Heat of Combustion of Phenyl-Beta-Naphthylamine (N-Phenyl-2-Naphthylamine)

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The heat of combustion of purified solid phenyl-beta-naphthylamine, (N-phenyl-2-naphthylamine) in forming gaseous carbon dioxide, liquid water, and gaseous nitrogen, has been determined from measurements with a bomb calorimeter. The value obtained ($-\triangle H_c^\circ$ at 25° C) is 37909.6 int j/g (1987.07 kcal/mole), with an estimated value of 8.3 int j/g (0.43 kcal/mole) for the standard deviation of the mean, obtained by making allowance for both accidental and systematic errors.

I. Introduction

Phenyl-beta-naphthylamine (N-phenyl-2-naphthylamine) is one of the most important materials used as stabilizers in the production of synthetic rubber. Stabilizers prevent continued polymerization, cross-linking, or cyclization, which would otherwise cause stiffening during storage of the unvulcanized synthetic rubber. The concentrations used range from 0.10 to 2.0 percent, depending on the type of rubber.

This material is also widely used as an antioxidant in the compounding of natural and synthetic rubbers prior to vulcanization. In this connection it retards oxidative deterioration of the product after vulcanization and improves its resistance to cracking and deterioration by heat. It is sold under the trade names Agerite Powder and Neozone D.

Data on the heat of combustion of phenyl-beta-naphthylamine are useful in interpreting the results of heat of combustion measurements on synthetic rubbers, and an accurate value may be desirable for other calculations.

II. Apparatus and Method

The measurements of the heat of combustion were made in a bomb calorimeter. The apparatus and procedure are the same as those described previously [1, 2, 3, 4, 5],[1] except in the following

[1] Figures in brackets indicate the literature references at the end of this paper.

respects: (1) The firing electrode was sealed into the head of the bomb with soda glass instead of the special glass previously used [3], (2) the bomb has two valves, and the carbon dioxide remaining in it after the pressure was reduced to atmospheric following a combustion was flushed out by passing purified oxygen through the bomb, instead of by alternately filling it to a pressure of several atmospheres and releasing the pressure [5].

The calorimetric system was calibrated with Bureau Standard Sample 39f of benzoic acid. The value used for the heat of combustion of this sample under the conditions of the standard bomb process was reported previously [4].

The amount of the combustion reaction in each measurement of heat of combustion was derived from the mass of carbon dioxide formed. The determination of the carbon dioxide, tests for carbon monoxide, and corrections for ignition energy, and for nitric acid formed were the same as described previously [6]. No carbon monoxide was detected in the gaseous products of combustion. A value of 60 kj/mole of nitric acid was used in correcting for the aqueous nitric acid (about 0.5 molar) formed in the bomb. This correction amounted to about 0.12 percent of the heat of combustion. The nitric acid represented about 7 percent of the total nitrogen present.

Using the procedure described by Washburn [7], modified so as to apply to 30° C and to the energy content of the gases at zero pressure instead of 1 atmosphere, the observed heat of combustion in

each experiment was reduced to the value of $-\Delta U_c^\circ$, the decrease in intrinsic energy accompanying the combustion reaction:

$$C_{16}H_{13}N(c) + \frac{77}{4} O_2(g) \rightarrow 16CO_2(g) +$$
$$\frac{13}{2} H_2O(l) + \frac{1}{2} N_2(g),$$
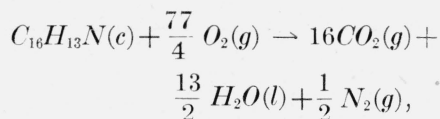
with each of the reactants and products in its thermodynamic standard state.

The energy unit used in the original calculation of the results is the international joule. Conversion of the results to terms of the conventional thermochemical calorie was made by use of the relation 1 calorie = 4.1833 int. j. Conversion to absolute joules may be made by use of the relation 1 int j = 1.000165 absolute j.

III. Material

The sample used was prepared by F. J. Linnig of this Bureau from a commercial grade material (Agerite Powder, supplied by the R. T. Vanderbilt Co.) by vacuum distillation and two recrystallizations from aviation gasoline. It consisted of nearly white needle crystals with a melting point of approximately 107° C.

Spectrochemical examination of the unpurified and purified samples of phenyl-beta-napthylamine was made by Martha E. Mayo of this Bureau to determine whether the recrystallized sample had been contaminated with lead from the aviation gasoline. Lead was not detected in either sample. Traces (less than 0.001%) of copper and silicon were found in the unpurified material.

IV. Results

The results of the calibration experiments with benzoic acid are given in table 1. The results of the measurements of heat of combustion of phenyl-beta-napthylamine are given in table 2, where $-\Delta U_B$ is the observed heat of combustion under the conditions of the bomb process [2], and $-\Delta U_c^\circ$ is the decrease in intrinsic energy accompanying the combustion reaction when the reactants and products are all in their thermo-

[2] The conditions of the bomb process are specified by the temperature (30° C) to which the combustion reaction is referred, the mass of water (1 g) placed in the bomb before each experiment, the internal volume of the bomb (377 ml), and the data given in columns 1 and 2 of table 2.

