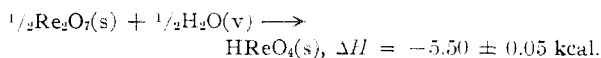


The slope of this curve gives the heat of the reaction



Using the value $\Delta H = -295.5 \pm 2$ kcal. mole⁻¹, determined by Roth and Becker⁶ for the heat of formation of rhenium heptoxide the heat of formation of solid HReO₄ from its elements is $\Delta H = -182.2 \pm 1$ kcal.

(6) W. A. Roth and G. Becker, *Z. physik. Chem.*, **A159**, 27 (1932).

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Condensation Product of Pyrrolidonecarboxylic Acid and Formaldehyde¹

BY J. B. STARK AND A. E. GOODBAN

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To determine composition changes during the processing of sugar beets a study has been made in this Laboratory of the acid constituents of sugar beet processing liquors.² This investigation revealed the presence of a previously unreported acid. Chemical analyses indicated it to be methylene bis-(N-pyrrolidone-2-carboxylic acid). This compound was synthesized and identified with the unknown by crystallographic analysis and X-ray diffraction patterns. A qualitative test was devised and derivatives were synthesized. By analyses of various sugar beet juices it was found that the acid was an artifact produced only in juices preserved with formaldehyde.

Experimental

Isolation.—The acids in the sugar-beet liquor were removed from the other components by passage through a cation exchange resin, D-50,³ and then through an anion exchange resin, IR4-B.⁴ The acids were eluted from the anion resin with 5% ammonium hydroxide. Excess ammonia was removed by boiling and the salts decomposed by treatment with D-50. The unknown acid was present in the fraction containing water-soluble, alcohol-insoluble calcium salts. This fraction was dissolved in water and the calcium removed with D-50. The acid crystallized from water after concentration of the solution.

Properties.—After repeated crystallizations from water the following chemical and physical properties of the purified acid were determined; m.p. 310° with decomposition (the melting point is dependent on the rate of heating). *Anal.* Calcd. for C₁₁H₁₃O₆N₂: C, 48.4; H, 5.22; N, 10.37. Found: C, 48.9; H, 5.25; N, 10.4. The neutral equivalent was 135.3.

The X-ray measurements show that the volume of the unit cell is 624 Å³. The density of single crystals determined by flotation in ethylene bromide and toluene is 1.44 g./ml. The molecular weight must be equal to 541.6 or some submultiple. Since at least two molecules must be in the unit cell, the maximum molecular weight would be 270.8. This is in excellent agreement with the minimum molecular weight of 270.2 calculated from the per cent. composition. X-Ray powder data for the compound are given in Table I.

(1) Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) J. B. Stark, A. E. Goodban and H. S. Owens, *Proc. Am. Soc. Sugar Beet Technol.*, 578 (1950).

(3) Dowex 50, a product of Dow Chemical Co. Mention of this and other products does not imply that they are endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.

(4) A product of Resinous Products Co.

TABLE I

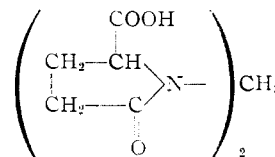
X-RAY POWDER DATA FOR METHYLENE BIS-(N-PYRROLIDONE-2-CARBOXYLIC ACID)

CuKα = 15418 Å.

<i>d</i>	<i>I</i> ^a	<i>d</i>	<i>I</i> ^a	<i>d</i>	<i>I</i> ^a
8.53	MS	3.24	MW	2.21	W
7.31	MW	3.14	M	2.09	MW
6.27	M	3.08	VW	2.04	W
5.73	S	3.02	MW	2.00	MW
4.64	VVS	2.82	MS	1.937	W
4.24	MW	2.72	MS	1.906	VW
4.07	S	2.62	VW	1.875	W
3.87	VS	2.55	W	1.849	VW
3.65	W	2.50	MW	1.823	W
3.65	MW	2.43	W	1.794	W
3.40	MW	2.36	W	1.715	VW
3.31	MW	2.28	MW		

^a Visually estimated: V = very; S = strong; M = medium; W = weak.

