methane, which arises from the reaction of methyl radicals. In conformity with the decomposition of *t*-butoxy radicals by the mechanism

$$(CH_3)_3CO— \longrightarrow CH_3 + CH_3COCH_3 \quad (6)$$

an almost equivalent amount of acetone (0.10 mole) was recovered by fractionation of the reaction product. *t*-Butyl alcohol (0.24 mole) and unreacted peroxide (0.08 mole) were also recovered by fractionation.

The product was filtered to separate the precipitated *meso*-diphenylethylene glycol dibenzoate which melted at 244–246° and had a saponification equivalent of 211 after washing with hot ethanol.

Benzaldehyde and Benzoyl Peroxide.—Benzaldehyde (106 g., 1.00 mole) and benzoyl peroxide (21 g., 0.09 mole) were heated at 80° for *ca.* eighteen hours, during which time all of the peroxide reacted. The evolved gas consisted of 0.009 mole of carbon dioxide and 0.007 mole of carbon monoxide. After removal of the excess aldehyde the liquid product yielded 6.0 g. (0.014 mole) of crystalline *meso*-diphenylethylene glycol dibenzoate (m. p. 244–245°). The residue was not further investigated.

Summary

1. A remarkably clean-cut disproportionation reaction of benzaldehyde leading to *sym*-diphenylethylene glycol dibenzoate is effected by either di-*t*-butyl peroxide or benzoyl peroxide.

2. The mechanism advanced for the formation of the diester is supported by the synthesis of the same compound from benzyl benzoate and di-*t*-butyl peroxide.

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[CONTRIBUTION NO. 10 FROM THE THERMODYNAMICS LABORATORY OF THE PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

The Heat of Combustion of 2,2′-bis-(4-Hydroxyphenyl)-propane

BY WARD N. HUBBARD, JOHN W. KNOWLTON AND HUGH M. HUFFMAN

Introduction

The heat of combustion of 2,2′-bis-(4-hydroxyphenyl)-propane was measured and the data combined with values for the heats of formation of water and carbon dioxide to obtain a value for the heat of formation of this compound. For brevity in the text, the above substance will be called by its trade name, "Bis-phenol-A."

Experimental

The Calorimeter and its Calibration.—The calorimeter was substantially of the type described by Dickinson.[1] The construction of the constant-temperature jacket differs from the Bureau of Standards model, but there was no change in operating principles or in the design of the calorimeter itself.

A schematic diagram of the apparatus is shown in Fig. 1. The calorimeter can E was enclosed in the constant-temperature jacket, which was a covered cylindrical tank. The inner boundary of the jacket was a copper vessel D, called the well. This was of such shape and dimensions that a 1-cm. air gap was provided between the well and the calorimeter, the form of which is shown by the isometric projection G. The well was isolated in the jacket, being anchored to three plastic supports. Two tubes attached to the water-tight cover extended through the top of the jacket to provide ports for insertion of the thermometer and for coupling the calorimeter stirrer to its drive pulley at A. All surfaces were nickel-plated and polished.

In operation the jacket was filled with water to the level indicated by the overflow C. Two propellers (as shown at B) provided vigorous circulation. Constant temperature was maintained by intermittently energized heaters, which were soldered to the flow tubes surrounding the propellers and controlled by a sensitive thermostat (not shown). The well was exposed for introducing and removing the calorimeter by draining water through cocks F. To avoid delay in starting an experiment, the jacket was drained only to the level of the upper of these cocks in between runs. This arrangement (which approaches the Richards submarine calorimeter[2] eliminates the troublesome water cap of the Dickinson model, and simplifies the construction.

Temperature measurements were made using a platinum resistance thermometer of the calorimetric type in conjunction with a Type G-2 Mueller resistance bridge and a sensitive galvanometer. By controlling the amount of material burned in each experiment, the temperature rise was held substantially constant. Each combustion was initiated at 24.000° and the temperature of the calorimeter rose to an average of 26.000 ± 0.003°. The improved ignition technique of Huffman and co-workers was used.[3]

