[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Heats of Combustion of Anthracene Transannular Peroxide and Dianthracene

BY PAUL BENDER AND JOSEPH FARBER

Heat of combustion measurements are reported which lead to the values +19.7 and +73.2 kilocalories for the standard heats of formation at 25° of anthracene transannular peroxide and dianthracene, respectively. Values are also reported for anthracene and phenanthrene.

Introduction

As part of a study of anthracene transannular peroxide and the photoöxidation of anthracene, the heats of combustion of the peroxide and dianthracene, its photochemical competitor, have been measured. For thermochemical calculations on this system the standard heat of formation of anthracene is also required. A difference large in comparison with the precision of the individual determinations was found in the previously reported values of the standard heats of combustion of anthracene; measurements on this compound were therefore included in the hope of resolving the discrepancy. In this effort it proved desirable to extend the work to phenanthrene as well.

Experimental Details

Calorimeter.—The isothermal jacket calorimeter employed was essentially of the design recommended by Dickinson.[1] A standard Emerson double valve combustion bomb of 550-ml. volume was used; the sample cup was fabricated from sheet platinum. The experimental conditions for the combustion reactions conformed to accepted modern practices as recommended by Washburn.[2] The bomb was filled with oxygen at 30 atmospheres pressure at 25°; 2 ml. of water was also added. To secure complete combustion of the anthracene transannular peroxide and dianthracene samples it was necessary to use an auxiliary substance. A vacuum pump oil was employed, as suggested for example by Huffman and Ellis.[3]

Temperature Measurements.—Temperature measurements were made with a calorimetric type platinum resistance thermometer constructed and calibrated by the Leeds and Northrup Company, and checked by comparison with standard research type platinum thermometers certified by the National Bureau of Standards. The Mueller bridge, made by the Rubicon Co., was thermostated, and calibrated before use. Time–temperature data were recorded photographically. The corrected temperature rise was calculated by the method of Dickinson.[1]

Calibration.—Benzoic acid, from Sample 39g of the National Bureau of Standards, was used as a standard for the determination of the heat capacity of the calorimetric system. The value used for the heat of combustion of the benzoic acid was 6317.83 calories per gram.[4] This calibration, done in accordance with the N.B.S. specifications, was checked by the electrical method. Because of the greater number of individual measurements involved in each of the electrical calibration runs, the random error in the latter determination was the greater, but the average values obtained by the two methods were in essentially exact agreement. The energy introduced in firing the charge was determined directly by means of blank runs, as recommended by Jessup.[4]

Miscellaneous.—All weighings were made with calibrated weights, and all weights reported have been corrected to vacuum. The values of Osborne, Stimson and Ginnings[5] were used for the specific heat of water. Time measurements were made with a conventional synchronous motor driven timer. All samples were kept under vacuum until used. Results are expressed in defined calories, where one defined calorie equals 4.1840 absolute joules.

Preparation of Samples. Anthracene Transannular Peroxide.—A solution of anthracene in carbon disulfide was irradiated (with an AH-6 mercury vapor lamp), while oxygen was bubbled through it.[6] The crude peroxide which separated from the solution on cooling was treated with Norite in carbon disulfide solution, then was recrystallized three times from carbon disulfide. This material exploded at temperatures of the order of 160°, in contrast to the explosion point of *ca.* 120° reported by Dufraisse.

Dianthracene.—The dianthracene which precipitated on irradiation, with an AH-6 mercury vapor lamp, of an oxygen-free solution of anthracene in xylene was washed repeatedly with toluene and dried in a vacuum oven at 35°. A second preparation was made from toluene solution.

Anthracene. A.—Eastman Kodak Co. "Blue-White Fluorescent" grade anthracene was found to give erratic results. On sublimation it gave in the initial condensate non-solidifying liquid droplets considered to be ethylene glycol. A slight amount of a solid impurity, probably dianthracene, insoluble in ethyl alcohol was also found. Purification of this starting material was therefore undertaken.

Sample 1.—The Eastman Kodak Co. anthracene was recrystallized three times from ethyl alcohol; the dianthracene was removed by filtration. The final product was dried under vacuum at room temperature.

Sample 2.—A benzene solution of anthracene and maleic anhydride in a 1:1 molar ratio was refluxed for ten minutes. Under these conditions, according to Bachmann and Kloetzel,[7] a 25% conversion to anthracene 9,10-*endo*-α,β-succinic anhyride is obtained. The precipitate formed was filtered off, to remove as adducts heavier condensed hydrocarbon impurities which react more rapidly and completely under these conditions. A fivefold excess of maleic anhydride was added to the filtrate, which was then refluxed for three hours. The anthracene adduct was filtered out and recrystallized from ethyl acetate to eliminate impurities which do not undergo the diene synthesis. Sublimation was used to dissociate the adduct; extensive decomposition and charring occurred. The sublimate, which was contaminated with undissociated adduct, was extracted with boiling sodium hydroxide solution. The residual anthracene was recrystallized three times from alcohol then dried under vacuum. The over-all yield in the direct pyrolysis was very poor. Better results are obtained by heating an intimate mixture of the adduct and finely powdered soda lime.

