Enthalpies of Combustion of Organic Compounds. I. 8-Quinolinol.

Minoru Sakiyama, Toshiro Nakano, and Syûzô Seki
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

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A rotating-oxygen-combustion bomb calorimeter equipped with a platinum lined bomb has been constructed and calibrated. The enthalpy of combustion of 8-quinolinol(c) was determined. Thermodynamic quantities obtained are as follows: $\Delta E_c^\circ = -4458.90 \pm 1.60$, $\Delta H_c^\circ = -4460.76 \pm 1.60$ and $\Delta H_f^\circ = -81.24 \pm 2.00$ kJ mol^{-1} for the crystalline state and $\Delta H_f^\circ = 27.6 \pm 2.6$ kJ mol^{-1} for the gaseous state.

Measurement of enthalpy of combustion is the standard experimental method in organic thermochemistry. It provides not only fundamental chemical-thermodynamic quantities but also the most reliable experimental means for determination of the total intramolecular energy if the enthalpy of vaporization or sublimation data are available. The usual static bomb calorimeter is sufficient for compounds containing carbon, hydrogen, oxygen and nitrogen. It is well-known that the use of a rotating bomb calorimeter is required in order to get accurate results for compounds containing halogen, sulfur or metal besides the above-mentioned elements. By rotating the bomb after the combustion reaction the internal bomb-wall is washed out thoroughly with bomb-liquid so that a thermodynamically well-defined state is established.

We have constructed an isoperibol, rotating-bomb calorimeter in order to carry out the measurement of enthalpy of combustion for various kinds of compounds with high precision and accuracy. In the present paper we report the construction, operation and calibration of the calorimeter as well as the enthalpy of combustion of 8-quinolinol. The idealized combustion reaction which the energy and enthalpy of combustion given in this paper refer to is as follows:

$$C_9H_7ON(c) + 10.25\ O_2(g) = 9\ CO_2(g) + 3.5\ H_2O(l) + 0.5\ N_2(g).$$

All the quantities refer to the reference temperature 298.15 K.

Experimental

Apparatus. The rotating-bomb calorimeter is similar in design to that used by Hubbard *et al.*[1,2] The principal calorimeter was based upon the design of the Argonne National Laboratory, U.S.A. (CAPE-432) with some modifications made by ourselves. The calorimetric apparatus consists of a calorimeter vessel surrounded by a jacket with a constant air gap of 10 mm width. The whole system is kept in a measuring-room thermostatted at 23.0±0.3 °C.

The jacket, 47 cm in diameter and 33 cm in height, is made of brass except for portions which face the calorimeter vessel and which are made of copper. The outer surface of the jacket is chromium-plated and polished. The jacket is filled with distilled water of *ca.* 46 dm^3 which is stirred by two stirrers positioned symmetrically. Two centrifugal pumps are installed at the base of the stirrers. The double walled jacket lid is divided into two parts, and a pump circulates the jacket water through each half. Each pair of stirrer and pump is driven simultaneously by an induction motor. A cold water nozzle, a manganin heater (30 V, 36 W) and a thermistor probe for temperature regulation are located at the upper, middle and lower portions, respectively, of a cylinder made of brass which surrounds the stirrer. A pipe heater (100 V, 1000 W) is attached to the bottom of the jacket for rapid heating of the jacket-water.

The calorimeter vessel is made of copper and is of a novel shape in order to minimize the heat capacity. The outer surface is chromium-plated and brightly polished to minimize heat transfer by radiation. The combustion bomb is placed in the vessel with the base upward in order to protect the bomb lid from possible damage due to the high temperature flame during combustion of the sample. The vessel is filled with 2850 g of water while the measurement is going on. The stirrer for circulation water is driven at the rate 200 rpm by a synchronous hysteresis motor attached to the lid of the jacket. The combustion bomb is driven by another synchronous hysteresis motor. The rotation motion of the combustion bomb can be stopped with a plug actuated by a solenoid if desired, after the bomb-drive-motor is switched off. The stirrer and the bomb-drive shaft are connected with each motor via Nylon couplers in the air gap space between the jacket and the vessel. The combustion bomb rotates around two axes perpendicular to each other. The modes of rotation are a spinning motion about the bomb axis at $4\,{}^4/_{17}$ rpm and an end-over-head motion at 10 rpm. A blade and a spring switch both made of phosphor bronze electrically connect the bomb with an outer AC power source for ignition of the sample contained. The calorimeter-water is heated up to a predetermined temperature with a cartridge heater (DC 22 V, 22 W). A quartz thermometer probe is inserted into the calorimeter can through tubing at the top of the vessel. The probe is in intimate contact with the jacket-lid by a metal-to-metal contact device. All the openings on the upper portion of the vessel are closed with rubber bushing, cork stopper and oil seals in order to minimize the possible evaporation of calorimeter-water.