The double-valved bomb was machined from S. A. E. 1040 steel, following the design of Atwater and Snell[4] and was lined with platinum. The arrangement of platinum firing electrodes was similar to that of Prosen and Rossini.[5] This consists in having one electrode in the form of a tube connected to one of the valves, and extending close to the bottom of the bomb, permitting continuous flushing with oxygen and convenient removal of the gaseous products of combustion for analysis whenever desired. The sealing gasket was made of du Pont Teflon (polytetrafluoroethylene). Repeated combustions of Bis-phenol-A, benzoic acid and certain chlorinated hydrocarbons (which form extremely corrosive combustion products) resulted in no visible attack on this material and no anomalous combustion data were obtained when such a gasket was used. The volume of the bomb was 0.328 liter, and all combustions were carried out under an initial oxygen pressure of 30 atmospheres and with 0.1 ml. of water added to the bomb.

The energy equivalent of the calorimeter was determined by combustion of benzoic acid (National Bureau of Standards Standard Sample 39f), having for its isothermal heat of combustion at 25°, and under standard specified conditions,[6] the value $-\Delta U_B/M$ = 26,429.4 N. B. S. international joules per gram. Since the conditions in these experiments were not quite those of the standard

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(1) Dickinson, *Bull. Bur. Standards*, **11**, 189 (1915).

(2) Richards and Jesse, THIS JOURNAL, **32**, 268 (1910).

(3) (a) Huffman and Ellis, *ibid.*, **57**, 41 (1935); (b) Stiehler and Huffman, *ibid.*, **57**, 1734 (1935); (c) Huffman, *ibid.*, **60**, 1171 (1938).

(4) Atwater and Snell, *ibid.*, **25**, 659 (1903).

(5) Prosen and Rossini, *J. Research Natl. Bur. Standards*, **27**, 289 (1941).

(6) Jessup, *J. Research Natl. Bur. Standards*, **29**, 247 (1942), revised for a new value for the density of benzoic acid. See Jessup, *ibid.*, **36**, 421 (1946), and Supplementary Note of February 12, 1946, to N. B. S. Certificate for Standard Sample 39f.

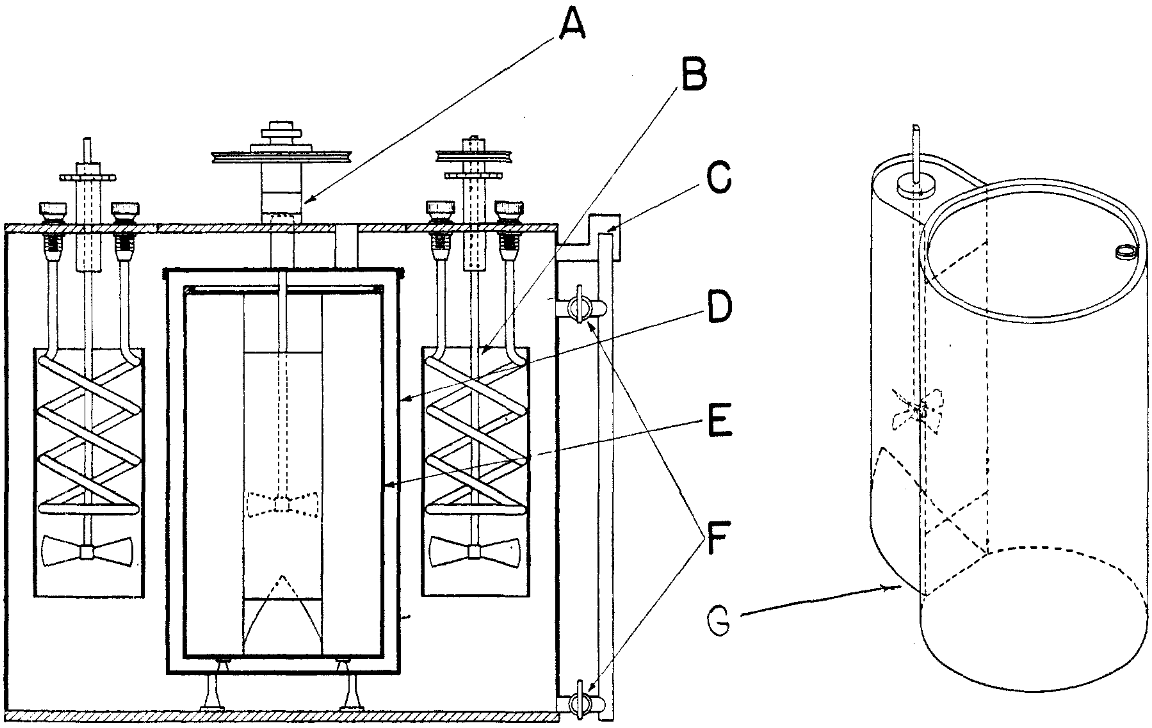

Fig. 1.

bomb process, the N. B. S. value was corrected[7] to 26,426.6 N. B. S. international joules per gram.