B. **Sample 3.**—A specimen of anthracene was obtained from the Harshaw Chemical Co. from their single crystal material grown for scintillation counters. This specimen was especially selected from the standpoint of probable freedom from impurities, through the courtesy of Dr. K. E. Long.

Phenanthrene.—A sample of highly purified phenanthrene was furnished by Dr. Milton Orchin, of the United States Bureau of Mines. This material was a recrystallized portion of that prepared by Feldman, Pantages and Orchin,[8] and used by them for the determination of some of the physical properties of the compound.

Naphthalene.—J. T. Baker "Resublimed" grade naphthalene was used as supplied. The residue from sublimation of this material was less than 0.02%.

Experimental Results

In Table I are summarized the results of the combustion

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(1) H. C. Dickinson, *Natl. Bureau of Standards Bull.*, **11**, 189 (1914).

(2) E. W. Washburn, *J. Research Natl. Bur. Standards*, **10**, 525 (1933).

(3) H. M. Huffman and E. L. Ellis, THIS JOURNAL, **57**, 42 (1935).

(4) R. S. Jessup, *J. Research Natl. Bur. Standards*, **29**, 247 (1942).

(5) N. S. Osborne, M. S. Stimson and H. F. Ginnings, *ibid.*, **23**, 197 (1939).

(6) C. Dufraisse and M. Badoche, *Compt. rend.*, **200**, 1103 (1935).

(7) W. E. Bachmann and M. C. Kloetzel, THIS JOURNAL, **60**, 481 (1938).

(8) J. Feldman, P. Pantages and M. Orchin, *ibid.*, **73**, 4341 (1951).

TABLE I

RESULTS OF HEAT OF COMBUSTION MEASUREMENTS AT 25°

Compound	Runs	Density	Mol. wt.	$-\Delta U_B$, cal. g.$^{-1}$	Average deviation, cal. g.$^{-1}$	$-\Delta U^0_R$, kcal. mole^{-1}	$-\Delta H^0_R$, kcal. mole^{-1}	ΔH^0, kcal. mole^{-1}
Anthracene transannular peroxide (s)	5	1.28[a]	210.22	7981.2	2.5	1677.1 ± 0.8	1678.0	+19.7
Dianthracene (s)	6	1.25[a]	356.44	9506.2	3.4	3386.9 ± 1.6	3389.8	+73.2
Anthracene (s)		1.25	178.22					
Samples 1, 2	9			9464.9	3.8	1685.6 ± 0.7	1687.1	+28.8
Sample 3	5			9474.9	1.7	1687.5 ± 0.5	1688.9	+30.6
Phenanthrene (s)	3	1.025	178.22	9454.0	2.0	1683.8 ± 0.7	1685.3	+27.0
Naphthalene (s)	3	1.145	128.16	9590.5	2.8			

[a] Estimated.

experiments, as calculated by the standard method.[9] The values used for the standard heats of formation of carbon dioxide gas and liquid water were −94,051.8 cal.[10] and −68,317.4 cal.,[11] respectively.

The data obtained lead to the following standard heats of reaction for the formation of dianthracene and anthracene transannular peroxide

$$2C_{14}H_{10(s)} \longrightarrow C_{28}H_{20(s)},\ \Delta H^0_{298} = +15.6 \pm 3 \text{ kcal.}$$

$$C_{14}H_{10(s)} + O_{2(g)} \longrightarrow C_{14}H_{10}O_{2(s)},\ \Delta H^0_{298} = -9.1 \pm 1.5 \text{ kcal.}$$

In these calculations the value given by Samples 1 and 2 for the standard heat of formation of anthracene has been used.

Discussion

The number of runs made on each of the compounds studied is not as large as sometimes is suggested, but is considered to be entirely sufficient to establish an adequate random error estimate for the heats of combustion. The accuracy of the measurements reported is primarily determined by the purity of the compounds; aside from this consideration an estimate of ±0.05% reliability is considered justified. This claim strengthened by the comparison of the present value for ΔU_B for naphthalene with that of Huffman and Ellis,[3] which is higher by 0.04%. The disadvantage of the volatility of naphthalene is offset by the relative ease with which it can be obtained in a pure state.

