

# Thermochemistry of Biologically Important Compounds

## Heats of Combustion of Solid Organic Acids

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Standard heats of formation, calculated from measured heats of combustion, have been obtained for the following compounds: oxalic acid, malonic acid, succinic acid, glutaric acid, maleic acid, maleic anhydride, fumaric acid, DL-malic acid, L-malic acid, and citric acid.

RAPID PROGRESS is being made in unravelling the intermediate steps in complex metabolic reactions which occur in living organisms. Attempts to develop quantitative and mathematical descriptions of these processes have pointed out the need for reliable thermodynamic information on the compounds which take part in these reactions. This is the first report of a series designed to furnish data needed to obtain heats and Gibbs free energies of formation of these compounds in the pure state and in solution. A series of Krebs cycle acids and related compounds is being studied first. Although heats of combustion of most of the compounds presented in this paper have been published previously by various authors we feel that it is desirable to repeat these measurements using modern techniques and to present a consistent set of data for the whole series of compounds. The heat of combustion of succinic acid has been measured many times and a review of this literature has been given by Pilcher and Sutton (10). Comparison

of their recommended value with our value for succinic acid furnishes a check on the accuracy of our measurements.

### EXPERIMENTAL

**Materials.** Most samples used in the heat of combustion measurements were obtained by further purification of high quality commercially available grades. Experiments have been carried out to determine the best procedure for each compound. Recrystallization from suitable solvents and sublimation under pressures of 20 to 40 microns were used in most cases. Brief descriptions of the purification procedures are shown in Table I. Each sample was given a final drying, just before being used in a combustion experiment, by heating the finely ground powder in a vacuum drying apparatus in the presence of silica gel. Conditions were selected to remove effectively all of the water without causing the formation of anhydride or other

Table I. Preparation and Properties of Samples

Sample	Starting Material	Recrystallizing Solvent	Range °C.		Observed - Calculated		
			Sublimation	Melting	Equiv. wt.	% C	% H
Oxalic acid, A	Fisher Cert. Reag. <sup>a</sup>						
Oxalic acid, B	Baker Anal. Reag.	water, twice	...	190.6-193	0.04	0.03	0.06
Oxalic acid, C	sample B	...	105-115	186.5-191	0.07	0.16	0.02
Malonic acid, A	EK No. 695 <sup>a</sup>			134.0-135.1		-0.11	-0.14
Malonic acid, B	sample A	methanol-CHCl <sub>3</sub> , isobutyl ketone	110-115			-0.05	-0.01
Malonic acid, C	sample A	cyclohexane-acetone, twice	...	134.8-135.0	0.06		
Malonic acid, D	sample C	...	110-112	134.5-135.0		0.07	0.01
Succinic acid, A	Fisher Cert. Reag. <sup>a</sup>			185.7-187.0	0.07	0.10	0.08
Succinic acid, B	sample A	water, twice; water- ethanol; water, twice	130-140	187.6-187.9	0.05	-0.04	0.01
Glutaric acid, A	EK No. 564	dichloroethane-acetane	...	96.1- 97.2	0.44	0.03	-0.11
Glutaric acid, B	sample A	...	100-110	96.5- 97.3	0.05	0.05	-0.13
Maleic anhydride, A	Fisher, A-168	benzene	50	52.6- 53.8	0.07		
Maleic anhydride, B	Fisher, A-168	chloroform, twice	...	52.5- 53.7	0.04		
Maleic acid, A	Mal. anhyd., A	water, twice	...	129.3-130.2	0.05	-0.04	0.03
Maleic acid, B	Fisher, A-168 Mal. anhyd. conv. to acid	water, methyl ethyl ketone	...	130.3-131.0	0.12		
Fumaric acid, A	Fisher, A-120	n-propanol, conv. to Na-salt then to acid	165	289.2-289.6	0.10	0.06	-0.01
Fumaric acid, B	Fisher, A-120	water, twice	...	284.9-289.6	0.26		
DL-Malic acid	Fisher, A-169	dioxane, twice	...	127.2-128	0.11	0.06	0.01
L-Malic acid	Cal. Corp. Biochem. Research, 4425	dioxane, twice	...	98.8-100.3	0.10	-0.04	-0.31
Citric acid	Baker Anal. Reag.	water at 48°, twice	...	152.9-155 (dec.)	0.04	0.03	-0.02

<sup>a</sup>Used with no further treatment.