Eight combustions of benzoic acid (using 1.020-g. samples) yielded a value of 3226.1 cal./deg. for the energy equivalent to the calorimeter. The average deviation from the mean of these experiments was ±0.01% with a maximum deviation of 0.02%.

Units of Measurement and Auxiliary Quantities.—The results of the combustion experiments are expressed in terms of the arbitrary calorie, which equals 4.1833 N.B.S. international joules, and refer to the isothermal process at 25° and for true mass. The molecular weight was computed from the 1947 table of atomic weights. For the correction to true mass, the density of Bis-phenol-A was estimated from the dimensions and weight of a pellet to be 1.13 g./cc.

The heats of formation of water and of carbon dioxide at 25° were taken to be 68,317.4 ± 9.6[8] and 94,051.8 ± 10.8[9] cal./mole, respectively. The correction, usually less than 1 calorie, for the small amount of nitric acid formed in each combustion was calculated using −13,960 cal. for the heat of the following reaction at constant volume

$$1/2N_2(g) + 5/4O_2(g) + 1/2H_2O(l) + aq = HNO_3(aq) \quad (1)$$

The amount of nitric acid was determined in each experiment by titration of the bomb washings with sodium hydroxide, using brom cresol green as the indicator.

Material.—The 2,2′-bis-(4-hydroxyphenyl)-propane used in this work was furnished by Dr. A. Farkas of the Barrett Division of the Allied Chemical and Dye Corporation, Frankford, Philadelphia, Pa. Carbon analysis based on the carbon dioxide produced in a calorimetric combustion, yielded 99.98% of the theoretical amount.

Heat of Combustion.—About 0.787 g. (weighed to 0.01 mg.) of Bis-phenol-A was burned in each experiment. It was found that the finely crystalline material, as received, was slightly hygroscopic. Attempts to dry it over phosphorus pentoxide *in vacuo* were unavailing, since on subsequent exposure to the air there was a rapid gain in weight of about 0.04% (which was approximately equal to the loss on drying). Successful weighing was accomplished after each sample had been converted to a solid mass by crystallizing from the melt, thus reducing the surface exposed to the atmosphere. Before each combustion, a tared platinum crucible containing sufficient material was placed in an oven held at 200°. The Bis-phenol-A melted almost immediately (m.p. ~ 151°), and after being in the oven for three minutes, the crucible and melt were rapidly transferred to a small desiccator which was immediately evacuated. Upon attaining room temperature, the crucible plus the crystalline sample was weighed, and introduced into the bomb. No significant gain in weight was ob-

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(7) Washburn, *Bur. Standards J. Research*, **10**, 525 (1933). Slight revisions have been made in order to obtain the Washburn correction at 25°.

(8) Wagman, Kilpatrick, Taylor, Pitzer and Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

(9) Prosen, Jessup and Rossini, *ibid.*, **33**, 447 (1944).

served in samples which were prepared in this manner and left exposed in the balance case for periods up to one hour. The carbon analysis reported above was obtained on such a sample.

The completeness of drying, as well as the possibility of thermal decomposition due to the treatment to which the Bis-phenol-A was subjected, was checked by a combustion of the original powdered material in which the mass burned was computed from the amount of carbon dioxide produced. As a further check, one sample for combustion was held at 200° for ten minutes before crystallization. There was no significant difference between the results of these and the other experiments.

The results of eight combustion experiments yielded for Bis-phenol-A the value $-\Delta U_B/M$ = 8184.1 cal./g. with an average deviation from the mean of ±0.01% and a maximum deviation of 0.02%. Consideration of the propagated uncertainty of the result, which is due to the respective precision error taken for the heat of combustion of benzoic acid, the calibration measurements, the combustions of Bis-phenol-A and the carbon analysis, resulted in an estimated accuracy uncertainty of ±0.03%. The derived data are presented in Table I. No value for the heat of combustion of Bis-phenol-A was found in the literature.

