Summary

Rates of inversion of sucrose measured by the reducing sugars produced were found to be slightly higher than the rates previously obtained by the dilatometric method at the same temperatures and concentrations of hydrochloric acid and sucrose.

The activation energy obtained is 25.9 kcal. and does not vary significantly with the temperature between 0 and 30°.

The logarithms of the velocity constants at 0° are a linear function of the concentration of hydrochloric acid between 0.1 and 4.4 *N*.

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CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Thermal Data. XII. The Heats of Combustion of Urea and Guanidine Carbonate and their Standard Free Energies of Formation

BY HUGH M. HUFFMAN

In continuation of our program,[1] involving the study of the thermal properties of organic compounds of physiological interest, we have determined the heats of combustion of urea and of guanidine carbonate. These data have been used in conjunction with other data to calculate the standard free energies of formation of these compounds.

Experimental

Calorimetric Method.—The calorimetric method has been described in previous publications.[2] Since no important changes have been made, only the essential details will be given. All of the combustions were made in a Parr bomb having a volume of 0.380 liter and with an initial oxygen pressure of 30 atmospheres and with 1 ml. of water in the bomb.

The energy equivalent of the calorimetric system was controlled throughout the investigation by frequent calibration with Bureau of Standards benzoic acid standard sample 39e, having for its isothermal heat of combustion under standard conditions[3] and at 25° the value of $-\Delta U_B/m = 26{,}419$[4] N.B.S. international joules. The conditions in our bomb are not quite standard, necessitating a correction of this value to 26,418 N.B.S. international joules.

A minor change was made in the calorimeter after the combustions on guanidine carbonate and hence a recalibration was required. The energy equivalent of the calorimetric system in the guanidine carbonate series was 3157.4 cal., mean of fifteen calibration experiments, with a standard deviation of 0.0016% and in the urea series 3157.0 cal., mean of seventeen calibration experiments, with a standard deviation[5] of 0.0021%. The results of all of our combustion experiments are expressed in terms of the defined conventional calorie which is derived from the N.B.S. international joule by dividing by 4.1833. The units and corrections are the same as those given in previous papers.[6] The molecular weights are based on the 1939 table of atomic weights. All of the thermal data are given for the isothermal process at 25° and for true mass.

Purification and Heats of Combustion

Urea.—Three combustion samples a, b and c were prepared from J. T. Baker C. P. urea by one and three crystallizations from redistilled water and by two crystallizations from purified methyl alcohol, respectively.

Guanidine Carbonate.—Material from Eastman Kodak Co. was dissolved in hot water and allowed to cool, it was then precipitated by the addition of about 2.5 volumes of purified ethyl alcohol. This process was repeated to give sample (a). Material from Hoffman–LaRoche was precipitated once as above to give sample (b).

Nitrogen determinations on the urea gave the theoretical results and the ash content was negligible. Titrations of the guanidine carbonate with dilute hydrochloric acid gave 99.7 and 99.8% of the theoretical. The ash content was about 0.03%.

The results of the combustions of these compounds are given in Table I. In the case of guanidine carbonate we have arbitrarily corrected the mass by subtracting from the observed mass the mass of ash found after each combustion. The uncertainties given in the table are the mean deviations from the mean.

In addition to the experimental values we have also calculated the quantities $-\Delta U_B$, $-\Delta U_R$, $-\Delta H_R$ and $-\Delta H_f^\circ$ which we have defined previously.[2b] To obtain the values of $-\Delta H^\circ_{f298}$ we have used for the heats of formation of water and carbon dioxide at 25° the value 68,318.1[7] and 94,030[8] calories, respectively.

Discussion

Urea has been burned by several workers (Berthelot 1890, Stohmann 1893, Krummacher 1904, Emery and Benedict 1911). It is not possible to make a careful comparison of our results

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(1) Huffman and Borsook, THIS JOURNAL, **54**, 4297 (1932).

(2) (a) Huffman and Ellis, *ibid.*, **57**, 41 (1935); (b) Stiehler and Huffman, *ibid.*, **57**, 1734 (1935).

(3) Washburn, *Bur. Standards J. Research*, **10**, 552 (1933).

(4) Jessup and Green, *ibid.*, **13**, 496 (1934).

(5) Rossini and Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

(6) Huffman, THIS JOURNAL, **60**, 1171 (1938).

(7) Rossini, *Bur. Standards J. Research*, **22**, 407 (1939).

(8) Rossini and Jessup, *ibid.*, **21**, 491 (1938).