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decomposition products. Temperatures to which samples could be heated without decomposition were determined from an examination of thermogravimetric curves, both in the atmosphere and at reduced pressure, and DTA curves. Temperatures at which gas evolution begins, as detected by a thermal conductivity cell, were also observed. Although it was not always possible to distinguish between sublimation and the onset of decomposition, no evidence of decomposition could be found below the following temperatures; oxalic acid, 100°; malonic acid, 120°; succinic acid, 150°; glutaric acid, 80°; maleic anhydride, 140°; maleic acid, 110°; fumaric acid, 240°; DL-malic acid, 120°; L-malic acid, 100°, and citric acid, 150°. Temperatures used for drying were always well below these temperatures and in no case could a relationship be found between temperature or time of drying and heat of combustion.

Results of several purity tests are also listed in Table I. Melting ranges were obtained by heating the sample in a sealed capillary tube completely immersed in a circulating oil bath at a rate of about 0.1 degree per minute. The temperatures reported are those at which the first indication of melting could be seen and those at which the last trace of solid material disappeared. Temperatures were measured with mercury thermometers graduated at 0.1° intervals which had been compared to a platinum resistance thermometer calibrated by the National Bureau of Standards. The melting range of fumaric acid was measured directly with the platinum resistance thermometer. There are indications that most of these compounds decompose at least slightly at the melting point so that melting ranges have limited value in indicating purity. Cooling curve experiments were made using an apparatus similar to that of Smit and Kateman (15) on several samples. Temperatures were measured with a calibrated thermistor. The melting point of the pure sample and the mole fraction of impurities were determined from a plot of temperature vs. fraction of sample melted. Three runs on maleic anhydride sample A gave melting points of 54.15°, 54.00°, and 53.95° C. and 0.15, 0.25, and 0.16 mole per cent impurity. Maleic anhydride sample B gave a melting point of 53.83° C. and 0.35 mole per cent impurity and glutaric acid, sample A gave melting point of 97.28° C. and 0.20 mole per cent impurity. Successive determinations on the same portion of succinic acid sample B gave melting points of 187.48° and 186.68° C. with 0.10 and 0.23 mole per cent impurity. Other similar experiments showed that repeat determinations on samples of succinic acid and malonic acid gave increasing amounts of impurity following each melting.

Equivalent weights were determined by first dissolving a weighed portion of the solid acid in 0.4M potassium bromide solution. Standard sodium hydroxide solution was then added from a weight burette until the acid was almost neutralized. The final end point was reached by means of a coulometric titration with a silver anode and platinum cathode. The end point was located by plotting the second derivative of the pH, as determined by a glass-electrode

pH meter, against equivalents of base generated by electrolysis. The sodium hydroxide was standardized against a N.B.S. sample of potassium acid phthalate using the same procedure. The values reported in Table I are the average of three or four determinations. The difference between the maximum and minimum in each set was usually about one part in a thousand so that the average is probably reliable to about one part in two thousand. The proportion of carbon and hydrogen was determined by a micro-combustion method using a special high accuracy procedure. Samples were dried prior to analysis in a manner similar to that used for the combustion measurements.

Infrared spectra using the KBr pellet technique, chromatography through a column containing silicic acid packing, and paper chromatography using several different solvent systems were used to test purity of these samples. None of these methods could detect any impurity in any of the samples used in the heat of combustion measurements. However tests with samples containing known quantities of impurities showed that, at best, these techniques could not detect impurities of the type likely to be present in amounts less than about 1 to 2%.

X-ray diffraction angles from powdered samples were used as a guide in developing purification procedures and in testing for decomposition. For the most part the diffraction angles were nearly the same for different samples of the same compound. The only exceptions for strong diffractions were as follows. Oxalic acid sample C showed a diffraction corresponding to 2.84A which was not present in sample B. Glutaric acid sample A gave a reflection at 6.37A which was not present in sample B and finally fumaric acid sample A gave a reflection at 4.19A which was not present in sample B.

