

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

## The Apparent Energy of the N-N Bond as Calculated from Heats of Combustion<sup>1</sup>

BY CARL M. ANDERSON AND E. C. GILBERT

Heats of combustion of suitable simple compounds in the gaseous state have offered the most direct approach to the calculation of bond energies,<sup>2</sup> and results recently obtained in this Laboratory on hydrazine<sup>3</sup> have been used thus to calculate the energy of the covalent N-N bond.<sup>2</sup> This calculation has also been made from data on the heat of combustion of phenylhydrazine and methylphenylhydrazine<sup>2,4</sup> giving somewhat different values. The combustion data on phenylhydrazine<sup>5</sup> are very discordant and it was thought that new and accurate data on combustion might give better agreement in the bond energy calculation. Redetermination of the heat of combustion was undertaken and in the meantime measurements on the velocity of dissociation of tetraphenylhydrazine by Cain and Wiselogle<sup>6</sup> indicated to them the possibility that the value for the N-N bond was subject to revision or re-interpretation of the data. Lewis and Lipkin<sup>7</sup> in turn have examined the conclusions of Cain and Wiselogle.

In an effort to provide additional data for the elucidation of this problem the heat of combustion of tetraphenylhydrazine has now been determined. Calculation of bond energies in the ordinary manner is precluded with such a compound since the heats of fusion and vaporization are unknown and presumably unobtainable. Were these available, there remains the question of resonance energy, which for complex molecules is still only a matter of estimate. This is true for instance with phenylhydrazine, which contains an undetermined amount of resonance energy.

An interesting approach is possible however in which the effect of several of these variables can be reduced to a minimum. This may be done by comparing the heat of combustion of structurally

similar molecules in pairs. For this purpose the following pairs were chosen and the various heats of combustion determined: (1) tetraphenylhydrazine and diphenylamine (2 moles); (2) phenylhydrazine and aniline; (3) benzamide (2 moles) and dibenzoyl hydrazide; (4) hydrazobenzene and aniline (2 moles). In the last instance the recent combustion data of Swietoslawski and Bobinska on hydrazobenzene were utilized.<sup>8</sup>

### Experimental

**The Calorimeter.**—The calorimeter used was of the adiabatic type and has been described previously.<sup>3,9</sup> It was recalibrated with the use of benzoic acid, Standard Sample No. 39e, Natl. Bur. Standards, and found to have the same heat capacity as reported in the earlier work, *i. e.*, 2607.3 cal. per degree. The precision attainable under optimum conditions with this calorimeter is 0.01–0.02%.

**Materials.**—The materials used in the combustions were prepared in the following ways. The physical constants given have only a general significance since the calorimetric measurements are much more sensitive to very small amounts of impurities than common criteria of purity.

**Aniline.**—A single sample, enough for twelve combustions, was prepared from Eastman Kodak Co. white label grade by vacuum distillation from zinc dust in a nitrogen atmosphere, collected over stick sodium hydroxide and redistilled.

**Benzamide.**—Benzamide was recrystallized from alcohol three times and dried at 60° in a vacuum oven twenty-four hours and over phosphorus pentoxide two days. The sample had a melting point of 130°.

**sym-Dibenzoylhydrazide.**—A large sample of dibenzoylhydrazide had been previously prepared by Albert Hughes of this Laboratory in 1938. A portion of this was recrystallized from ethanol and ethanol-water, dried in vacuum at 60° twenty-four hours and over phosphorus pentoxide three days. A melting point of 237–238° was found.

**Diphenylamine.**—Samples of diphenylamine were purified by each of the following methods: (1) recrystallized four to six times by precipitation from ethanol solution by adding water. (2) recrystallized three to four times from high boiling petroleum-ether. (3) the residues from the above procedure were steam distilled and recrystallized once from ethanol-water. The samples were dried over phosphorus pentoxide for two to four days before using them. Each of the samples had a melting point of 53°.

**Phenylhydrazine.**—Eastman Kodak Co. white label grade of phenylhydrazine was crystallized in a nitrogen atmosphere by cooling with cold water. About one-half of the material was crystallized out and the mother liquor was removed with a filter stick by suction. A given sample was crystallized four to six times before filling the bulbs

(1) Taken from the thesis submitted by C. M. Anderson in partial fulfillment of the requirements for the Ph.D. June 1942. Published with the approval of the Monographs Publication Committee, Oregon State College, as Research Paper No. 62, School of Science, Department of Chemistry.