TABLE I

THE EXPERIMENTAL DATA AT 25°

Sample	Desiccation, hours P_2O_5	Vac. 70°	Oven 100°	True mass	Total heat evolved, cal.	Cal. from HNO_3	Cal. from oil	Cal. from paper and Elt	$-\Delta U_B/m$ cd. g^{-1}	Dev.
					Urea					
(a)	2160			2.45335	6330.9	24.4	101.8	18.1	2521.7	0.1
(a)	4150			2.45231	6341.7	24.9	117.6	16.8	2521.0	.6
(a)	4100	90		2.43084	6355.1	24.2	183.8	17.4	2521.6	.0
(b)	2160			2.45441	6313.3	25.2	80.4	17.3	2522.2	.6
(c)	2160			2.45406	6335.4	24.7	104.6	17.6	2521.7	.1
(c)	4100	24		2.43823	6345.8	24.9	155.6	17.6	2521.4	.2
								Mean	2521.6	± .3
					Guanidine Carbonate					
(a)	1248			2.41774	6345.9	24.8	116.2	16.9	2559.4	0.4
(a)	1440			2.41750	6344.0	23.6	116.1	16.6	2559.5	.5
(a)	1080	168		2.41688	6337.5	23.5	111.9	17.4	2559.0	.0
(a)	408		72	2.40356	6350.6	22.2	162.5	17.6	2558.0	1.0
(a)			264	2.44756	6413.0	23.0	110.1	16.9	2558.9	0.1
(b)	1248			2.41717	6331.6	22.7	106.6	16.4	2559.1	.1
(b)	1440			2.29695	6419.2	25.0	499.5	17.9	2558.5	− .5
(b)	1248		120	2.41085	6327.0	24.0	114.9	17.9	2559.3	.3
								Mean	2559.0	± .4

with those of the earlier workers because of insufficient data. We have made a rough recalculation of the data of Emery and Benedict[9] and find that their value of $-\Delta H_R$ is about 0.2% higher than that of this investigation. So far as we are aware there are no existing data for the combustion of guanidine carbonate.

The derived data are given in Table II. The uncertainties assigned to these data are calculated from the standard deviations of the experimental data multiplied by two and combined with the uncertainties assigned to the various auxiliary data which were used. See reference (5) for details of these calculations. As far as we are aware there are no factors which would cause any absolute error in these determinations hence the assigned uncertainties may be taken as a measure of the absolute accuracy of these data.

TABLE II

SUMMARY OF DERIVED DATA AT 25°

Substance	Urea	Guanidine carbonate
Formula	CH_4ON_2	$C_3H_{12}O_3N_6$
Molecular weight	60.058	180.175
Density	1.335	1.251
$-\Delta U_B$, kcal. mole^{-1}	151.44 ± 0.04[a]	461.07 ± 0.13[a]
$-\Delta U_R$, kcal. mole^{-1}	151.29 ± .04	460.67 ± .13
$-\Delta H_R$, kcal. mole^{-1}	151.00 ± .04	459.77 ± .13
$-\Delta H_f^\circ$, kcal. mole^{-1}	79.67 ± .05	232.22 ± .15
$d\Delta U_R/dT$, mole^{-1} deg.$^{-1}$ cal.	−18	−59

[a] Calculated uncertainty interval.

The Free Energies.—We have also calculated the free energies of these compounds using the entropy of urea as determined by Parks, Huffman and Barmore[10] and the value of Huffman, Ellis and Borsook[11] for guanidine carbonate. The values of the free energies and other necessary data are tabulated in Table III. To obtain ΔS we have used for the entropies of C (graph), H_2, O_2 and N_2 the values 1.36,[12] 31.23,[13] 49.03[14] and 45.79[15] cal. degree^{-1} mole^{-1}, respectively. We have assigned uncertainties to the tabulated free energies but in this case this is only an estimate since we are unable to evaluate precisely the uncertainty in the entropies of the compounds. We do feel however that this is a very conservative estimate, especially in the case of urea.

TABLE III

THERMAL DATA AT 298.1°K.

Substance	ΔH°, kcal.	S, cal. deg^{-1} mole^{-1}	ΔS, cal. deg^{-1} mole^{-1}	ΔF°, kcal.
Urea	− 79.67	25.2	−108.9	− 47.21 ± 0.18[a]
Guanidine carbonate	−232.22	70.6	−331.7	−144.34 ± 0.45

[a] Estimated maximum uncertainty.

Urea was used by Parks, Huffman and Barmore[10] to test the third law of thermodynamics.

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[9] Emery and Benedict, *Am. J. Physiol.*, **28**, 311 (1911).

[10] Parks, Huffman and Barmore, THIS JOURNAL, **55**, 2733 (1933).

[11] Huffman, Ellis and Borsook, *ibid.*, **62**, 297 (1940).

