

# Heat of Combustion of Resorcinol and Enthalpies of Isomerization of Dihydroxybenzenes

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The heat of combustion of crystalline resorcinol in the standard state at 25°C.,  $\Delta H_c^\circ(c)$ , was found to be  $-631.30 \pm 0.10$  kcal. per mole. With the use of appropriate auxiliary data, this gives  $\Delta H_f^\circ(c) = -87.95$  kcal. per mole and  $\Delta H_f^\circ(g) = -65.7$  kcal. per mole.

THE LARGE NUMBER of very accurate heats of combustion measurements on hydrocarbons and sulfur compounds which have accumulated during the past 30 years has formed the basis of very effective semi-empirical bond energy schemes, which include the effect of nonbonded intramolecular interactions (2, 3, 5, 7, 8). As a result, we can now predict with confidence the heats of formation of most alkanes, cycloalkanes, alkyl benzenes, alkanethiols, and thiaalkanes in the gas phase to an accuracy of 0.1 to 0.2 kcal. per mole.

The correlation and prediction of the standard enthalpies of oxygen-containing compounds have not yet been so successful. This lack of success is due partly to the additional complexity introduced by the oxygen atom and partly to the scarcity of correspondingly accurate experimental measurements of heats of formation. Resorcinol, 1,3-dihydroxybenzene, is one of the key compounds for establishing the effect of substitution of hydroxyl groups on the benzene ring. The recent availability of a high purity sample has permitted us to determine the heat of combustion of resorcinol with a much greater accuracy than has previously been possible.

## EXPERIMENTAL

The sample was supplied by the Research Department, Koppers Co., Monroeville, Pa. Starting with USP grade material which melted at 109.68°C., it was zone-refined by 130 passes in a 36-inch column. An initial freezing point of 109.770°C. was obtained for the purified material by thermal analysis using a calibrated platinum resistance thermometer. By extrapolating the freezing points of several samples of resorcinol of varying purity to the pure material, the staff at Koppers has concluded that pure resorcinol freezes at 109.78°C. On this basis, the assumption of ideal behavior leads to the conclusion that the zone-refined sample contains 0.017 mole % impurity. The most likely impurities are water, phenol, and pyrocatechol. The Koppers Co. has also prepared a different sample of purified resorcinol by sublimation from this same USP starting material and deposited the sample with the Office of Standard Reference Materials, National Bureau of Standards. The initial freezing point of the sublimed sample is 109.744°C. Infrared spectra of both these samples have been published (10). No significant differences can be seen between these two spectra. The combustion measurements were made on the zone-refined sample as received, except that after the pellets had formed, the surface moisture was removed by heating in a vacuum at 40° to 50° C. for 8 hours. The pellets were protected from moisture until they were weighed.

The samples were burned in a Parr Instrument Co. 1106 bomb, having an internal volume of 340 ml., which was

initially filled with oxygen at  $30.00 \pm 0.01$  atm. Combustible impurities were removed from the oxygen by passing it through a furnace packed with copper oxide at 500°C. The pellets were weighed to an accuracy of 0.05 mg. and corrections for air buoyancy applied. The bomb was placed in a Precision Scientific Co. No. 3028 calorimeter, and the water around the jacket adjusted to within 0.02° of 27.34°C., whereas the temperature was controlled to  $\pm 0.002^\circ$  C. The temperature of the water in the calorimeter bucket was measured with a Leeds & Northrup, knife-type, platinum resistance thermometer. The resistance was measured with a Leeds & Northrup G2 Mueller bridge and Keithly No. 147 Nanovolt electronic null detector. The thermometer had a resistance of 28.0545 ohms at 25°C. and a coefficient of 9.921 deg. per ohm. To follow the temperature of the calorimeter, the times were recorded when the indicator of the null detector passed through zero following a series of equal increments of the bridge setting. This procedure was used to establish the initial and final temperatures to a relative accuracy of at least  $5 \times 10^{-5}$  degree.

