The Heats of Combustion of the Methyl Substituted Hydrazines and Some Observations on the Burning of Volatile Liquids

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The method of burning volatile reactive liquids in a combustion bomb is discussed. A modified method is outlined in which a small soft-glass cylindrical vial is used as the sample container, and a small pellet of benzoic acid acts as an auxiliary ignitor in the combustion process. Values for the heats of combustion are reported as follows: methylhydrazine, 311.711 kcal./mole; symmetrical dimethylhydrazine, 473.454 kcal./mole; unsymmetrical dimethylhydrazine, 472.648 kcal./mole.

Introduction

The interest in substituted hydrazines both as jet engine fuels and from a theoretical point of view makes it desirable to have values for the heats of combustion of methyl substituted hydrazines. The heat of combustion of hydrazine has been determined by Hughes, Corruccini and Gilbert.[1]

While the third law entropies of methylhydrazine and symmetrical dimethylhydrazine have already been determined in this Laboratory,[2,3] values of the heats of formation required to calculate reliable values of the free energy of formation are lacking.

The present paper describes the experimental work involved in the determination of heats of combustion of these two compounds and of unsymmetrical dimethylhydrazine and gives the values so obtained.

During the work, evidence was obtained about the function of thin flat-walled bulbs in burning of liquids. It is shown that such bulbs seldom, if ever, stand the pressure of oxygen in the bomb. Rather, they operate through breaking gently without splashing the liquid out of the crucible. This is discussed in further detail in the experimental section.

Experimental

Apparatus and Method.—The apparatus and method were similar to those used by many previous investigators.[4,5] The bath was essentially like that described by Dickinson[4] except that it was made to accommodate twin calorimeter assemblies.

All temperature measurements were made with a flat calorimetric type resistance thermometer (Leeds and Northrup, Catalog No. 8160, Serial No. 326349).

The pressure-tight seal in the electrode assembly of the combustion bomb, described by Dewey and Harper[6] was first tried. The quartz washer was ground to optical flatness and the gold washers were pressed between plane paralleled steel blocks which had been lapped until they were optical flats. The illium surfaces which bear on the gold were ground as true as possible, yet no permanent tight seal could be obtained even when Sauereisen insulating cement was used between the gold washers. We finally learned that workers at the Bureau of Standards had had the same trouble with all such assemblies except the first and abandoned them.

The body of the present electrode (see Fig. 1) is a conical piece of illium which clears the body of the bomb by $^1/_{32}$ inch, thus shielding the teflon gasket from the combustion zone.

The gold gasket between the top and body of the bomb was replaced by a teflon gasket.

In the determination of the energy equivalent of the calorimetric system, the time of energy input was measured on a clock activated by the output from a vacuum tube precision fork (General Radio Company). The circuit is arranged so that the heating and timing are switched on and off simultaneously. The error in the timing was estimated as 0.03 second, and the heating time was 300 seconds.

Calibration.—In a series of six determinations, the mean energy equivalent for the system was 128,386.3 ± 27.8 joules per ohm, with a maximum deviation from the mean of 41.0 joules per ohm.

As a check, the heat of combustion of benzoic acid (standard sample N.B.S. 39F) was determined. In four determinations, the heat produced in the bomb process at 30° was found to be 26,426.2 ± 6.4 joules per gram of benzoic acid burned. Jessup[7,8] reports a mean value of 26,427.3 ± 2.7 joules per gram.

On Burning Volatile Liquids.—Initially a soft glass bulb, heat-flattened on both sides, with a capillary neck was used for the sample since such bulbs (weight between 10 and 100 mg.) had proved reasonably satisfactory in burning liquid hydrocarbons.[1,6,9,10]

In theory, when a slight excess pressure is exerted on a bulb, weighing less than 120 mg., the internal volume of the bulb is reduced until the liquid sample supports the excess pressure. The flexibility of the flattened sides allows the initial distortion without breakage. This is true, but only under strictly limited conditions.

In tests made on the bulbs an excess pressure of 0.1 atmosphere outside a sample bulb of 1 ml. capacity, weighing 80–100 mg., caused the meniscus to rise approximately 1 mm. in a 1-mm. capillary. Most of the bulbs tested broke when the excess pressure reached 0.3 to 0.5 atmosphere. Thus an excess pressure of 0.1 atmosphere produced a change in volume of 0.0008 ml. and the change of volume possible without breaking the bulb is between 0.0024 and 0.0040 ml.

When an external pressure, P_2, is exerted on a bulb of volume V, which contains a volume, v_s, of liquid and a volume, v_g, of non-condensible gas, the liquid will support the external pressure when V has been reduced by an amount equal to

$$\Delta V = v_s B_s (P_2 - P_1) + v_g (1 - P_1/P_2) \qquad (1)$$

where B_s is the coefficient of compressibility of the liquid.