TABLE 1. *Calibration of calorimeter with benzoic acid*

Observed energy equivalent at 28.5° C int j/° C
13724. 7
13727. 6
13723. 9
13725. 0
13723. 1
13724. 5
13727. 5
13724. 2
13730. 4
13727. 0
13723. 2
13729. 3
13726. 8
Mean _____ 13725. 9
Standard deviation of the mean [1], s_E. 0. 6

[1] Standard deviation of the mean, as used here and in table 2, is defined as $[(\Sigma d^2)/n(n-1)]^{1/2}$, where d is the difference between a single observation and the mean, and n is the number of observations. In the case of the final values of heat of combustion given in table 3, the values given for the standard deviation include the effects of estimated systematic errors, as well as accidental errors. These values were calculated from the relation

$$s = Q[(s_E/E)^2 + (s_Q/Q)^2 + B^2 + R^2]^{1/2},$$

where s_E is the standard deviation of the mean of the experiments with benzoic acid to determine E, the energy equivalent of the calorimetric system; s_Q is the standard deviation of the mean of the results of the experiments to determine Q, the heat of combustion of the sample; B is an allowance of 5×10^{-5} for the standard deviation of the value used for heat of combustion of benzoic acid; and R is an allowance of 2×10^{-4} for systematic errors associated with the impurities in the sample and the determination of the amount of the combustion reaction from the mass of carbon dioxide.

TABLE 2. *Bomb-calorimetric measurements on phenyl-beta-naphthylamine*

Mass of sample	Initial O_2 pressure at 30° C	Mass of CO_2	Heat of combustion at 30° C	
			$-\Delta U_B$	$-\Delta U_c^\circ$
g	atm	g	int j/g CO_2	int j/g CO_2
0. 99480	32. 4	3. 19305	11802. 8	11795. 7
. 96981	32. 2	3. 11248	11801. 5	11794. 4
. 96304	32. 0	3. 09107	11799. 7	11792. 7
. 98986	32. 7	3. 17725	11801. 8	11794. 6
Mean _____				11794. 4
Standard deviation of the mean,[1] s_Q _____				0. 6

[1] See footnote 1, table 1.

dynamic standard states at 30° C. In table 3 are given values of heat of combustion per gram and per mole calculated from the mean value given in table 2, on the assumption that 16 moles (16 x 44.010 g) of carbon dioxide corresponds to 1 mole (219.272 g) of phenyl-beta-napthylamine ($C_{13}H_{13}N$.

TABLE 3. *Heat of combustion of phenyl-beta-naphthyl-amine*

	int j/g	int kj/mole	cal/g	kcal/mole
$-\Delta U_c^\circ (30°C)$	37875.8	8305.10	9054.05	1985.30
$-\Delta H_c^\circ (30°C)$	37907.4	8312.03	9061.60	1986.96
$-\Delta H_c^\circ (25°C)$	37909.6	8312.51	9062.12	1987.07
Standard deviation of mean[1], s	8.3	1.81	1.97	0.43

[1] See footnote 1, table 1.

The values obtained for the mass of carbon dioxide formed in combustion of phenyl-beta-naphthylamine were lower than the stoichiometric amounts calculated from the corresponding masses of sample burned by an average of 0.053 percent, indicating that some impurity was present in the samples. Several measurements of the carbon dioxide formed in combustion of Bureau Standard Sample 39f of benzoic acid yielded results in agreement with calculated values within less than 0.01 percent on the average. Both the benzoic acid samples and the phenyl-beta-naphthylamine samples were compressed into pellets, which burned completely, leaving no residue.

Two experiments on unpurified Agerite Powder yielded a value for heat of combustion per gram of carbon dioxide formed, which was 0.062 percent lower than that of the purified material. With the unpurified samples, the values obtained for the mass of carbon dioxide formed in combustion were lower than the stoichiometric amounts calculated from the corresponding masses of sample burned by an average of 0.135 percent.

The use of the mass of carbon dioxide formed as a measure of the amount of the combustion reaction is equivalent to assuming that the material burned consists of phenyl-beta-naphthylamine plus inert impurity. If this were true for both the purified and unpurified material, the same value of heat of combustion per gram of carbon dioxide formed would be obtained for both. The fact that different values were obtained for the purified and unpurified materials indicates that the assumption is not true for both materials, and it is not certain that it is true for either. It is possible, therefore, that the results for the purified material reported in tables 2 and 3 may be systematically in error by a few hundredths of a percent due to impurity in the material.

V. Previous Work

Lemoult [8] reported the values 9153.39 and 9166.79 cal/g (mean 9160.1 cal/g) as the results of calorimetric measurements of the heat of combustion of phenyl-beta-naphthylamine. His calorimeter was calibrated with naphthalene using 9,664 cal/g for its heat of combustion. No experimental details were given. His sample melted at 107.5° C and contained 6.18 percent of nitrogen (theoretical, by present atomic weights 6.39 percent). In terms of the energy unit used in the present work, the mean of Lemoult's results is calculated to be $-\Delta H_c = 1,999$ kcal/mole. This value was calculated with the aid of the values reported by Lemoult for naphthalene and phenyl-beta-naphthylamine, a value for the ratio of the heats of combustion of naphthalene and benzoic acid derived from the work of Dickinson [1], and the value [4] for the heat of combustion of benzoic acid used in the present work.

VI. References

[1] H. C. Dickinson, Bul. BS **11**, 189 (1914) S230.
[2] E. F. Mueller, Bul. BS **13**, 547 (1916) S288.
[3] R. S. Jessup and C. B. Green, J. Research NBS **13**, 469 (1934) RP721.
[4] R. S. Jessup, J. Research NBS **29**, 247 (1942) RP1499.
[5] R. S. Jessup, J. Research NBS **18**, 115 (1937) RP966.
[6] D. E. Roberts, W. W. Walton, and R. S. Jessup, J. Research NBS **38**, 627 (1947) RP1801.
[7] E. W. Washburn, BS J. Research **10**, 525 (1933) RP 546.
[8] P. Lemoult, Ann. chim. phys. [8] **10**, 395 (1907).

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