Ignition was accomplished by an iron wire fuse which produced 8.2 cal., as determined by blank runs. All samples burned completely and cleanly, with no evidence of soot or of any products other than water, carbon dioxide, and a trace of nitric acid derived from the nitrogen initially mixed with the oxygen. The carbon dioxide produced in two of the runs was collected and absorbed on Indicarb, following the procedure of Prosen and Rossini (6). The recovery was 99.99 and 99.97% of the theoretical amount. The uncertainty in these measurements was about 0.02%. The final solution was titrated with standard sodium hydroxide, using bromothymol blue indicator to determine the quantity of nitric acid.

One gram of water was placed in the bomb and the initial temperature adjusted to  $25.060^\circ \pm 0.001^\circ$  C. The mass of sample was chosen to give a temperature rise in the range of  $2.11^\circ \pm 0.05^\circ$  C. The effective thermal conductivity between the jacket and calorimeter was always in the range of  $(1.59 \pm 0.02) \times 10^{-3}$  per minute. All calculations, including conversion of temperature and time measurements to initial and final temperatures, corrections for heat exchange between calorimeter and jacket, and reduction to the standard state, were carried out on a digital computer programmed to follow the procedure of Hubbard, Scott, and Waddington (4). The density of resorcinol was taken as 1.278 grams per ml., the specific heat as  $0.301 \text{ cal. g.}^{-1} \text{ deg.}^{-1}$ , and the energy coefficient as  $-5 \times 10^{-3} \text{ cal. atm.}^{-1} \text{ g.}^{-1}$  in these calculations. Additional pertinent experimental quantities for a typical run are shown below.

Mass of sample, $m'$ , g.	1.62434
Bath temperature, $t$ , ohms	28.2800
Initial temperature of calorimeter, $t_i$ , ohms	28.054348
Heat exchange correction, $\Delta t_{corr}$ , ohm	0.000639
Corrected final temperature, $t_f + \Delta t_{corr}$ , ohms	28.270112
Mole of nitric acid formed, $n'(\text{HNO}_3)$	$1.35 \times 10^{-4}$
Correction for nitric acid, $\Delta E'_{decomp}(\text{HNO}_3)$ , cal.	1.90
Isothermal bomb energy, $\Delta E_B$ , cal.	-10056.68
Correction to standard state, $\Delta E_s$ , cal.	-7.91
Energy of combustion at 25°C., $\Delta E_c^\circ/M$ , cal. g. <sup>-1</sup>	-6185.20

The apparent heat equivalent of the calorimeter,  $\epsilon$  (calor.), was determined by burning benzoic acid sample 39i as obtained from the National Bureau of Standards. The heat of combustion was certified as 26,434 absolute joules per gram when burned under certificate conditions. The average result for ten calibration runs was 46601.2 cal. per ohm, with the value of twice the standard deviation of 6.0 cal. per ohm. Heat of combustion is reported in units of the defined thermochemical calorie (4.1840 joules) and a molecular weight of 110.1135 based on the carbon-12 1961 table of atomic weights.

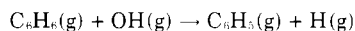
## RESULTS

Of the eight measurements, all except one fell in the range of -6183.55 to -6185.41 cal. per gram. The one result of -6187.10 cal. per gram was discarded. The average of the remainder gave  $\Delta E_c^\circ(c)/M = -6184.58$  cal. per gram with twice the standard deviation of the mean of 0.56 cal. per gram. This gives  $\Delta H_c^\circ(c) = -681.30 \pm 0.10$  kcal. per mole for crystalline resorcinol at 25°C. The uncertainty interval includes the effect of uncertainty in calibration and in ignition energy. This set of measurements was more consistent than our original estimates of uncertainties in experimental variables had predicted. Using the heats of formation of water and carbon dioxide reported in the National Bureau of Standards tables (13) gives  $\Delta H_f^\circ(c) = -87.95 \pm 0.12$  kcal. per mole. ( $\Delta H_f^\circ(\text{H}_2\text{O}, l) = -68.315$  kcal. per mole;  $\Delta H_f^\circ(\text{CO}_2, g) = -94.051$  kcal. per mole). The heat of sublimation listed in the Thermodynamics Research Center Data Project tables (11) is 22.3 kcal. per mole. Combination of these last two values gives  $\Delta H_f^\circ(g) = -65.7$  kcal. per mole.