According to equation (1), if a bulb of the dimensions given above be filled with acetone ($B_s = 1.11 \times 10^{-4}$) and sealed off under nitrogen 2 mm. above the level of the liquid, the change in volume necessary so that the acetone would support an external pressure of 30 atmospheres is 0.0048 ml. Since this value of ΔV is larger than that which the flexibility of the bulbs would normally allow, the bulb should break as the bomb is being charged with oxygen.

Were it experimentally feasible the conditions could be improved by reducing v_g, although if the coefficient of compressibility is in the higher part of the usual range the bulb would break even if v_g were zero.

When the bulb was filled with acetone, the bomb charged with oxygen, and the sample fired in the normal manner, it appeared from the nature of the combustion that the bulb had functioned properly although according to the above

(1) A. M. Hughes, R. J. Corruccini and E. C. Gilbert. THIS JOURNAL. **61**, 2639 (1939).

(2) J. G. Aston, H. L. Fink, G. J. Janz and K. E. Russell, *ibid.*, **73**, 1939 (1951).

(3) J. G. Aston, G. J. Janz and K. E. Russell, *ibid.*, **73**, 1943 (1951).

(4) H. C. Dickinson, *Bulletin Bur. Standards*, **11**, 189 (1915).

(5) R. S. Jessup and C. B. Green, *J. Research Natl. Bur. Standards*, **13**, 469 (1934).

(6) P. H. Dewey and D. R. Harper, III, *ibid.*, **21**, 457 (1938).

(7) R. S. Jessup, *ibid.*, **36**, 421 (1946).

(8) R. S. Jessup, *ibid.*, **29**, 247 (1942).

(9) R. S. Jessup, *ibid.*, **18**, 115 (1937).

(10) J. Coops, D. Mulder, J. W. Dienske and J. Smittenberg, *Rec. trav. chim.*, **66**, 153 (1947).

TABLE I

HEATS OF COMBUSTION

Substance burned	Mass of sample, g.	Total heat produced, int. joules	Nitric acid formation, int. joules	Ignition energy, int. joules	$\frac{CO_2(exp.)}{CO_2(calc.)}$, per cent.	Heat produced by combustion of benzoic acid burned, int. joules	Observed heat of combustion, int. joules/g.
Methyl-	0.47705	16648.5	−114.6	−40.2	99.47	2982.8	28321.8
hydra-	.50908	16905.8	−78.9	−56.6	99.88	2362.3	28302.0
zine	.52533	19894.5	−84.6	−51.4	99.81	4901.3	28281.7
						Mean	28301.9 ± 13.1
Unsym-	.34469	16840.4	−92.1	−33.7	99.83	5361.4	32937.4
metrical-	.42847	17571.4	−72.9	−45.6	99.84	3354.1	32905.0
dimethyl-	.38349	14654.3	−66.7	−50.8	100.09	1918.0	32905.2
hydrazine	.41091	19752.7	−86.1	−43.3	99.22	6044.5	33045.7
						Mean	32948.3 ± 48.7
sym-Dimethylhydrazine[a]	.71346	26091.5	−80.9	−48.6	99.92	2414.6	33004.5

[a] This was the only run of 15 which gave satisfactory combustion.

calculation breakage must have occurred when the oxygen was introduced.

When bulbs weighing between 75 and 175 mg. were filled with hydrazine the bulbs broke during filling and the sample ignited spontaneously or did not burn at all.

Coops and his co-workers[10] actually tested thin bulbs (about 100 mg.) by submitting them to 35 atmospheres of oxygen pressure without firing them. On reopening the bomb some of these bulbs were still intact. This could be due to a summation of favorable factors (e.g., the compounds they studied had lower compressibilities) in equation (1) as well as fortuitously favorable structural details in the glass bulb.

Since acetone or liquid hydrocarbons do not usually react with the oxygen even after the bulb breaks, whenever the sample is fired successfully the breakage escapes detection but is unimportant because with the bulb practically full of liquid, breakage occurs without shattering.

The bulb chosen is a soft glass cylindrical bulb with a rounded end and a capillary neck (weight, 500 mg.; diameter of cylindrical part, 10 mm.; over-all volume, 0.5 ml.).

Since a bulb of this size is not readily broken with a small fuse wire, as an auxiliary ignitor, a thin pellet of benzoic acid (standard sample, N.B.S. 39F), is placed in the crucible with the sample. The average weight of the benzoic acid pellet is 0.1 g., and of the hydrazine sample is 0.6.

When pure hydrazine was burned with benzoic acid, a dark residue was detected after a combustion, both in the crucible and on the walls of the bomb. It is quite probable that the hydrazine sample is ignited before the benzoic acid pellet has burned completely. When the unburned benzoic acid strikes the wall of the bomb it is cooled enough to cause incomplete oxidation and the residue remains on the wall. Since it would be very difficult to weigh this unburned residue, it is necessary to depend on the carbon analysis to determine the extent of combustion.