In order to correct the heat of combustion to the standard state the effect of pressure on the energy of the compound should be known. This may be approximately related to the coefficient of expansion by the formula,  $(\partial E/\partial P)_T = -RT (\partial V/\partial T)_P$ . Although this is a minor correction very little data of this type can be found for solid organic compounds. Table II shows the results of the measurements of the specific volume of some compounds as a function of temperature. A weighed portion of the solid was placed in a glass dilatometer and the remaining space filled with xylene, was boiled under reduced pressure to remove all air bubbles. The volume of the solid was then calculated from the volume of xylene present and the amount of xylene expelled as the temperature was raised. The specific volume of the solid was calculated and fitted to a power series in temperature by a least squares procedure.

**Calorimetry.** A Parr Instrument Co. model 1106 bomb with platinum fittings and 1221 adiabatic calorimeter which had been modified in several respects were used for the heats of combustion measurements. The principal modifications made on the calorimeter are as follows. The plastic ring around the top of the water bucket was removed and replaced by four sharp steel pins attached to fittings at the top. The bucket is supported inside the adiabatic jacket by

Table II. Coefficients in the Specific Volume Formula,  $V = a + bt + ct^2$  ( $V$  in ml. gm.<sup>-1</sup> and  $t$  in ° C.), Coefficient of Expansion, and Coefficient of Internal Energy for Some Solid Organic Acids

Compound	Temp. Range, ° C.	$a$	$b \times 10^4$	$c \times 10^6$	$(\partial V/\partial T)_P \times 10^4$	$(\partial E/\partial P)_T \times 10^3$
					Ml. Gm. <sup>-1</sup> Deg. <sup>-1</sup> at 25° C.	Cal. Gm. <sup>-1</sup> Atm. <sup>-1</sup> at 25° C.
Oxalic acid	20-80	0.5758	2.137	-0.705	1.784	-1.29
Malonic acid	20-80	0.6250	0.900	0.446	1.123	-0.81
Succinic acid	20-80	0.6349	1.097	0.398	1.296	-0.94
Glutaric acid	0-50	0.7137	1.965	0.194	2.062	-1.49
Maleic acid	0-80	0.6215	1.776	0.050	1.801	-1.30
Fumaric acid	20-80	0.6074	0.480	0.937	0.948	-0.68
Malic acid	20-80	0.7173	1.291	-0.459	1.062	-0.77
Citric acid	20-80	0.6415	-0.477	2.363	0.704	-0.51

means of these pins, which rest on small cups attached to the inside of the jacket. A chromium plated brass cover was installed on the bucket to reduce evaporation of water. This cover contains a probe and electrical contacts for a Leeds and Northrup type 8164 platinum resistance thermometer, an electrical contact for the ignition circuit and a small hole for the multi-junction thermocouple used for adiabatic control. A piece of 0.5 inch copper rod was soldered to the inside of the cover and conducts heat from the water to the cover and thus helps to reduce the temperature lag of the cover. The thermometer resistance was measured with a Leeds and Northrup model 8069 Mueller Bridge and highly sensitive mirror galvanometer located about 15 feet from the scale. Using a current reversal method for balancing the bridge and using the galvanometer scale to interpolate between the settings on the lowest decade of the bridge, a sensitivity of  $5 \times 10^{-6}$  ohms, corresponding of  $5 \times 10^{-5}$  degrees, was achieved.

The difference in temperature between the water in the jacket and the bucket was monitored by an 8-junction copper-constantan thermopile connected to an electronic galvanometer. The junctions which were immersed in the bucket were encased in a glass tube and those immersed in the jacket in a copper tube. Both sides were made compact to reduce temperature lag. The complete unit, including a switch for opposing the two 4-junction halves, was made in one piece which could be raised when removing the bucket. The system is sensitive to about 0.001 degree. An adjustable reference voltage connected in series with the galvanometer made it possible to maintain a constant temperature difference between the jacket and bucket. In practice this temperature difference was adjusted until a drift rate of not more than  $5 \times 10^{-5}$  degrees per minute was attained, and then held constant throughout the experiment. Because of the heat of stirring this resulted in a jacket temperature of 0.05 to 0.1 degree cooler than the bucket. Manual addition of hot or cold water was used to control the jacket temperature. A system of copper tubes was installed to distribute the incoming water uniformly throughout the jacket.