(2) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, New York, 1940; O. K. Rice, "Electronic Structure and Chemical Binding," 1st ed., McGraw-Hill Book Company, Inc., New York, N. Y., 1940.

(3) Hughes, Corruccini and Gilbert, *THIS JOURNAL*, **61**, 2639 (1939).

(4) Sidgwick, Sutton and Thomas, *J. Chem. Soc.*, 406 (1933).

(5) Kharasch, *J. Research Natl. Bur. Standards*, **2**, 359 (1929).

(6) Cain and Wiselogle, *THIS JOURNAL*, **62**, 1163 (1940).

(7) Lewis and Lipkin, *ibid.*, **63**, 3232 (1941).

(8) Swietoslawski and Bobinska, *C. A.*, **24**, 1790 (1930).

(9) Davies and Gilbert, *THIS JOURNAL*, **63**, 2730 (1941).

The freezing point of each sample was 19.6° for at least the last two crystallizations. Phenylhydrazine purified in this manner retained a faint yellow color and slight odor.

Colorless and odorless samples were obtained by vacuum distillation in a nitrogen atmosphere of 400–500 cc. of the material collecting the middle 100-cc. fraction over stick sodium hydroxide and redistilling. These samples had a freezing point of 19.6° and rapidly turned yellow in contact with air.

Additional amounts of phenylhydrazine were prepared in this Laboratory according to the procedure given by Coleman.<sup>10</sup>

**Tetraphenylhydrazine.**—Tetraphenylhydrazine was prepared by the oxidation of diphenylamine with potassium permanganate in acetone solution according to the procedure given by Gattermann and Wieland.<sup>11</sup> Samples were recrystallized from benzene by precipitation with ethanol and were well washed with cold ether. These were then dried in the vacuum desiccator over phosphorus pentoxide for twenty-four hours. After standing three to four days the samples were rewashed with cold ether or recrystallized again. Melting points anywhere in the range of 145–175° could be obtained depending upon the rate of heating the melting point bath and the temperature at which the melting point tube was placed in the bath.

**Calculations.**—All weighings were *in vacuo*. The data are referred to a standard temperature of 25°. The energy unit used is the arbitrary calorie obtained by multiplying the international joule by the factor 4.1833. The technique and precautions were the same as described in the earlier work.<sup>3,9</sup>  $-\Delta U_B$ , the heat experimentally evolved in the bomb process per gram formula weight was first calculated. From this was obtained  $-\Delta U_R$  the decrease in energy for the combustion reaction at the standard state at constant volume, as defined by Washburn.<sup>12</sup> In making this calculation it was assumed that the nitrogen produced in the reaction may be treated as if it were oxygen and the correction equations modified appropriately.  $-\Delta H_R$ , the heat evolved in the isothermal process in the standard state at constant pressure was also calculated. The 1941 table of atomic weights was used.

## Results

The combustion data are shown in Tables I–VI, and collected values for the isothermal heats of combustion in comparison to earlier results in Table VII. Of the substances investigated the latent heat of vaporization at 25° is obtainable for only two, aniline<sup>13</sup> (*ca.* 12,000 cal./mole) and phenylhydrazine<sup>14</sup> (14,690 cal./mole). Utilizing these data and the accurately established heats of formation of water and carbon dioxide,<sup>15</sup>  $\Delta H_{298.1}$  for formation of aniline in the gaseous state is

(10) O. M. Coleman, "Organic Syntheses," Collective Volume I. John Wiley and Sons, Inc., New York, N. Y., 1941, p. 442.

(11) L. Gattermann and H. Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Co. New York, N. Y., 1937, p. 355.

(12) Washburn, *J. Research, Natl. Bur. Standards*, **10**, 544 (1933).

(13) Garrick, *Trans. Faraday Soc.*, **23**, 560 (1927).

(14) Williams, G. E., M.S. Thesis, 1942, Oregon State College.

(15) Rossini, *J. Research Natl. Bur. Standards*, **22**, 407 (1939).

TABLE I  
HEAT OF COMBUSTION OF ANILINE<sup>a</sup>

True mass of sample in grams	$\Delta T$ , <sup>b</sup> °C.	Total <sup>b</sup> heat, cal.	Heat from HNO <sub>3</sub> , cal.	$-\Delta U_B/m$ , cal./g.	Dev. from mean
0.84186	2.8107	7339.2	18.20	8696.2	-3.9
.74038	2.4729	6457.0	17.84	8697.7	-2.4
.73698	2.4623	6429.9	16.25	8702.7	+2.6
.81119	2.7103	7077.5	17.85	8702.9	+2.8
.86075	2.8748	7507.3	17.97	8700.9	+0.8

Mean  $\Delta U_B/m = -8700.1$  cal./g.