Preparation and Purification of Samples.—The methyl substituted hydrazine samples were prepared according to the methods outlined in reference 11. The methylhydrazine was then purified and used for heat capacity determinations.[2]

From melting point data taken during the heat capacity determinations the methylhydrazine was shown to contain 0.25 mole per cent. impurity. Difficulties in removing this sample from the calorimeter necessitated further purification of the methylhydrazine used for combustion determinations by distillation through a forty-plate column packed with glass helices, and maintained at a pressure of 680 mm. using oxygen-free nitrogen.

No calorimetric melting point data have, as yet, been determined on this newly purified methylhydrazine. Since, however, the column proved very effective in a test distillation of acetonitrile, it is assumed that the methylhydrazine fraction used has less impurity than stated above.

The symmetrical dimethylhydrazine sample was that used in the heat capacity measurements.[3] From the data taken during melting it was found to be 99.6% pure.

The final purification of the unsymmetrical dimethylhy-

(11) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 395, 211, 208.

drazine sample consisted also in distillation through the column used for the methylhydrazine sample. Since the heat capacity data have not yet been taken, its exact purity is not known, but the impurity should be less than 0.5%.
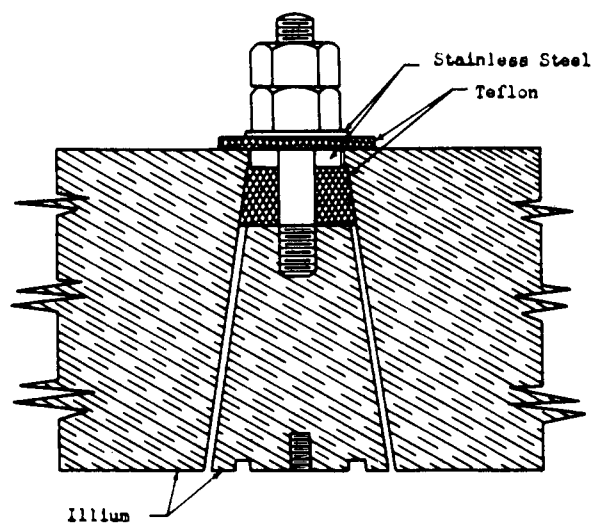

Fig. 1.—New electrode assembly.

Results

The value reported by Hughes, Corruccini and Gilbert[1] for the heat of combustion of hydrazine at 25° is 148,635 ± 30 cal./mole. The value determined in this Laboratory, using benzoic acid as an auxiliary ignitor, is 148,619 cal./mole. This we consider as a check on the technique employed.

The results are listed in Table I. The amount of benzoic acid burned was derived from the carbon analysis. Only those experiments in which the ratio CO_2 (experimental)/CO_2 (calculated) is 99% or above have been considered. It is assumed that the low carbon analyses are due solely to the incomplete combustion of benzoic acid (that is, that the hydrazine sample burned completely).

The final value for the heat of combustion under the conditions of the bomb process (initial pressure, 30 atmospheres; final temperature, 30°) for methylhydrazine is 311.711 ± 0.144 kcal./mole, and for unsymmetrical dimethylhydrazine it is 472.648 ± 0.699 kcal./mole. In the case of symmetrical dimethylhydrazine, a preliminary value is given

as 473.454 kcal./mole. The accuracy does not justify the correction outlined by Washburn.[12]

On investigation after heat of combustion determinations using the compounds discussed previously, the sample bulb was found either fused or more often shattered. After symmetrical dimethylhydrazine combustions (about fifteen runs were attempted on this compound) the bulb was in some cases so badly shattered that it appeared powdered. This indicated a tendency for the latter sample to burn more violently. Such a

(12) E. W. Washburn, *J. Research Natl. Bur. Standards.* **10**, 529 (1933).

tendency could explain the fact that only one combustion resulted in a reasonable carbon analysis. This determination alone is used to calculate the value reported here; however, all other values lay within 1% of this mean.

The errors are estimated on the basis that the correction for unburned benzoic acid is good to only 20.0% of its value, and that compared to this, all other errors are negligible. As a matter of fact the deviation from the mean is roughly proportional to this correction. Accordingly, the average deviation from the mean is given as the error.