The solid samples were ground to a fine powder, dried, formed into pellets and weighed to an accuracy of 0.05 mg. with weights which had been checked against a set calibrated by the National Bureau of Standards. All weighings were reduced to vacuum. Since oxalic and citric acids would not burn in the bomb when pure they were mixed with a primary standard grade of benzoic acid prior to forming the pellet. Because of its high vapor pressure all samples of maleic anhydride were sealed in bags of 0.001 inch thick polyester film. The cylindrical shaped bags were made to fit snugly around the pellet and were sealed with a small soldering iron. Since oxalic and citric acids form stable

hydrates some of these samples were also sealed in such bags to prevent absorption of water by the sample before combustion. Samples were ignited by passing current from a constant current supply through a platinum wire coiled around a strip of filter paper. Wire, 26 gage, was used in the early experiments but 0.004 inch wire was used in all the others. The smaller wire melted through during each ignition but required much less electrical energy. Electrical energy was measured with a voltage integrating circuit. The following standard state heats of combustion,  $\Delta E_c^\circ$ , were determined in separate experiments and used in correcting for the effects of these items; benzoic acid,  $-6310.0$  cal. gm.<sup>-1</sup>; paper,  $-4152$  cal. gm.<sup>-1</sup> and polyester film,  $-5456.3$  cal. gm.<sup>-1</sup>.

In every case one-ml. of water was placed in the bomb and, after sealing, the bomb was flushed and filled with regular commercial grade oxygen which was passed through a furnace packed with copper oxide at around 700°C. The initial pressure was measured with a precision Bourdon gage sensitive to 0.03 atm and was adjusted to 30 atm. in all cases except that 25 atm. was used in four of the experiments with glutaric acid. The bucket was filled with 2042.8 grams of water weighed to an accuracy of 0.05 grams.

The initial temperature of the water in the bucket was adjusted to within 0.05° of 24° C. and the fore-period drift rate determined. The slow drift rates which could be obtained by the adiabatic technique made accurate time measurements unnecessary. The resistance of the thermometer was calculated as the average of the normal and reverse readings of the bridge and the time was taken as midway between the time when these two readings were obtained. In most cases the sample weight was adjusted to produce about 6500 cal. of heat, resulting in a temperature rise of about 2.5°. The principal calorimetric error was probably the result of lack of adiabatic control during the two or three minute period after ignition. The temperature of the water in the bucket became sufficiently stabilized within about 12 minutes to begin recording the after-period drift. The temperature rise was obtained by extrapolating the fore-period and after-period drifts to the time of ignition of the sample.

Heats of combustion were reduced to the standard state by the procedure of Hubbard, Scott, and Waddington (6), using a digital computer for the actual computations. An uncertainty interval, representing the 95% confidence limit, was estimated for each experimental variable. The computer program then computed the corresponding uncertainty interval in the standard state heat of combustion. The computation procedure was based on the usual statistical formulas, as given by Rossini (12), in which the estimated uncertainty intervals were interpreted as twice the standard deviation. Examples of these computed uncer-

Table III. Examples of Experimental Data for the Combustion Experiments

	Succinic Acid, Sample B	Citric Acid
Weight of sample, $m_1$ , grams	2.15806	1.65486
Weight of auxiliary material, $m_2$ , grams	...	0.35935
Weight of plastic film, $m_3$ , grams	...	0.05265
Weight of paper fuse, $m_4$ , grams	0.01456	0.01142
Initial temp., ° C.	24.02	24.05
Ignition energy, cal.	0.50	0.54
Total bomb energy, cal.	6585.9	6654.2
Heat of combustion of items other than sample, cal.	60.4	2602.2
Heat of decomposition of nitric acid, cal.	0.67	1.06
Correction to standard state, cal.	8.62	8.92
Constant volume heat of combustion in the standard state, $\Delta E_c^\circ$ cal. gm. <sup>-1</sup>	3019.5	2442.5
Computed uncertainty interval, s, cal. gm. <sup>-1</sup>	1.04	1.67