A Parr 1004C stainless steel combustion bomb with platinum-lining *ca.* 0.5 mm thick was used. A platinum-10% rhodium dish (*ca.* 11.14 g in weight) is placed on a gimbal and its ring. Ignition current flows between an insulated electrode and the bomb proper *via* a platinum-ignition-wire (diam. 0.1 mm). Two needle valves are attached to the lid of the bomb, one for introduction and the other for discharge of a gas. One end of a cotton fuse is connected with the ignition wire and the other with the sample. On the outer wall of the bomb proper, miter gears and ball bearings are attached for the biaxial rotational motion mentioned above. It was found from separate experiments that rotation energy is 0.0505 J s^{-1}.

The temperature of the jacket is maintained at 25.300± 0.003 °C throughout the experiment by regulating the electrical current through the jacket heater against a constant flow of cold water from outside. The electrical current is regulated in proportional mode by a vacuum tube regulator similar in principle to that used by Skinner *et al.*[3] The jacket-water is recycled with a rate of *ca.* 20 cm^3 min^{-1} by a metering pump through a spiral copper tube immersed in an ice bath. The temperature of the jacket is monitored by a Beckmann thermometer having the finest division of 0.001 K in its scale.

A sample is ignited by heating the platinum wire to red with AC current supplied from a transformer, with output voltage 4 V and current capacity of the secondary coil 10 A. Under these conditions, ignition can be carried out without fusion of the platinum wire in most cases. The ignition energy is measured by an integrating ammeter, which is similar in principle to that used by Mackle and O'Hare[4] but designed for use of integrated circuits. It was found from calibration-experiments that the full deflection of the meter corresponds to 9.03 J. For the measurement of temperature of the calorimeter a Hewlett-Packard model 2801A quartz thermometer with a model 2850 D sensor was used. The temperature is measured with a 0.000 01 K resolution at constant intervals of *ca.* 101.5 s with the use of an option M40 and is recorded on a Hewlett-Packard model 562 A digital printer.

Experimental Procedure. In the case of solid material, the pelletted sample, cotton fuse and platinum dish are weighed separately. The pelletted sample is tied to one end of the fuse, and measurement is then made of the total weight of the sample and fuse contained in the dish. Buoyancy correction is made to the final weight. The dish with the sample and fuse is attached to the gimbal ring of the bomb, the platinum ignition wire being tied to the other of the fuse. A predetermined amount of water is then added to the bomb and finally the bomb is closed tightly. The bomb is flushed with *ca.* 3.5 dm^3 oxygen at the rate of *ca.* 400 $\text{cm}^3\ \text{min}^{-1}$. Combustible impurities in the oxygen are removed by passing it over Deoxo M (0.5% Pt on γ-alumina) kept at 150 °C. Water and carbon dioxide formed are removed by Ascarite (NaOH on asbestos), Dehydrite ($Mg(ClO_4)_2$) and phosphorus pentoxide, contained in a train of purification-tubes. The bomb is then charged with oxygen up to 3.040 MPa at 25 °C. The bomb is weighed on a large chemical balance (measurable up to 20 kg with *ca.* 3 mg resolution). The combustion bomb is set up in an inverted position in the calorimeter vessel, 2850 g of distilled water is added to the vessel and the total weight is measured. After the outer surface is wiped clean with chamois-leather, the can is fixed on pegs in the hollow of the jacket and then the ignition and heater wires are connected. The calorimeter is heated up to 22.80 °C with the cartridge heater. It is then subjected to a gradual temperature-rise by heat exchange with the surrounding jacket wall and stirring. When it reaches 23.00 °C, the recording of the temperature is started. The temperature rise in the main period is *ca.* 1.8 °C, when the calibration experiment with the standard benzoic acid is carried out under standard bomb conditions (see next section). In combustion experiments mass of a sample is adjusted so that the temperature rise may be as equal as possible to that in the calibration experiments. The anticipated initial temperature T_i of the main period is chosen so that the final temperature of the main period is close to 25 °C. The sample is ignited around T_i and the deflection of the integrating ammeter is recorded. Twenty readings of temperature preceding the ignition compose the initial period. After forty readings following the ignition are recorded, the bomb is taken out from the calorimeter. The bomb surface and external accessories are burst with a hot blaster in open air in order to dry them completely. The bomb is then placed in a sealed-metal-tank which is evacuated ($\sim$ 0.1 Pa) by an oil rotary pump for an hour. After the gas is released, the bomb is opened and the internal wall together with the fittings are washed thoroughly with distilled water. After collecting the washings, which is adjusted to 100 cm^3, the nitric acid formed as a by-product of combustion from a nitrogen containing sample and/or the nitrogen remaining in oxygen is analyzed with 0.02 M sodium hydroxide solution.