<sup>a</sup> Professor H. M. Huffman of the California Institute of Technology very kindly communicated his own values for the heat of combustion of aniline obtained some years ago. The few results here shown agree, perhaps fortuitously, almost exactly with his more precise determinations (see Table VII). <sup>b</sup> Corrected for the heat of stirring and for the combustion of the iron wire.

TABLE II  
HEAT OF COMBUSTION OF BENZAMIDE

True mass of sample in grams	$\Delta T$ , <sup>a</sup> °C.	Total <sup>a</sup> heat, cal.	Heat from HNO <sub>3</sub> , cal.	$-\Delta U_B/m$ , cal./g.	Dev. from mean
0.98378	2.4052	6280.9	16.51	7008.8	+1.4
.75424	2.0291	5298.4	13.93	7006.3	-1.1
.74775	2.0112	5251.9	12.40	7006.9	-0.5
.91260	2.4553	6411.5	16.39	7007.6	+0.2
.76797	2.0671	5395.0	14.13	7006.7	-0.7
.83282	2.2389	5846.4	14.18	7002.9 <sup>b</sup>	
.87296	2.3488	6133.4	15.89	7007.8	+0.4

Mean  $\Delta U_B/m = -7007.4$  cal./g.

<sup>a</sup> Corrected for the heat of stirring and for the combustion of the iron wire. <sup>b</sup> Not used in calculating the mean value.

TABLE III  
HEAT OF COMBUSTION OF DIBENZOYLHYDRAZINE

True mass of sample in grams	$\Delta T$ , <sup>a</sup> °C.	Total heat, cal.	Heat from HNO <sub>3</sub> , cal.	$-\Delta U_B/m$ , cal./g.	Dev. from mean
0.41701	1.11687	2916.2	8.28	6973.2	-0.1
.57335	1.53517	4008.5	10.29	6973.4	+0.1
.87038	2.4195	6084.1	14.13	6973.9 <sup>b</sup>	+0.6
.85797	2.3845	5996.1	13.74	6972.7 <sup>b</sup>	-0.6

Mean  $\Delta U_B/m = -6973.3$  cal./g.

<sup>a</sup> Corrected for heat of stirring and for the combustion of the iron wire. <sup>b</sup> These values were obtained previously by Hughes.

TABLE IV  
HEAT OF COMBUSTION OF DIPHENYLAMINE

True mass of sample in grams	$\Delta T$ , <sup>a</sup> °C.	Total heat, cal.	Heat from HNO <sub>3</sub> , cal.	$-\Delta U_B/m$ , cal./g.	Dev. from mean
0.75908	2.6347	6880.0	11.45	9048.6	+1.2
.75902	2.6352	6881.2	10.87	9051.6	+1.8
.97940	3.4008	8880.9	16.99	9050.3	+0.5
.74002	2.5677	6705.1	8.89	9048.7	-1.1
.71390	2.4792	6473.9	13.89	9048.8	-1.0
.94402	3.2765	8556.4	11.59	9051.5	+1.7
.85398	2.9635	7738.9	10.85	9049.4	-0.4

Mean  $\Delta U_B/m = -9049.8$  cal./g.

<sup>a</sup> Corrected for the heat of stirring and for the combustion of the iron wire.

TABLE V  
 HEAT OF COMBUSTION OF PHENYLHYDRAZINE

True mass of sample in grams	$\Delta T, ^\circ\text{C.}$	Total <sup>a</sup> heat, cal.	Heat from HNO <sub>3</sub> , cal.	$-\Delta U_B/m$ , cal./g.	Dev. from mean
1.03210	3.1937	8340.4	25.81	8056.0	+0.6
0.68679	2.1259	5551.5	19.52	8054.8	-.6
.60413	1.8705	4884.3	17.99	8055.1	-.3
.81049	2.5084	6550.4	19.75	8057.7 <sup>b</sup>	...
.86707	2.6812	7001.8	19.13	8053.2 <sup>b</sup>	...
.99564	3.0804	8044.5	24.30	8055.3	-.1
1.00967	3.1253	8161.7	27.54	8056.2	+.8
0.79900	2.4736	6459.4	23.65	8054.7	-.7
Mean $\Delta U_B/m = -8055.4$ cal./g.					