tainty intervals,  $s_i$ , are listed in Table III. The value of  $2\sigma$  ( $\sigma$  = standard deviation) for the mean of a series of such measurements on the same quantity may be computed from the  $s_i$ 's by formulas given by Rossini. These values are listed under the heading  $s_a$  in Table IV. Thus the values of  $s_a$  should represent the 95% confidence limit resulting from calorimetric errors only, assuming that the original estimates were reliable. Additional errors may be introduced into the final values by variations in the properties of the samples. If this happens the value of  $2\sigma$  for the mean of a series of measurements as calculated from the individual results will be larger than  $s_a$  for the same series. Values of  $2\sigma$  obtained in this way and including the effect of uncertainty in the calibration of the calorimeter are also listed in Table IV. Complete detailed experimental data for all the measurements reported in this paper may be obtained from the American Documentation Institute.

**Calibration and Units.** The heat capacity of the empty calorimeter, obtained as the average six combustion of N.B.S. benzoic acid, sample 39h, was 24440.9 cal. ohm.<sup>-1</sup> with  $2\sigma = 6.3$  cal. ohm.<sup>-1</sup>. The calibration was based on the value of 26434 abs. joules gm.<sup>-1</sup> for the heat of combustion of benzoic acid when burned under conditions specified in the N.B.S. certificate. All heats of combustion are reported in units of the defined thermochemical calorie and are referred to 25°C. Molecular weights were calculated from the 1961 atomic weight scale based on carbon 12.

## DISCUSSION

The average values of heats of combustion listed in Table IV were obtained by weighing the individual results in proportion of  $1/s_a$ . Measurements have been made on additional samples of succinic acid, DL-malic acid, and citric acid. However, tests have indicated that these samples may not be pure so that they have not been included in the results shown in Table IV. The observed values of  $2\sigma$  for the calibration runs with benzoic acid, for the succinic acid data, and, considering the effect of uncertainty in calibration, the

malonic acid data are about what would be expected for the errors in calorimetric measurements as represented by the values of  $s_a$  in Table IV. However in all other cases  $2\sigma$  is appreciably larger than  $s_a$ . This is probably the result in variations in the properties of the sample from one run to the next. The large variation shown by the oxalic acid and citric acid data may be the result of mixing these compounds with benzoic acid prior to combustion.

The heat of combustion of oxalic acid sample C is significantly higher than that of samples A and B. Sample C was obtained by sublimation whereas samples A and B were obtained by recrystallization from water. Oxalic acid exists in two polymorphic forms (2, 4, 8). The  $\alpha$ -form (rhombic) is thermodynamically stable at room temperature while the  $\beta$ -form (monoclinic) is metastable. Measurements of refractive indices by the immersion technique using a polarizing microscope give  $\beta = 1.540$  and  $\gamma = 1.638$  for the sodium D-line at room temperature for sample B; and  $\beta = 1.535$  and  $\gamma = 1.632$  for sample C. These results indicate that both samples consist of the  $\alpha$ -phase although the discrepancy between values reported by different authors seems to be about as large as the difference between refractive indices for the  $\alpha$ - and  $\beta$ -phases. Since the method of preparation suggests that sample C may consist, at least partly, of the  $\beta$ -phase it seems likely that the data for samples A and B represent the heat of combustion of the stable form of oxalic acid and this has been used to calculate the values for oxalic acid in Table V. Malonic acid exists in three forms (1, 5, 8). The  $\alpha$ -form (triclinic) is stable at room temperature. This changes to a monoclinic form at 94°. A second monoclinic form can also be prepared. All samples of monoclinic acid have, within experimental error, the same heat of combustion. Refractive indices of 1.448, 1.488, and 1.577 for samples C and D identify them as the triclinic modification. Succinic acid exists in two crystalline forms (3, 5, 8, 11). The  $\beta$ -form (monoclinic) is stable at room temperature while the  $\alpha$ -form (triclinic) is stable above 135°C. Refractive indices of 1.447, 1.534, and 1.610 identify samples A and B as the  $\beta$ -form. The

Table IV. Average Heats of Combustion

Compound	Samples	Number of Measurements	Average $-\Delta E^\circ$ Cal. Gm. <sup>-1</sup>	$2\sigma$	$s_a$
Oxalic acid	A, B	5	654.7	2.5	0.4
Oxalic acid	C	2	679.0		
Malonic acid	A, B, C, D,	10	1983.5	0.9	0.3
Succinic acid	A, B	9	3019.6	1.0	1.0
Glutaric acid	A, B	5	3891.1	2.2	1.3
Maleic acid	A, B	5	2795.5	1.5	0.9
Maleic anhydride	A, B	5	3392.8	1.8	1.1
Fumaric acid	A	5	2753.3	1.8	0.5
Fumaric acid	B	2	2742.2		
DL-Malic acid		4	2367.7	1.1	0.4
L-Malic acid		2	2371.4		
Citric acid		8	2443.7	5.7	0.6

Table V. Heats of Formation from Elements in Their Standard States at 25°C.