Establishment of the Standard Calorimeter System. The energy equivalent of the calorimeter ε°(calor.) is determined by the combustion of benzoic acid (Standard Reference Material 39 i, National Bureau of Standards, U.S.A.). The certificated value for the energy of combustion of the benzoic acid is $26434 \pm 3\ \text{J g}^{-1}$ under standard bomb conditions[9] where the uncertainty is the uncertainty interval.[11] Deviation from the standard bomb conditions is made as small as possible and correction is made for it by the expression given by Jessup.[5] The energy equivalent is defined for the total system consisting of the calorimetric vessel containing 2850.00 g of water and the bomb where the gimbal and platinum ignition wire are installed. Total weight of the calorimetric system is *ca.* 10682 g in the case of calibration.

Material: 8-Quinolinol (Kishida Chemicals Co.) was used without further purification. The sample was prepared as the organic micro-analytical standard substance. The makers assert that the sample is purified by recrystallization (three times) using two kinds of solvents or solvent mixtures. It is certificated by the subcommittee of organic microanalysis of the Japan Society for Analytical Chemistry. The substance is known to have four crystalline modifications with melting points of 73.5, 65, 57—58, and 38—39.5 °C.[6] The present sample was examined with a Perkin-Elmer DSC-1B and no thermal anomaly was detected below 73 °C. It is therefore considered to have the most stable modification. Horton and Wendlandt[7] reported the sublimation pressure of 8-quinolinol. The maximum amount of 8-quinolinol lost by flushing with 10 dm^3 of oxygen was *ca.* 2.7×10^{-5} g at 300 K, corresponding to *ca.* 0.003% of the sample burnt. It was decided to burn the sample pellet without enclosing it in a polyester bag.

Calculations

Corrected Temperature Rise. The corrected temperature rise $\Delta T (= T_f - T_i - \Delta T_c)$, where T_i and T_f are the initial and final temperatures of the main period, respectively, and ΔT_c the temperature rise during the main period due to heat absorbed from the jacket wall and to that caused by stirring (and bomb-rotation), was calculated in the following way.

Temperature readings in the initial and the final periods are fitted to the following integrated form of Newton's cooling law: $T = T_\infty - (T_\infty - T_0)\exp[-k \cdot (t - t_0)]$, where T is the temperature at time t, T_0 the temperature at a reference time t_0, k the cooling constant (thermal leakage modulus), and T_∞ the convergence temperature. The fitting procedures were made as follows: (1) An appropriate practical value for k, a mean value ($= 3.734 \times 10^{-5}\ \text{s}^{-1}$), was first assumed from preliminary analyses. Linear least-square analysis between T and $\exp[-k(t - t_0)]$ was then carried out for the initial and final periods separately. In this case the time of onset of the initial period and that of the final period are taken as the reference time t_0. A curvature correction is applied since the temperature reading of the quartz thermometer shows a mean value during 100 s before display. The effect of rest periods (*ca.* 1.5 s) between each sample period

(100 s) is not taken into consideration in order to conform with the procedure adopted for the main period. From the values of T_∞ and T_0 thus obtained, temperatures $\overline{T}_i$ and $\overline{T}_f$ and the rates of temperature rise G_i and G_f are calculated for the time midway in the initial period and that in the final period, respectively. New values of k and T_∞ are obtained by the expressions: $k=(G_i-G_f)/(\overline{T}_f-\overline{T}_i)$ and $T_\infty=(G_i\overline{T}_f-G_f\overline{T}_i)/(G_i-G_f)$. (2) By using the newly derived values of k, the same linear least-squares analysis described above is carried out again and new values of k and T_∞ are obtained. (3) The temperatures T_i and T_f are calculated as the ending temperature of the initial period and the beginning temperature of the final period from the final set of k and T_∞ by taking the reference time midway in the initial period and that in the final period, respectively.