The purities of the peroxide and dianthracene are very difficult to establish. Conventional melting range techniques are useless here because of decomposition of the former and depolymerization of the latter. The peroxide was examined microscopically and spectrophotometrically for impurities, especially anthracene and anthraquinone, with negative results. Samples from two preparations were used; the combustion runs were made as soon as possible after the syntheses were completed to avoid difficulty from the decomposition of the compound which takes place slowly even at room temperature. Purity of the dianthracene is favored by its low solubility and the absence of competing reactions in its preparation; in addition, the logical contaminants, anthracene and toluene, have heats of combustion very close to that of dianthracene.

Through correction to a common basis of defined calories at 25° (due allowance being made for differences in the values of the heat of combustion of benzoic acid used for calibration purposes), the following comparison values of $-\Delta U^0_R$ are obtained for anthracene: Beckers,[12] 1684.25 kcal. mole^{-1}, specified precision ±0.01%; Milone and Rossignoli,[13] 1684.4 ± 0.5%; Fries, Walter and Schilling,[14] 1686.8 ± 0.01%; Richardson and Parks,[15] 1683.9 ± 0.01%; Parks, West, Fujii and McLaine,[16] 1682.4 ± 0.01%; present work, 1685.6 ± 0.04% (Samples 1, 2), 1687.5 ± 0.02% (sample 3).

The discrepancies noted here must be ascribed primarily to differences in sample purity. In particular, the measurement by Parks, *et al.*, was reported as prompted by the belief that the Eastman Kodak Co. "Blue-Violet Fluorescent" grade anthracene which they used was of higher quality than the sample used by Richardson and Parks, which was specified as "slightly yellowish." The low value reported by Parks, *et al.*, is believed to be due to the presence of glycol (*vide supra*) in their sample.

The present work is considered to confirm that of Fries, Walter and Schilling. Because the experimental conditions employed in the latter work differed considerably from those now conventional, the usual allowance for a 10% uncertainty in the Washburn correction would correspond to over 0.1% uncertainty in their final result; their value hence cannot be used to substantiate a preference for one of the two results here reported. The values given by our samples 1 and 2 were entirely equivalent and hence were grouped together; this agreement forms the basis for our previously stated preference for this result. The infrared spectra of carbon disulfide solutions of Samples 2 and 3, as obtained with the Baird Associates spectrometer, were essentially superimposable; we cannot account for the difference in the two heat of combustion values, but are convinced that it was real.

Work on phenanthrene was required because the agreement of our results on anthracene with those of Fries, *et al.*, would otherwise have been clouded by the extreme disagreement of their value for the heat of combustion of phenanthrene with other

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[9] J. M. Sturtevant in Weissberger's "Physical Methods of Organic Chemistry," Vol. I, Part I, 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1949.

[10] E. J. Prosen, R. S. Jessup and F. D. Rossini, *J. Research Natl. Bur. Standards*, **33**, 447 (1944).

[11] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, *ibid.*, **34**, 143 (1945).

[12] M. Beckers, *Bull. Soc. chim. Belg.*, **40**, 518 (1931).

[13] M. Milone and P. Rossignoli, *Gazz. chim. ital.*, **62**, 644 (1932).

[14] K. Fries, R. Walter and K. Schilling, *Ann.*, **516**, 248 (1935).

[15] J. W. Richardson and G. S. Parks, THIS JOURNAL, **61**, 3543 (1939).

[16] G. S. Parks, T. J. West, B. F. Naylor, P. S. Fujii and L. A. McLaine, *ibid.*, **68**, 2524 (1946).

reports. The several values of $-\Delta U^0_R$ at 25° for phenanthrene compare as follows: Milone and Rossignoli,[13] 1673.1 kcal. mole^{-1}, specified precision ±0.5%; Fries, *et al.*,[14] 1681.6 ± 0.01%; Richardson and Parks,[15] 1674.1 ± 0.01%; present work, 1683.8 ± 0.02%.

Again the discrepancies are assigned to differences in sample purity since phenanthrene is notoriously difficult to purify. The material used in the present work was probably of as high quality as any ever prepared in quantity; this purity is considered responsible for the higher result here reported, which again confirms, relatively at least, that of Fries, *et al.* The considerable attention given in the latter work to sample purification is noteworthy.

It is obvious that for neither anthracene nor phenanthrene has a definitive value for the standard heat of combustion been established as yet. Further measurements should be carried out on samples of established high purity.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Studies on the System Iron–Ethylenediamine Tetraacetate[1]

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The system iron–ethylenediamine tetraacetate has been studied polarographically over the *p*H range 1–11. Waves corresponding to reversible reduction of the ferric complex to the ferrous state are obtained up to *p*H 9; in more alkaline solution the reaction proceeds irreversibly. The ferrous complex yields reversible anodic waves under proper conditions. The diffusion currents are proportional to concentration of the complex. The half-wave potential of the system is constant and equal to −0.13 v. *vs.* S.C.E. in the *p*H region 3.5–6.5; outside this range the half-wave potential is *p*H dependent. The stability constant of the ferric complex has been obtained from a spectrophotometric analysis of its dissociation equilibrium in 0.6–1 *M* perchloric acid. The value is close to 5 × 10^{23}.

