where $[HCrO_4^-] = (-K' + \sqrt{(K')^2 + 8K'(m_2 + 2S)})/4$

The results are given in Table V.

A comparison of the results of columns 11 and 5 indicates that chromic acid is incompletely dissociated. Column 13 gives the calculated values of the classical dissociation constant, $K_1' = [H^+][HCrO_4^-]/(m_2 - [H^+])$.

It is obvious that a small error in $[H^+]$ will cause a relatively large error in K_1'. However in all cases but one, the individual values of K_1' agree with the mean within a magnitude equivalent to the experimental error of 0.2 millivolt.

Calculations of the liquid junction potentials by the Henderson equation[17] gave values of about −0.2 millivolt for the first six cells of Table V. The maximum value, −1.0 millivolt, was calculated in the case of cell 9. It is realized that such calculations can give approximate values only. If a correction for the junction potential is applied, the mean value of K_1' becomes somewhat greater, but is still definitely finite, 0.29 ± 0.08.

Summary

The glass electrode has been applied to the measurement of hydrogen ion activity in solutions of chromic acid and its salts at 25°.

The second ionization constant of chromic acid is 3.20×10^{-7} with an estimated error of 3%.

The equilibrium constant of the reaction

$$Cr_2O_7^{=} + H_2O \rightleftharpoons 2HCrO_4^-$$

is 0.023 with an estimated error of about 9%.

The ionization of the first hydrogen of chromic acid has been studied. The reaction is not quite complete. The classical ionization constant at an ionic strength of about 0.16 was found to be 0.18 ± 0.04.

NEW BRUNSWICK, N. J. RECEIVED JULY 2, 1934

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[17] Henderson, *Z. physik. Chem.*, **63**, 325 (1908).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

A Thermochemical Study of *d*-Gluconic Acid and its Modifications

BY ROYCE H. LEROY AND B. CLIFFORD HENDRICKS

Nef[1] showed that *d*-gluconic acid exists in two modifications other than the free acid form, *d*-gluconic-δ-lactone and *d*-gluconic-γ-lactone, and described methods of preparing them.

Hedenburg[2] used the polariscope to study the interconversion of each of these modifications into the equilibrium mixture in water solution. His data indicated that the free *d*-gluconic acid, when dissolved in water, is converted into *d*-gluconic-δ-lactone to the extent of about 20% at the end of twenty-four hours and that this quasi-equilibrium is maintained for three days. By that time the *d*-gluconic-γ-lactone is being formed at an appreciable rate. This change is shown by the specific rotation of the solution, which begins to increase slowly. At the end of eleven days the specific rotation reaches a constant value. This is interpreted as representing an equilibrium condition which exists between the three forms of the acid.

This same final equilibrium is reached at the end of fourteen days when *d*-gluconic-γ-lactone is dissolved in water. The specific rotation of the solution gradually and steadily decreases from the high initial value characteristic of the gamma form to that of the equilibrium mixture. When *d*-gluconic-δ-lactone is dissolved, two and one-half hours are required to attain an equilibrium point similar to that which is reached in twenty-four hours in the case of the free acid. This temporary equilibrium lasts for about twenty hours and then the specific rotation gradually increases and approaches the same final equilibrium point at the end of about eight days.

Hedenburg's findings were confirmed by Rehorst[3] and a third check was made of his results in the course of this investigation. Hedenburg's investigation also included *d*-mannonic acid and its lactones, and Upson, Sands and Whitnah[4] extended the study to *l*-mannonic and *l*-gluconic acid and their related lactones. In each case a relation similar to that encountered in the study of the *d*-gluconic acid was found to exist.

Levene and Simms[5] made a comprehensive examination of *d*-gluconic, *d*-glucoheptonic, *d*-

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[1] Nef, *Ann.*, **403**, 273, 306 (1914).

[2] Hedenburg, THIS JOURNAL, **37**, 345 (1915).

[3] Rehorst, *Ber.*, **61**, 163 (1928).

[4] Upson, Sands and Whitnah, THIS JOURNAL, **50**, 519 (1928).

[5] Levene and Simms, *J. Biol. Chem.*, **65**, 31 (1925).

mannonic and *d*-galactonic acids. This examination was based upon the postulate that "the linkage involving the hydroxyl group on carbon atoms (4) and (5) may be expected to involve different energy changes owing to the greater proximity of the carboxyl group to the former." From their polariscopic studies, the general conclusion was drawn that "normal monocarboxylic acids derived from hexoses (and also from heptoses) are practically identical in the rates of their lactone formation." In explanation, "the mono-carboxylic acids form two lactones simultaneously: one with a 6-membered ring, which reaches an equilibrium of 20 to 30% in a few hours, and another with a 5-membered ring, which attains an equilibrium of 75 to 80% after several hundred hours."