<sup>a</sup> Corrected for the heat of stirring and for the combustion of the iron wire. <sup>b</sup> Not used in calculating the average value.

 TABLE VI  
 HEAT OF COMBUSTION OF TETRAPHENYLHYDRAZINE

True mass of sample in grams	$\Delta T, ^\circ\text{C.}$	Total <sup>a</sup> heat, cal.	Heat from HNO <sub>3</sub> , cal.	$-\Delta U_B/m$ , cal./g.	Dev. from mean
0.36953	1.2843	3353.4	5.14	9060.8 <sup>b</sup>	+0.8
.36252	1.2612	3293.1	7.93	9062.0	+2.0
.33084	1.1509	3005.1	7.68	9060.0	+0.0
.57309	1.9936	5205.5	13.76	9059.1	-0.9
.36897	1.2829	3349.7	7.50	9058.1	-1.9
Mean $\Delta U_B/m = -9060.0$ cal./g.					

<sup>a</sup> Corrected for the heat of stirring and for the combustion of the iron wire. <sup>b</sup> A heavy nickel crucible was used in the bomb and the combustion was carried out under 20 atmospheres pressure of oxygen. Appropriate corrections were made in the calculations.

 TABLE VII  
 SUMMARY OF THE HEATS OF COMBUSTION MEASURED AND THE VALUES RECORDED IN THE LITERATURE

Substance	Heat of combustion, $\Delta H_R$ kcal./mole		Observer
	Found	reported <sup>b</sup>	
Aniline	- 810.55	- 812.7	Stohmann
		- 811.7	Lemoult
		- 816.7	Swartz
		- 810.48	Huffman <sup>c</sup>
Benzamide	- 848.76	- 847.6	Stohmann and Schmidt
Dibenzoylhydrazide	-1675.5		
Diphenylamine	-1531.9	-1536.2	Stohmann
		-1530.2	Lemoult
Phenylhydrazine	- 871.68	- 875.4	Lemoult
		- 805.4	Petit
Tetraphenylhydrazine	-3048.7		

<sup>b</sup> These values are those reported by Kharasch.<sup>5</sup> <sup>c</sup> Private communication (1942).

found to be +48.91, and for phenylhydrazine +19.25, kcal./mole. From the structures of the two compounds it is seen that the difference  $\Delta H = 29.66$  kcal./mole, involves any difference in resonance energies, the formation of an atom

of hydrogen and an atom of nitrogen, respectively, from their molecules ( $\Delta H = 136.7$  kcal.),<sup>2</sup> the formation of one N-H bond and the formation of one N-N bond. If the approximation used by Pauling is now made for the formation of the N-H bond, *i. e.*,  $\Delta H = 83.7$  kcal. (one-third of the energy required to dissociate the ammonia molecule completely in the gaseous state) the apparent energy of formation of the N-N bond becomes  $\Delta H = 23.3$  kcal. That the assumption of equality of resonance energy in the two molecules and the equivalence of the 3 N-H bonds in ammonia to each other and to N-H bonds in substituted ammonias is only an approximation is shown by the appreciable lack of agreement between the figure thus obtained for the N-N bond and that derived from combustion data on hydrazine itself ( $\Delta H = -20.0$  kcal.).<sup>2</sup>

If the heat of formation of gaseous phenylhydrazine alone is used, assuming a resonance energy of 6 kcal. per mole (the same as aniline<sup>2</sup>) and using Pauling's values for the remaining bonds, the energy of the N-N bond is 23.7 kcal.

The remaining compounds investigated are solids (except for aniline whose heat of fusion is known) and examination of the pairs chosen shows that in each case the difference in the heat of formation lies in the energy of two N-H bonds and one N-N bond. For solids however objection may be made to the simple assumption used previously that the energy of the N-H bond is one-third of the total required to dissociate the gaseous ammonia molecule, although such an assumption serves as a basis to show definite trends in the apparent value of the N-N bond in different compounds. A reasonable compromise can be made however by combining the heat of vaporization and fusion with the gaseous data on ammonia to arrive at an energy for the reaction (N-H) in solid ammonia  $\rightarrow$  N(g) + H(g)  
 $\Delta H = -85.9$  kcal.

By the use of this value qualitative allowance is made for lattice energies, etc. To test the comparative effect of such assumption the fusion and vaporization data for hydrazine<sup>16</sup> were also incorporated with the gaseous data on that compound and calculation made for the N-N bond in solid hydrazine. A value N-N = 22.3 kcal. was thus obtained, compared to 20.0 kcal. from the gaseous data.