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Some Catalytic Exchange and Hydrogenation Reactions of Acetylene and Ethylene[1,2]

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A series of experiments on the hydrogenation and exchange of acetylene and ethylene on nickel catalysts has provided the following information. (1) Contrary to previously published results, exchange between ethylene molecules has been found to occur. (2) Isomerization of *trans*-ethylene-d_2 takes place more rapidly than exchange. (3) Acetylene is adsorbed on the catalyst in part as a carbon complex and self-hydrogenates to ethylene. (4) Acetylene exchanges rapidly with itself and with residual hydrogen on the catalyst. (5) Addition of deuterium to acetylene at $-80°$ yields a preponderance of *cis*-ethylene-d_2. (6) Hydrogenation of acetylene by one-step addition appears to be ruled out. The results are discussed.

In connection with a study of the thermal *cis–trans* isomerization of ethylene-d_2 a supply of *cis*-ethylene-d_2 was desired. Preparation by the catalytic addition of deuterium to acetylene appeared highly feasible. Farkas and Farkas[3] have pointed out that the catalytic addition of hydrogen to disubstituted acetylenes yields the *cis*-ethylenic derivative in large preponderance (except for those cases where the *cis*-isomer is highly unstable) and they suggested an explanation. Sheridan[4] has also suggested a similar mechanism. Moreover, Farkas and Farkas[5] found that during the platinum-catalyzed addition of deuterium to acetylene to form ethylene, exchange was slight as judged by the return of light hydrogen to the gas phase.

The catalytic synthesis of *cis*-ethylene-d_2 on palladium was attempted by Arnett and Crawford[6] who obtained a mixture of all possible deuteroethylenes. We also attempted the catalytic preparation on nickel using experimental conditions believed to be conducive to formation of a pure *cis* product. However, only mixtures of all possible deuteroethylenes were obtained.

To clarify this finding, a series of qualitative experiments on the catalytic hydrogenation and exchange reactions of acetylene and ethylene was undertaken, together with some related work on more general aspects of these reactions.

(1) Presented before the Northwest Regional Meeting of the American Chemical Society, Seattle, June, 1951.

(2) Abstracted from a portion of a thesis to be submitted by John E. Douglas in partial fulfillment of the requirements for the Ph.D. degree at the University of Washington.

(3) A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **33**, 837 (1937).

(4) J. Sheridan, *J. Chem. Soc.*, 133 (1945).

(5) A. Farkas and L. Farkas, THIS JOURNAL, **61**, 3396 (1939).

(6) R. L. Arnett and B. L. Crawford, *J. Chem. Phys.*, **18**, 118 (1950). We thank Prof. Crawford for communicating his results to us prior to publication.

Experimental

Materials.—Deuterium was prepared by electrolysis of 99.8% D_2O, obtained on U. S. Atomic Energy Commission allocation. The acetylene was Matheson purified grade and was purified further by conventional methods. The ethylene was Matheson C.P. grade, used without further treatment. Dideuteroacetylene was prepared by the distillation of D_2O over a pure grade of calcium carbide. Mass spectrographic analysis showed that 1% of C_2HD was present. A sample of asymmetric-ethylene-d_2, containing 6.5% ethylene-d_1, was obtained from Dr. R. G. Inskeep of the University of Minnesota. *trans*-Ethylene-d_2 was prepared by reducing dideuteroacetylene with chromous chloride.[7] Mass spectrographic analysis showed the product to be 98.8% ethylene-d_2; the infrared spectrum showed no *cis*- or asymmetric-ethylene-d_2 and 1% ethylene-d_1 was the major impurity. Ethylene-d_4 was obtained by the addition of deuterium to acetylene-d_2 on a nickel catalyst previously flushed with the reagents. Mass spectrographic analysis showed the product to be 97.4% pure with 1.5% ethylene-d_3 and 0.8% ethane-d_6 as the major impurities.

Catalysts.—Nickel catalysts supported on kieselguhr were prepared by calcination of nickel nitrate followed by reduction in hydrogen at 400°.[8] They contained 17 to 19% Ni. A nickel wire catalyst was prepared by cutting 1400 cm. of #18 Ni wire into 1-cm. lengths which were treated alternately with O_2 and H_2 at 330°. Catalysts were regenerated by oxidation in O_2 at 500° followed by reduction in the usual manner. Prior to use, a catalyst was evacuated at room temperature or at 400° as indicated in the tables of results. Catalysts of palladium-on-kieselguhr were made by passing hydrogen through a suspension of kieselguhr-in-palladium chloride solution. The palladium content varied from 7 to 14%.

Apparatus and Procedure.—A conventional glass vacuum apparatus was employed. Apiezon M stopcock grease was used. No special precautions were taken to keep mercury or grease vapor away from the catalyst.

Flow Experiments.—Reactants were placed in a mixing bulb and allowed to flow over a catalyst at the desired rate and pressure. The catalyst was contained in a water-

(7) W. Patterson and V. du Vigneaud, *J. Biol. Chem.*, **123**, 327 (1938).

(8) F. De Pauw and J. C. Jungers. *Bull. soc. chim. Belg.*, **57**, 618 (1948).