These data and theoretical considerations furnish evidence that the energies of the formation of the 5-membered and 6-membered rings of the lactones from the free *d*-gluconic acid would be different and might be detected and measured by means of the adiabatic calorimeter developed in this Laboratory. This calorimeter[6] and its manipulation[7] have been described elsewhere.

Materials

The *d*-gluconic-δ- and the *d*-gluconic-γ-lactones were Pfanstiehl products and were recrystallized from glacial acetic acid. The constants were: *d*-gluconic-δ-lactone, $[\alpha]^{25}_{D}$ +65.0° (two minutes); m. p. 151–152°; *d*-gluconic-γ-lactone, $[\alpha]^{25}_{D}$ +67.75°, m. p. 134°.

Free *d*-gluconic acid was made from the *d*-gluconic-δ-lactone according to the procedure described by Brackenbury and Upson,[8] and the constants were $[\alpha]^{25}_{D}$ −4.25° (five minutes) m. p. 127°.

Sodium *d*-gluconate was prepared from *d*-gluconic-δ-lactone according to the method of Brackenbury,[9] which is essentially as follows: neutralization of the δ-lactone solution with normal sodium hydroxide, evaporation of the excess water under diminished pressure, and precipitation of the salt by the addition of 95% alcohol. The salt was purified by repeating the precipitation and the constants obtained were: $[\alpha]^{25}_{D}$ −11.7°, decomposition temperature 205°.

Experimental

For use in this work the calorimeter stirrer was modified by soldering a second disk about 9 cm. from the original disk. This extra disk was notched so that in the reciprocating motion of the stirrer it would move clear of the thermometer, and experiment showed that its use increased both the rate of the solution of the sample and the efficiency of the stirring. The whole stirrer was plated with silver and given a thin coating of paraffin.

The heat capacity of the calorimeter was determined by the electrical method in the manner previously described in which the energy delivered in to the calorimeter system was calculated by $I^2Rt/4.1818$. In this study the heat capacity was determined each time with the temperature bracketing 25° upon the thermometer. For six consecutive determinations the average ΔT was 0.2131 ± 0.0013°, t was 660 seconds, R was 3.0202 ohms, the average I was 0.6844 ± 0.0028 ampere and the average capacity of the calorimeter charge of water was 993.4 ± 0.3 gram calories per degree. In the six trials a mean value for the heat capacity of the calorimeter, 55.4 ± 1.7 calories per degree, was obtained.

The heats of solution of free *d*-gluconic acids, *d*-gluconic-δ-lactone, *d*-gluconic-γ-lactone and sodium *d*-gluconate were determined in the manner previously described. Care was taken that the temperature drop should "bracket" the exact 25° mark on the precision metastatic thermometer (B. S. No. 35605) used in the calorimeter. This point was established by comparison with a second precision thermometer, range 18 to 28°, which was calibrated by the Bureau of Standards (B. S. No. 51442). These data and the heats of solution in water for the sugars indicated are presented in Table I. The average sample weight for each different solute was, in the order given in the table, 2.5206 ± 0.0200, 3.5761 ± 0.0155, 2.9879 ± 0.0409 and 2.8462 ± 0.2800 g. and the weight of the solvent, water, was 993.3 ± 0.3 g. for all. Thus, the dilution was, in the order given in the table, 0.00023, 0.00033, 0.00028 and 0.00040 mole of solute per mole of water.

TABLE I

HEATS OF SOLUTION OF *d*-GLUCONIC ACID AND ITS MODIFICATIONS

Solute	Measurements	Mean heat of soln.	Av. dev.	Max. dev.
d-Gluconic acid	4	5.46	0.07	0.14
d-Gluconic-δ-lactone	4	4.72	.06	.07
d-Gluconic-γ-lactone	3	5.59	.06	.09
Sodium *d*-gluconate	5	5.16	.12	.22

The heats of the neutralization reactions of the free gluconic acid, *d*-gluconic-δ-lactone, and *d*-gluconic-γ-lactone with sodium hydroxide were then determined. In each experiment 0.0102 mole of sodium hydroxide in one liter of solution was placed in the calorimeter. The calorimeter solution was prepared by diluting to one liter the proper quantity of a sodium hydroxide solution which had previously been standardized according to proper analytical methods. The procedure then was the same as in the determination of the heat of solution. The specific heat of the 0.0102 normal sodium hydroxide solution was taken as 0.99725 calorie per gram and was obtained by extrapolating the heat capacity curve obtained by Steinbach[10] at 25° to the value for the heat capacity of water at 25°. As in the determination of the heats of solution, care was taken that the temperature change should bracket the exact 25° mark on the calorimeter thermometer.