Ethylenediamine tetraacetic acid is denoted by Schwarzenbach[2] as complexone III and abbreviated as H_4Y. Its tetrasodium and disodium salts are commercially available in this country under the respective trade names Versene and Disodium Dihydrogen Versenate; for the sake of simplicity we shall refer to both the acid and all of its salts as Versene. The ferric iron complexes were first prepared by Brintzinger, *et al.*,[3] and inferences as to their structure were drawn both from their qualitative chemical behavior[3] and from magnetic measurements.[4]

The solution chemistry of Versene and of its complexes with a large number of metal ions was studied most extensively by Schwarzenbach and co-workers. Analysis of the protolytic equilibria established the following successive pK values for the tetraacid (concentration constants at 20° and ionic strength 0.1): pK_1 2.00, pK_2 2.67, pK_3 6.16, pK_4 10.26.[2a] Similar studies led to the elucidation of the acidic and/or basic properties of a large number of complexes including those of ferrous and ferric iron, and also to the evaluation of some of the stability constants.[2b,c,d] The following stability constant was reported for ferrous iron[2c]

$$K_{\mathrm{red}} = \frac{[\mathrm{FeY}^{=}]}{[\mathrm{Fe}^{++}][\mathrm{Y}^{\equiv}]} = 10^{14.26}$$

Schwarzenbach also made a potentiometric study of the system iron–Versene over a wide *p*H range.[2d] The polarography of the system has been considered briefly by Furness and co-workers[5] who were interested in analyzing commercial Versene preparations.

The present paper is devoted mainly to the polarographic properties of the system iron–Versene over the *p*H range 1.0–10.9. In addition, a spectrophotometric method for determining the stability constant of the ferric complex is given.

Experimental

A stock solution of ferric iron was obtained from A. R. ferric chloride and standardized by the stannous chloride–dichromate method. A chloride free solution was prepared by dissolving a weighed amount of high purity iron powder in perchloric acid and oxidizing with hydrogen peroxide. Ferrous ammonium sulfate hexahydrate, found to assay 99.7%, served as source of ferrous iron.

Approximately 0.1 *M* stock solutions were prepared from A.R. Disodium Dihydrogen Versenate, $Na_2H_2Y \cdot 2H_2O$ (Hach Chemical Co., Ames, Iowa). They were standardized by adding excess calcium chloride solution to an aliquot portion and titrating with standard base to the same mixed methyl red–brom cresol green end-point obtained with a blank containing calcium in the absence of Versene.

High purity Airco or Linde nitrogen, further purified by passage through alkaline pyrogallol or vanadous sulfate[6] solution, was employed.

Unless otherwise specified, the *p*H of the solution was adjusted without the use of a special buffer system, by appropriate additions of perchloric acid or sodium hydroxide. *p*H values of 2 and above were measured with a glass electrode (Leeds and Northrup *p*H Meter, Model No. 7661); those below were calculated, using the activity coefficients given by Latimer.[7] The ionic strength was kept at either *ca.* 0.15 or 1.0 by addition of sodium perchlorate or nitrate. All polarographic experiments were performed at 25 ± 0.2° in a thermostatically controlled water-bath.

The ferrous complex was found to be extremely rapidly air oxidized. In order to prevent this the procedure finally developed for solutions containing this complex makes use of a 3-neck modification of the 2-compartment rapid mixing

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[1] This work was carried out under the sponsorship of the Reconstruction Finance Corporation, Synthetic Rubber Division, in connection with the Synthetic Rubber Program of the United States Government.

[2] (a) G. Schwarzenbach, *et al.*, *Helv. Chim. Acta*, **30**, 1798 (1947); (b) *ibid.*, **31**, 459 (1948); (c) *ibid.*, **32**, 1543 (1949); (d) *ibid.*, **34**, 576 (1951).

[3] H. Brintzinger, H. Thiele and U. Müller, *Z. anorg. allgem. Chem.*, **251**, 285 (1943).

[4] W. Klemm, *ibid.*, **252**, 225 (1944).

[5] W. Furness, P. Crawshaw and W. Cole Davis, *Analyst*, **74**, 629 (1949).

[6] L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

[7] W. M. Latimer, "Oxidation Potentials," Prentice–Hall, Inc., New York, N. Y., 1938, p. 323.