Similarly for use with some of the pairs for (16) Hieber and Woerner. *Z. Elektrochem.*, **40**, 252 (1934).

which liquid data or heats of fusion are available a value of



may be obtained.

A summary of the apparent values of the N-N bond calculated from the various pairs, and using the three assumptions for the N-H bond is shown in Table VIII.

TABLE VIII  
CALCULATED ENERGY OF N-N BOND

Compounds compared	Assumption N-H = 85.9 kcal.	Assumption N-H = 83.7 kcal.	Assumption N-H = 85.4 kcal.
Tetraphenylhydrazine	solids 14.8	(10.5)	..
Diphenylamine	..	..	..
Dibenzoylhydrazide	solids 22.1	(17.7)	..
Benzamide	..	..	..
Hydrazobenzene	solids 29.4	(25.0)	..
Aniline	..	..	..
Hydrazobenzene	liquid ..	..	28.4
Aniline	..	..	..
Phenylhydrazine	gas ..	23.3	..
Aniline	..	..	..
Phenylhydrazine	liquid ..	..	24.5
Aniline	..	..	..
Phenylhydrazine	solids 25.9	..	..
Aniline	..	..	..
Hydrazine—solid	22.3	..	..
Hydrazine—liquid	..	..	23.3
Hydrazine—gas	..	20.0	..

These values, calculated on any basis, support the contention of Lewis and Lipkin<sup>7</sup> that the apparent strength of the N-N bond is dependent upon the substituents in the molecule. Further

work is under way in this Laboratory which it is hoped will throw additional light on this issue. By all calculations the value of the N-N bond in tetraphenylhydrazine thus obtained is considerably less than in any of the other compounds. The values for hydrazobenzene are somewhat out of line. Previous experience with the data of Swietoslowski and Bobinska indicate that their results may be on the low side.<sup>17</sup> Upward revision of their combustion data would reduce the value assigned to the N-N bond.

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### Summary

1. New data for isothermal heats of combustion of tetraphenylhydrazine and *sym*-dibenzoylhydrazide are reported.

2. Revisions of earlier data for the heat of combustion of aniline, benzamide, diphenylamine and phenylhydrazine are given.

3. Using certain arbitrary assumptions, values are computed for the energy of the N-N bond in tetraphenylhydrazine, *sym*-dibenzoylhydrazide, hydrazobenzene, and phenylhydrazine. The apparent value thus obtained depends on the substituents attached to the nitrogen.

(17) Corruccini and Gilbert, *THIS JOURNAL*, **61**, 2925 (1939).

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## The Heat Capacity of Organic Vapors. III. A Comparison of Flow Calorimeters

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The constant-flow calorimeter for measuring the heat capacity of vapors was devised by Callendar and adapted by Swann<sup>2</sup> to measure the specific heat of air. An improved calorimeter was described by Scheel and Heuse.<sup>3</sup> An outstanding example of good design is the calorimeter used by Osborne, *et al.*<sup>4</sup> Typical of the calorimeters used

(1) Present address; Hercules Experiment Station, Wilmington, Del. This paper is an abstract from the thesis submitted by J. B. Montgomery in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The second paper of this series appeared in *THIS JOURNAL*, **64**, 1224 (1942).

(2) Callendar and Barnes, *Trans. Roy. Soc. (London)*, **199A**, 55-263 (1902); Swann, *Proc. Roy. Soc. (London)*, **82A**, 147 (1909).

(3) Scheel and Heuse, *Ann. Physik*, (4) **37**, 79 (1912).

(4) Osborne, Stimson, Sligh and Cragoe, *U. S. Bur. of Standards, Sci. Papers*, **20**, 65-110, 119-151 (1925).

recently for measuring the heat capacity of organic vapors have been those described by Bennewitz and Rossner, De Vries and Collins, and Pitzer.<sup>5</sup>

In this investigation modifications of the flow calorimeter were studied as part of a general program to measure the heat capacity of organic vapors.

### Experimental

Flow calorimeters may be arbitrarily classified on the basis of the method used for correcting for heat losses. In

(5) Bennewitz and Rossner, *Z. physik. Chem.*, **B39**, 126 (1938). De Vries and Collins, *THIS JOURNAL*, **63**, 1343 (1941); Pitzer, *ibid.*, **63**, 2413 (1941).