benzoic acid having a heat of combustion at constant volume of 6318 cal. per gram under certificate conditions. Seven combustions of benzoic acid yielded a value of 2478 cal. per degree for the energy equivalent of the calorimeter at 25° C. The average deviation from the mean in these experiments was 0.2% and the maximum deviation was 0.4%.

Procedure. The assembled bomb containing the sample was flushed several times with carbon monoxide at 30 atm. pressure in order to eliminate atmospheric oxygen. The bomb was then charged with carbon monoxide at 30 atm. pressure and allowed to come to thermal equilibrium. Subsequent operations were identical to those used in conventional oxygen bomb calorimetry.

The tetranitromethane was contained in a specially fabricated deep cylindrical cup (SS 316) to minimize evaporation losses during the weighing and flushing operations. These losses in sample exposure time and number of flushing operations were determined in blank runs and corrections were applied to the sample weight in the combustion experiments. Preliminary work with glass ampule and borosilicate glass sample holders indicated no significant improvement in precision over the metal cup.

A high heat input was needed to assure ignition of the tetranitromethane with the carbon monoxide; therefore, a 12.5-cm. length of No. 30 B. & S. Nichrome wire was substituted for the conventional 10-cm. length of No. 34 B. & S. Chromel C fuse wire. These wire types are essentially the same composition. The electrical energy input by the fuse wire was determined calorimetrically as a function of ignition time in a series of blank runs. A correction was then applied for the excess energy input of the nichrome fuse above that of the chromel fuse employed in the calorimeter calibration.

In contrast with conventional combustion experiments in an oxygen atmosphere, the oxidation of the fuse wire is a result of reaction with the tetranitromethane sample. As a consequence, less carbon monoxide is oxidized to carbon dioxide by the tetranitromethane, and less heat is evolved than would be expected according to Equation 1. From the known heat of combustion of the wire, 1400 cal. per gram, this correction was calculated to be 0.19 cal. per cm. of fuse wire consumed.

Complete combustion of the tetranitromethane was obtained in each of the experiments given in Table I as evidenced by infrared analysis of the product gases sampled by venting into an evacuated system. Incomplete combustions were easily noted by the presence of nitrogen oxides in the gas phase, and the runs were rejected. No residual or partially-burned material was found in the bomb after any run.

Table I. Heat of Combustion of Tetranitromethane in Carbon Monoxide

		Cor., Cal.		ΔE_c	
Sample Wt., G.	Temp. Rise, ° C.	Elec. input	Fuse wire	Cal.	Cal./g.
1.7221	1.816	2.87	0.72	4490	2607
1.7750	1.883	32.61	0.49	4626	2606
1.7173	1.823	32.61	0.57	4476	2606
1.7149	1.816	32.61	0.67	4462	2602
1.8237	1.928	23.69	0.72	4748	2603
1.7839	1.880	14.77	0.80	4639	2600
				Mean	2604
				Standard deviation	2.52

RESULTS

The data are summarized in Table I. Columns under ΔE_c, give the change in internal energy on combustion under standard conditions and include Washburn corrections calculated by the procedures of Hubbard, Scott, and Waddington (*2*) but with modifications due to the carbon monoxide–rich reactant and product gases.

The enthalpy of combustion at 25° C. calculated from these data is −508.7 kcal. per mole with an estimated over-all uncertainty of ±0.7 kcal. per mole. The largest single source of error is the limited accuracy of the mercury thermometer used to measure the temperature increments.

Using the values −26.4157 and −94.0518 kcal. per mole for the standard heats of formation of CO and CO_2 (*3*), the standard heat of formation of tetranitromethane at 25° C. is calculated to be +8.8 ± 0.7 kcal. per mole, and is in agreement with the results obtained by Roth and Isecke.

LITERATURE CITED

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Heat of Vaporization and Vapor Pressure of 1,4-Dioxane

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The heat of vaporization and the vapor pressure of 1,4-dioxane were measured at 100.1 and 100.5° C. The heat of vaporization was compared with a value from the literature and with a value from the Clapeyron equation. All of the published vapor-pressure data were correlated with an equation which was then differentiated to obtain the slope *dP/dT* needed in the Claypeyron relation. The over-all comparison indicates the vapor pressure between 0.5 and 1.5 atm. may be slightly in error.

BECAUSE DIOXANE is a widely used solvent, it is useful to know its latent heat of vaporization and to have a correlation of the vapor pressure over a wide temperature range. Only one measurement of the latent heat of vaporization has been reported (*9*) previously, while three investigators (*1, 2, 5*) have studied the vapor pressure. The vapor pressure data have not been correlated, however, and the latent heat has not been independently corroborated.

APPARATUS AND PROCEDURE

The equipment (*10*) is a flow device with vapor generated continuously in a calorimeter which is supplied with liquid slightly below the boiling point. The calorimeter is is thermally shielded by being situated inside a second continuous vaporizer. During a determination the vapor from the calorimeter is withdrawn from the system and condensed. The weight of condensate collected in a given time is compared with the electrical power input to obtain the latent heat. A very small correction is required for the sensible heat of the liquid in being raised to the boiling point.

The accuracy of the apparatus was checked by determining the latent heat of vaporization of doubly distilled water and Baker reagent-grade methanol. The latent heat of water was found to be 540.2 cal. per gram at 741 mm. (99.3° C.), which compares favorably with the most precise literature (*7*) value of 539.9 cal. per gram. The latent heat of vaporization of methanol was measured as 263.1 cal. per gram at 744 mm., which may be compared with reported (*4, 8*) values of 264.1 and 262.9 cal. per gram at 760 mm.

The sample of 1,4-dioxane (Carbide and Carbon Chemicals Co.) was allowed to stand over calcium chloride for several weeks before use. The boiling temperature showed no rising or declining trends over several consecutive determinations, while a mass spectrometer analysis, discussed later, showed 0.04% water.

RESULTS

Of eight determinations of the latent heat of vaporization of dioxane, four at 744 mm. and 100.5° C. gave an average latent heat of 96.53 cal. per gram with a standard deviation of 0.31 cal. per gram. The other four at 736 mm. and 100.1° C. gave an average latent heat of 96.56 cal. per gram with a standard deviation of 0.23 cal. per gram. In all cases the small sensible heat correction, always less than 2%, was made using a liquid specific heat estimated from a published (*3*) value.

The above results are consistent, but differ considerably from a published (*9*) value of 105.08 cal. per gram measured at 760 mm. To determine a further independent value, all available vapor pressure data were fitted with an equation which was then used in the Clapeyron relation to calculate the latent heat. The equation of Martin, Kapoor, and Shinn (*6*) was chosen because of its ability to fit general vapor pressure behavior with a high order of precision. The equation is

$$\log_{10} P = A + \frac{B}{T} + C \log_{10} T + DT + E\left(\frac{F-T}{T}\right)\log_{10}(F-T)$$

The constants were selected to give a good fit of the average vapor pressure data of the three published investigations. With pressure (*P*) in atmospheres and temperature (*T*) in ° K., the constants are:

A = 20.776007
B = −3205.5402
C = −5.0537764
D = 0.00064574875
E = 0.39512067
F = 596