TABLE I

HEAT OF COMBUSTION OF 2,2'-BIS-(4-HYDROXYPHENYL)-PROPANE, $C_{15}H_{16}O_2$, Mol. Wt. = 228.278

Derived data at 25° in kcal./mole

$-\Delta U_B = 1868.2 \pm 0.4^a$

$-\Delta U_R = 1867.3 \pm 0.4$

$-\Delta H_R = 1869.1 \pm 0.4$

$-\Delta H_f = 88.2 \pm 0.5$

[a] Precision uncertainty.

Summary

The isothermal heat of combustion at 25° of 2,2'-bis-(4-hydroxyphenyl)-propane has been determined. From this value the heat of formation has been calculated.

BARTLESVILLE, OKLAHOMA

RECEIVED MAY 13, 1948

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Cuprous Chloride Complexes of Maleic and Fumaric Acids

BY L. J. ANDREWS AND R. M. KEEFER

A study of the relative tendencies of different olefins to form cuprous chloride complexes as influenced by the nature of substituents at the double bond is in progress in this Laboratory. In this connection it seemed desirable to compare the degree to which certain *cis–trans* isomers will form such complexes. This paper reports the results of a study of the reaction of cuprous chloride with maleic and fumaric acids.

By measurements of the solubility of cuprous chloride in aqueous solutions of allyl alcohol,[1] it has been demonstrated that an equilibrium is established with respect to the formation of a 1–1 water soluble complex ($CH_2{=}CH{-}CH_2OH \cdot CuCl$). Using a similar procedure the solubility of cuprous chloride in aqueous solutions of maleic and fumaric acids at different hydrogen ion concentrations has been determined. Supporting evidence for the conclusions as to structure of the complexes and equilibria involved as based on these solubility measurements has been obtained by an investigation of the absorption spectra of the intensely yellow solutions of the complexes.

Experimental

Cuprous Chloride.—This material was prepared in 5-g. batches according to the procedure of Keller and Wycoff.[2] Each batch was divided into 1-g. samples which were placed in sample vials and stored in a desiccator until used.

Maleic and Fumaric Acids.—These were prepared from maleic anhydride according to the directions of Robertson.[3]

Solubility Determinations.—The method for determination of the solubility of cuprous chloride in fumaric or maleic acid solutions was essentially that used in previous work.[1] To minimize chances of oxygen entering the reaction flasks during shaking the glass stoppers were sealed with paraffin. Solutions of maleic and fumaric acids which had been standardized against standard sodium hydroxide solution were used. The analyses for water-soluble cuprous complexes in the solutions at equilibrium were determined volumetrically as described elsewhere.[4] All reported concentrations (Cu_c^+) were corrected for the slight solubility of cuprous chloride in the organic acid-free medium. All runs were temperature controlled at 25 ± 0.5°.

When solutions of maleic acid which had been partially neutralized with sodium hydroxide were shaken with cuprous chloride, a crystalline yellow solid was formed. The solid was washed with water by decantation to remove traces of cuprous chloride and was transferred to a filter and washed with absolute alcohol and anhydrous ether. After air drying the water insoluble yellow solid showed negative tests for chloride and sodium ions. Analyses of the solid by dissolving weighed portions in hydrochloric acid and titrating for cuprous content indicated that it was cuprous acid maleate dihydrate.

Anal. Calcd. for $CuC_4H_3O_4 \cdot 2H_2O$: eq. wt., 215. Found: eq. wt., 209, 215.

A yellow solid of this type was also isolated in runs using partially neutralized fumaric acid solutions. It was, however, never isolated free from cuprous chloride.

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[1] Kepner and Andrews, *J. Org. Chem.*, **13**, 208 (1948).

[2] Keller and Wycoff, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Company, Inc., New York, N. Y., 1946, pp. 1–4.

[3] Robertson "Laboratory Practice of Organic Chemistry," The Macmillan Company, New York, N. Y., 1943, pp. 316–317.

[4] Hatch and Estes, THIS JOURNAL, **67**, 1730 (1945).