The data for the heats of neutralization are presented in Table II. The weights of the samples averaged 1.8775 ±

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(6) Hendricks, Dorsey, LeRoy and Moseley, *J. Phys. Chem.*, **34**, 418 (1930).

(7) Hendricks and Steinbach, *ibid.*, **36**, 1279 (1932).

(8) Brackenbury and Upson, THIS JOURNAL, **55**, 2512 (1933).

(9) Brackenbury, Thesis, University of Nebraska, 1933.

(10) Steinbach, Thesis, University of Nebraska, 1931.

0.1225 g. and the average heat capacity of the reacting sodium hydroxide solution was 993.3 ± 0.9 gram calories per degree. The heat of reaction is expressed in kilogram calories per mole of organic reactant.

TABLE II

HEATS OF REACTION OF SOLID *d*-GLUCONIC ACID AND ITS MODIFICATIONS WITH 0.0102 *N* SODIUM HYDROXIDE

Acid reactant	Measurements	Mean heat of reaction	Av. dev.
d-Gluconic acid	2	− 6.91	0.03
d-Gluconic-δ-lactone	2	− 9.73	.03
d-Gluconic-γ-lactone	2	−10.22	.00

Discussion

From the data above the heats of reaction of the three forms of *d*-gluconic acid (aq.) with sodium hydroxide (aq.) have been calculated and are as follows:

d-Gluconic acid (aq.), $\Delta H = -12.37$ Cal.
d-Gluconic-δ-lactone (aq.), $\Delta H = -14.45$ Cal.
d-Gluconic-γ-lactone (aq.), $\Delta H = -15.81$ Cal.

In a similar manner, by proper treatment of the data, it can be shown that the thermal relations (ΔH in kg. cal.) of the three modifications in water solutions and in solid state are:

	Reaction	Aqueous	Solid
1	*d*-Gluconic = *d*-gluconic-δ-lactone	2.08	2.82
2	*d*-Gluconic = *d*-gluconic-γ-lactone	3.54	3.41
3	*d*-Gluconic-δ-lactone = *d*-gluconic-γ-lactone	1.46	0.59

The lower heat of conversion, 2.08, of *d*-gluconic acid into *d*-gluconic-δ-lactone than that, 3.54, for converting it into *d*-gluconic-γ-lactone gives experimental support to the inferences of Hedenburg and of Levene and Simms that the free acid dissolved in water attains an equilibrium between itself and *d*-gluconic-δ-lactone before the equilibrium with *d*-gluconic-γ-lactone.

Summary

1. The heats of solution in water to a dilution of 0.0003 ± mole of solute per mole of water at 25° for *d*-gluconic acid, *d*-gluconic-δ-lactone, *d*-gluconic-γ-lactone and sodium *d*-gluconate have been determined, as well as the heats of neutralization of the first three substances with 0.0102 *N* sodium hydroxide.

2. The thermal relations of the three modifications of *d*-gluconic acid in water solutions and in solid states have been calculated and it has been found that the transformation of *d*-gluconic-δ-lactone into *d*-gluconic-γ-lactone is an endothermic change.

3. The inferences of Hedenburg and of Levene and Simms concerning the equilibrium of the *d*-gluconic acid and its lactones find experimental support in the present work.

LINCOLN, NEBRASKA RECEIVED JULY 9, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Photochemistry of Mixtures of Chlorine and Ozone

BY A. C. BYRNS AND G. K. ROLLEFSON

In a recent article[1] we showed that, even at temperatures as high as 20°, pressure measurements were not an accurate measure of the amount of ozone decomposed when mixtures of chlorine and ozone were illuminated with blue light, due to the condensation of chlorine trioxide on the walls of the reaction vessel. This was shown by a comparison of the amount of oxygen calculated from the pressure increase with that found by freezing out all other gases with liquid air. There was also the qualitative observation that drops of liquid chlorine trioxide could be seen on the walls of the vessel. At the same time it was shown that chlorine trioxide acted as a catalyst for the thermal decomposition of ozone. A further study has now been made of the behavior of chlorine–ozone mixtures at 30°, where there should be no condensation of chlorine trioxide. The apparatus and technique used were essentially the same as in the earlier article, except for the use of a modified ozonizer which has been described by one of us. The temperature was hand regulated and a large Pyrex test-tube was used as a thermostat. For the work on stoichiometry, readings were taken at 0° so as to minimize the error due to thermal reaction before the gases could be frozen out with liquid air. The pressures of chlorine used varied from 10–50 cm. of sulfuric acid, and of ozone 30–82 cm.

At no time could any chlorine trioxide be observed on the walls of the reaction vessel at 30°, nor even when cooled to room temperature. However, there was in a few runs some evidence of

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[1] Rollefson and Byrns, THIS JOURNAL, **56**, 364 (1934).