[12] Jacobs and Parks, *ibid.*, **56**, 1513 (1934).

[13] Giauque, *ibid.*, **52**, 4816 (1930).

[14] Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

[15] Giauque and Clayton, *ibid.*, **55**, 4875 (1933).

In view of our new combustion data and also of the availability of more reliable free energy data for water and carbon dioxide it is interesting to again compare the free energy of urea as calculated from equilibrium data and from third law data.

The calculation from the equilibrium data may be summed up as follows

$CO_2(g)+2NH_3(g) = H_2O(g)+CO(NH_2)_2(s);\ \Delta F_{298} = 290$[16]

$H_2O(g) = H_2 + 1/2O_2;\ \Delta F = 54{,}638$[7]

$C(graph) + O_2 = CO_2(g);\ \Delta F = -94{,}239$[8]

$N_2 + 3H_2 = 2NH_3;\ \Delta F = 7820$[17]

$C(graph) + 2H_2 + N_2 + 1/2O_2 = CO(NH_2)_2(s);\ \Delta F = -47{,}131$

This result is only 80 calories higher than the third law value and is less than the uncertainty in the $T\Delta S$ term due to the uncertainty in the entropy of urea.

In conclusion we wish to thank Dr. E. L. Ellis for the purification of the compounds used in this investigation.

Summary

1. The isothermal heats of combustion of urea and guanidine carbonate have been determined at 25°.

2. The free energies of urea and guanidine carbonate have been calculated.

3. A comparison of the free energy of urea from equilibrium data and third law data has been made.

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[16] Lewis and Burrows, THIS JOURNAL, **34**, 1515 (1912).

[17] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 557.

[CONTRIBUTION FROM THE RYERSON PHYSICAL LABORATORY, UNIVERSITY OF CHICAGO]

The Crystal Structure of Sodium Formate, $NaHCO_2$[1]

BY W. H. ZACHARIASEN

The present investigation was undertaken primarily to obtain accurate values for the structure of the formate group.

Crystals of sodium formate, $NaHCO_2$, are reported[2] to have monoclinic-holohedral symmetry with crystallographic elements $a'_1:a'_2:a'_3 = 0.9196:1:1.6512$, $\alpha'_2 = 93°37'$. In this article another coördinate system, a_1, a_2, a_3, will be used. The correlation between the two sets of axes is $a_1 = a'_1$, $a_2 = a'_2$, $a_3 = {}^1/_2(-a'_1 + a'_3)$, and one finds readily $a_1:a_2:a_3 = 0.9196:1:0.9700$, $\alpha_2 = 121°51'$.

The crystals studied were obtained by recrystallization from aqueous solutions. Most of the specimens obtained proved to be twinned with (001) as the twinning plane. The single crystals were elongated in the direction a_3 and showed the faces (010), (110) and (001). The compound is somewhat hygroscopic.

A great many oscillation photographs, using CuKα radiation, were prepared. The directions [001], [100], [101] and [010] served as rotation axes. The crystals were shaped into approximate cylinders along the various rotation axes so that corrections for absorption readily could be applied. The structure determination was based upon the reflections in the equator layer lines for which the intensity was set proportional to

$$|F_H|^2 \frac{1 + \cos^2 2\theta}{\sin 2\theta} A$$

where A is the absorption factor.

The dimensions of the unit cell were found to be $a_1 = 6.19 \pm 0.01$ Å., $a_2 = 6.72 \pm 0.01$ Å., $a_3 = 6.49 \pm 0.01$ Å., with $\alpha_2 = 121°42' \pm 10'$. The reported density of 1.91–1.93 gives four molecules of sodium formate in the unit cell. No reflections appear for which $H_1 + H_2$ is odd, so the translation lattice is base centered. Furthermore, reflections H_1OH_3 are absent if H_3 is odd, showing that the symmetry plane is a glide-plane rather than a reflection plane. On the assumption that the reported point group is correct, the space group becomes $C2_1/n(C_{2h}^6)$.

In order to obtain a reasonable structure for the formate group, carbon and hydrogen atoms must lie on the twofold rotation axes. A Patterson analysis of the reflections H_1OH_3 proved conclusively that the sodium atoms also occupy positions on the twofold axes while the eight oxygen atoms are in a set of general positions of the space group. The distribution of the atoms is accordingly as follows: 4 Na in $\pm({}^1/_4, u_1, {}^1/_4)$, 4 H in

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[1] Some of the results of this investigation were published in an abstract which appeared in *Phys. Rev.*, **53**, 917 (1938).

[2] P. Groth, "Chemische Krystallographie," Vol. III, Leipzig, 1901.