Compound	Molecular Weight	Heat of Formation, $-\delta H_f^\circ$ Kcal. Mole <sup>-1</sup>			
		Experimental	Other Data		
Oxalic acid	90.04	198.36 ± 0.23	196.2(16)	196.31(17)	
Malonic acid	104.06	212.97 ± 0.09	211.4(16)	211.6 (9)	212.42(17)
Succinic acid	118.09	224.87 ± 0.12	224.3(16)	226.7 (9)	224.33(17)
Glutaric acid	132.12	229.44 ± 0.29	226.2(16)	228.87(17)	
Maleic acid	116.08	188.95 ± 0.17	186.3(16)	185.9 (9)	188.29(14)
Maleic anhydride	98.06	112.43 ± 0.17	109.6 (9)		188.21 (7)
Fumaric acid	116.08	193.84 ± 0.21	192.5(16)	194.1 (9)	193.84(14)
DL-Malic acid	134.09	264.27 ± 0.15			
L-Malic acid	134.09	263.78			
Citric acid	192.13	369.0 ± 1.1	362.7 (9)		193.68 (7)

heats of combustion of the two fumaric acid samples differ appreciably. The reason for this is not obvious, however, the melting points and equivalent weight data in Table I indicate that sample A is more nearly pure than is sample B. It may be that sample B was not completely dry. The data for sample A was used in Table V.

The experimental heats of formation listed in Table V were calculated from the data in Table IV using the heats of formation of water and carbon dioxide given in the N.B.S. Circular 500 (13). The uncertainty intervals listed were based on the values of  $2\sigma$  in Table IV. Data from previous literature reported in Table V have been recalculated to correspond, as nearly as possible, to the units and conditions used in this report.

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## Mutual Solubilities in Water-Permethylosiloxane Systems

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**The solubility of tritiated water in pure hexamethyldisiloxane, I; hexadecamethylheptasiloxane, II; and octamethylcyclotetrasiloxane, III, at 25.0°C. is less than one part per million. On a weight basis this value represents the lower limit of water detectable in these experiments. The solubility of carbon-14 labeled octamethylcyclotetrasiloxane, IV, in water at 25.0°C. was 2.0 parts per million by weight. This latter value suggests that hydrogen bonding forces between water and siloxanes are weaker than the hydrogen bonding forces for most oxygenated functions such as diethyl ether.**

**T**HE HYDROPHOBIC nature of the siloxane bond in organosiloxanes is no longer surprising to the organosilicon chemist. There is, however, a paucity of reliable quantitative data in the literature which demonstrates this fact. Our present paper briefly reports the findings from an investigation of mutual solubilities in water-permethylosiloxane systems.

#### EXPERIMENTAL

**Materials.** Hexamethyldisiloxane, I, hexadecamethylheptasiloxane, II, and octamethylcyclotetrasiloxane, III, were fractionally distilled and then stored for at least three days in contact with chromatographic grade alumina.

Purified water was prepared by redistilling distilled water from a solution of alkaline potassium permanganate, through a tin condenser, into polyethylene bottles.

Tritiated water was obtained from New England Nuclear Corp. at a specific activity of 100 mc. per gram and diluted with purified water to the convenient activity level of 8  $\mu$ c. per gram before use.

Carbon-14 labeled octamethylcyclotetrasiloxane, IV, specific activity for these experiments 15  $\mu$ c. per gram, b.p. 171°C., was synthesized via conventional reactions starting from carbon-14 labeled methyl iodide purchased from Tracerlab. Further purification just prior to use was attained by injecting 1 cc. of IV into the preparative attachment available for the F & M Model 500 GLC unit. The