In each case examined, the variation in k was found to be less than 1×10^{-9} s^{-1} and that in T_∞ less than 1×10^{-5} K, after the procedure in stage (1) had been adopted.

The temperature rise ΔT_c during the main period due to heat exchange with the jacket and the heat of stirring (and rotation) is calculated by: $\Delta T_c=k\int_{t_i}^{t_f}(T_\infty-T)\mathrm{d}t$, where t_i and t_f are the beginning and ending times, respectively, of the main period. Calculation is simple as the temperature readings are mean temperatures during 100 s before display. In the main period it is difficult to estimate the effect of the rest periods on ΔT_c. However, the effect is estimated to be negligible and is not taken into consideration for the final determination of ΔT_c.

Determination of the duration of the main period should satisfy the following requirements:[8] 1) attainment of a state in which the effect of evolution of heat due to combustion is no more detectable, and 2) minimization of heat exchange as well as heat of stirring correction which may be a cause of experimental error. The corrected temperature-rise was calculated by increasing the length of the main period from eight to twenty readings. A compromise between the two contradictory requirements has been found to be twelve readings both in calibration (using benzoic acid) and in combustion experiments. Thus, twenty readings after the main period have been assigned to the final period.

Energy Equivalent and Energy of combustion. The energy equivalent of the standard calorimetric system ε°(calor.) was calculated by the procedure described by Coops *et al.*[9] The mean and standard deviation of the mean for the energy equivalent was found to be 15162.8±1.3 J K^{-1} from six calibration experiments interspersed between combustion experiments, where uncertainty is the standard deviation of the mean. The standard energy of combustion ΔE°_c was calculated by the method of Hubbard *et al.*,[10] the final overall precision of the ΔE°_c mean values being estimated as recommended by Rossini[11] following the scheme presented by Bjellerup.[12] All procedures in the calculation of ΔT, ε°(calor.) and ΔE°_c were incorporated in a Fortran program*, the computations being carried out with a NEAC 2200 computer of Osaka University.

Table 1. Auxiliary quantities used in the calculation of energy of combustion

Substance		ρ	C_p	$(\partial E/\partial P)_T$
		g cm^{-3}	J K^{-1} g^{-1}	J kPa^{-1} g^{-1}
8-Quinolinol	C_9H_7ON	1.57	(1.21)[a)]	(−1.19)[a)]
Fuse	$CH_{1.860}O_{0.930}$	1.50	1.70	−2.94

a) Estimated value.

The standard energy of combustion of the cotton fuse ΔE°_c(fuse) was determined by separate combustion experiments and found to be −16507 J g^{-1}.

Auxiliary Quantities. Molecular weight were computed from the 1961 Table of Relative Atomic Weights. Auxiliary data necessary for calculating weights *in vacuo* from weights in air, for correcting the energy of bomb reaction to that of an isothermal reaction at 25 °C and for making the reduction to standard states are given in Table 1. The density and specific heat capacity of the dish (Pt–Rh alloy) were estimated to be respectively 20.50 g cm^{-3} and 0.1464 J K^{-1} g^{-1}.

Results and Discussion

The results of six combustion experiments on 8-quinolinol are given in Table 2. Symbols in the table are similar to those used by Hubbard *et al.*[10] except for $\Delta m(H_2O)$, ΔE_{rot}, and ΔE(std. state). $\Delta m(H_2O)$ is the mass of excess water in the calorimeter can, ΔE_{rot} the energy evolved by the rotation of the bomb and ΔE(std. state) the sum of items 81—86, 87—89, 91 and 93—94 designated by Hubbard *et al.*[10] From these results the following thermodynamic quantities were derived: ΔE°_c(c) = −4458.90±1.60, ΔH°_c(c) = −4460.76±1.60, ΔH°_f(c) = −81.24±2.00 and ΔH°_f(g) = 27.6±2.6 kJ mol^{-1}, where the uncertainties are uncertainty intervals defined by Rossini.[11] The standard enthalpy of combustion ΔH°_c has been calculated by the use of the expression: $\Delta H^\circ_c=\Delta E^\circ_c+\Delta n_g RT$, where Δn_g is the increase in moles of gaseous species in an idealized combustion reaction and R is the gas constant. In the calculation of the standard enthalpy of formation, CODATA key values[13] for $\Delta H^\circ_f(CO_2,g)$ and $\Delta H^\circ_f(H_2O, l)$ and the enthalpy of sublimation value of Horton and Wendlandt[7] for 8-quinolinol have been used. These values are as follows: $\Delta H^\circ_f(CO_2, g) = -393.51\pm0.13$ and $\Delta H^\circ_f(H_2O, l) = -285.830\pm0.042$ kJ mol^{-1}, where uncertainties are those at 95% confidence level and $\Delta H_{subl}=108.8\pm1.7$ kJ mol^{-1}, where uncertainty is the uncertainty interval.