## DISCUSSION

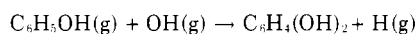
Three values of the heat of combustion of resorcinol have been found in the literature. When converted to modern units these are: -683.4 (9), -683.8 (14), and -683.9 (1) kcal. per mole, compared with our value of -681.30  $\pm$  0.1 kcal. per mole. The uncertainty in the data of Stohman and Langbein is about 1 kcal. per mole, while the information published with the other two values is not sufficient to allow any estimate of uncertainty.

The group contribution method of Cox (2) predicts a heat of formation of phenol of -23.0 kcal. per mole and of resorcinol of -65.9 kcal. per mole in the gas phase. This value for phenol is close to the -22.98 kcal. per mole listed in the TRC tables (11), which is based on experimental measures. The predicted value for resorcinol also falls within the experimental uncertainty in the experimental heat of formation in the gas phase. The changes in enthalpy for the substitution of a hydroxyl radical for one of the hydrogens on benzene to produce phenol



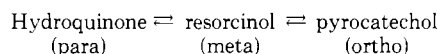
can be calculated from the data in the TRC tables (11), NBS tables (13), and API 44 tables (12). The result is

$\Delta H^\circ = -0.03$  kcal. Similarly, the enthalpy change for hydroxylation in the conversion of phenol to a dihydroxybenzene



is 0.1 kcal. for resorcinol, 0.8 kcal. for pyrocatechol, and -0.1 kcal. for hydroquinone.

The four enthalpies of hydroxylation of benzene and phenol to the corresponding hydroxybenzenes are essentially zero within  $\pm 0.2$  kcal., except for pyrocatechol. From a slightly different point of view, the gas phase enthalpies of isomerization among the three dihydroxybenzenes—namely,



are +0.2 and +0.7 kcal., respectively. The enthalpy of formation of pyrocatechol should be more negative by about 2 to 3 kcal. if intramolecular H-bond formation is present. However, these data imply that the repulsive and strain effects for the two ortho hydroxyl groups on a benzene ring are larger than one would ordinarily expect. More reliable values of enthalpies of formation and sublimation for pyrocatechol are needed to resolve these points.

## ACKNOWLEDGMENT

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## LITERATURE CITED

- (1) Barker, M.F., *J. Phys. Chem.* **29**, 1345 (1925).
- (2) Cox, J.D., *Tetrahedron* **18**, 1337 (1962).
- (3) Greenshields, J.B., Rossini, F.D., *J. Phys. Chem.* **62**, 271 (1958).
- (4) Hubbard, W.N., Scott, D.W., Waddington, G., in "Experimental Thermochemistry," F.D. Rossini, ed., Vol. 1, Chap. 5, Interscience, New York, 1956.
- (5) McCullough, J.P., Good, W.D., *J. Phys. Chem.* **65**, 1430 (1961).
- (6) Prosen, E.J., Rossini, F.D., *J. Res. Natl. Bur. Std.* **27**, 289 (1941).
- (7) Skinner, H.A., *J. Chem. Soc.* **1962**, 4396.
- (8) Somayajulu, G.R., Zwolinski, B.J., *Trans. Faraday Soc.* **62**, 2327 (1966).
- (9) Stohman, F., Langbein, H., *J. Prakt. Chem.* **45**, 305 (1892).
- (10) Thermodynamics Research Center Data Project, Thermodynamics Research Center, Texas A&M University, College Station, Tex. "Catalog of Selected Infrared Spectral Data," Serial No. 326 (loose-leaf data sheets, 1967).
- (11) Thermodynamics Research Center Data Project, Thermodynamics Research Center, Texas A&M University, College Station, Tex. "Selected Values of Chemical Compounds" (loose-leaf data sheets, 1967).
- (12) Thermodynamics Research Center, Texas A&M University, College Station, Tex. "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, (loose-leaf data sheets, 1967).
- (13) Wagman, D.D., Evans, W.H., Halow, I., Parker, V.B. Bailey, S.M., Schumm, R.H., *Natl. Bur. Std., Tech. Note* **270-1** (1965).
- (14) Wolf, K.L., Trieschmann, H.G., *Z. Physik. Chem. (Leipzig)* **B27**, 376 (1934).

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