Combustion experiments were carried out with and without the rotation of the combustion bomb after ignition. No significant difference was found in ΔE°_c values for both modes. In some experiments nitric acid was analyzed separately for the solutions formed on the side wall and on the upper and lower walls of the bomb. The results in an experiment are 5.6×10^{-4} and 2.1×10^{-4} mol for the solutions on the side

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* The Washburn correction portion of the program was rewritten with a slight modification from an ARGOL program supplied by courtesy of Professor S. Sunner, University of Lund, Lund, Sweden.

TABLE 2. RESULTS OF COMBUSTION EXPERIMENTS ON 8-QUINOLINOL

m^i(compd.)g	0.83862	0.85140	0.84207	0.85751	0.81135	0.82038
m^i(fuse)/g	0.00252	0.00284	0.00296	0.00306	0.00328	0.00271
m^i(H_2O tot.)/g	0.982	1.081	1.076	1.092	0.971	0.986
m(Pt)/g	11.142	11.142	11.142	11.142	11.142	11.142
Δm(H_2O cal.)/g	0.159	0.237	−0.070	0.259	0.293	−0.294
p^i(gas)/MPa	3.044	3.041	3.037	3.040	3.034	3.040
T_i/°C	23.25499	23.24191	23.25053	23.22730	23.32311	23.30232
T_f/°C	24.98287	24.99775	24.98751	24.99433	24.99748	24.99438
ΔT_{corr}/°C	0.02310	0.02467	0.02460	0.02380	0.02501	0.02455
n^f(HNO_3)/mol	0.000722	0.000798	0.000727	0.000767	0.000709	0.000709
ΔE_{ign}/J	6.14	7.77	8.13	7.86	1.86	6.86
ΔE_{rot}/J	10.61	10.33	10.59	0.0	10.60	0.0
ΔE_{diln}(HNO_3)/J	−0.12	−0.13	−0.11	−0.12	−0.11	−0.11
ΔE_{decomp}(HNO_3)/J	42.52	46.99	42.81	45.17	41.75	41.75
ΔE(std. state)/J	15.99	16.40	16.17	16.53	15.37	15.60
ε^i(cont.)/J K^{-1}	16.95	17.36	17.32	17.41	16.84	16.93
ε^f(cont.)/J K^{-1}	17.78	18.20	18.16	18.26	17.64	17.74
ΔE_c°/J g^{-1}	−30719.7	−30716.1	−30717.9	−30721.5	−30707.0	−30718.9
Mean and standard deviation of the mean $= -30716.9 \pm 4.4$ J g^{-1}						

wall and on the upper and lower walls, respectively. Judging from the relative availability of water on both portions, nitric acid is more concentrated in the solution on the side wall. The nitric acid solution on the side wall is formed by the reaction of nitrogen oxides with water from the sample. The fact that nitric acid is more concentrated on the side wall is in good agreement with the observation of Armstrong and Marantz[14] that most of nitrogen oxides from the combustion of organic nitrogen compounds not containing hydrogen may not be absorbed by bomb water effectively unless a device to vaporize the water after the combustion is made. The localization of nitric acid in the bomb, however, does not cause a significant systematic error in the determination of the standard energy of combustion because the contribution of the energy of dilution of nitric acid to the total energy is not significant and in addition the energy of dilution does not depend seriously on the concentration in the range 5—10%.

The enthalpy of combustion of 8-quinolinol was reported only briefly by Sullivan and Hunt[15] and Wood and Jones.[16] A large difference of *ca.* 12 kJ· mol^{-1} (*ca.* 0.3%) was found between their values. Our value does not agree with either of them within the assigned uncertainty intervals, but agrees fairly well with the mean of these values ($\Delta H_c^\circ = -4458.9$ kJ· mol^{-1}) cited as a selected value by Domalsky.[17]

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