On acid hydrolysis the compound yields formaldehyde and nearly two moles of glutamic acid. Since the compound gives a negative ninhydrin test, the glutamic acid portion probably is present as the lactam, α-pyrrolidonecarboxylic acid. Both PCA and formaldehyde were present in the sugar beet extract. From these data the following structure was postulated.



Methylene-bis-(N-pyrrolidone-2-carboxylic acid)

Synthesis.—The acid was synthesized from a 5% water solution of pyrrolidonecarboxylic acid treated with a 2-fold excess of formaldehyde. The solution was allowed to evaporate at room temperature for about a week. The material was recrystallized from water and the crystals were identical with the unknown as shown by neutral equivalent (135.2), X-ray diffraction patterns and crystallographic analysis. The solubility of the compound in water and 95% ethyl alcohol at 25° was determined to be 1.33 g./100 ml. of water solution and 0.63 g./100 ml. of alcohol solution.

Detection and Derivatives.—The acid can be detected in the presence of pyrrolidonecarboxylic acid by the following procedure. Two ml. of 2,7-dihydroxynaphthalene (0.01 g./100 ml. of concd. sulfuric acid) solution and 0.5 ml. of water are added to 0.1 ml. of the unknown solution in a test-tube. The mixture is heated in a boiling water-bath for 20 minutes. The presence of a faint lavender to deep violet indicates the presence of formaldehyde or formaldehyde-forming materials. Glycolic, lactic, malic and tartaric acids and some aldehydes give colored reaction products with the reagent.⁵ In the absence of interfering substances 0.004 mg. of the acid in 0.1 ml. of water could be detected. The chromotropic acid test for formaldehyde is also applicable but is not so sensitive.⁵ Paper chromatography will differentiate between methylene-bis-(N-pyrrolidone-2-carboxylic) and lactic, malic, tartaric or glycolic acids.⁶ The acid may also be separated from these acids and others including pyrrolidonecarboxylic acid by the use of anion exchange resins.

The following derivatives of pyrrolidonecarboxylic acid (PCA) and of methylene bis-(N-pyrrolidone-2-carboxylic acid) (Me N-PCA) were prepared:

p-Nitrobenzyl ester of PCA: m.p. 122–123°. *Anal.* Calcd. for C₁₂H₁₂O₆N₂: C, 54.54; H, 4.58; N, 10.60. Found: C, 54.7; H, 4.61; N, 10.6.

p-Nitrobenzyl ester of Me N-PCA: m.p. 93–94°. *Anal.*

(5) Feigl, "Qualitative Analysis by Spot Tests," 3rd Ed., Elsevier Publishing Corp., New York, N. Y., 1946, pp. 395–399.

(6) J. B. Stark, A. E. Goodban and H. S. Owens, *Anal. Chem.*, **23**, 412 (1951).

Calcd. for $C_{25}H_{24}O_{10}N_4$: C, 55.55; H, 4.48; N, 10.37. Found: C, 55.4; H, 4.60; N, 10.3.

Quinine salt of PCA: m.p. 207–209°. *Anal.* Calcd. for $C_{25}H_{31}O_5N_3$: C, 66.20; H, 6.89; N, 9.27. Found: C, 66.3; H, 6.90; N, 9.3.

Quinine salt of Me N-PCA: m.p. 159–160°. *Anal.* Calcd. for $C_{51}H_{62}O_{10}N_6$: C, 66.65; H, 6.80; N, 9.15. Found: C, 66.5; H, 6.76; N, 9.1.

Acknowledgments.—The authors are grateful for the cooperation of K. J. Palmer on the X-ray studies, F. T. Jones on the optical measurements, and Geraldine Secor and Mary Kilpatrick on the composition analyses.

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Reaction of Tantalum with Hydrogen Chloride, Hydrogen Bromide and Tantalum Pentachloride; Action of Hydrogen on Tantalum Pentachloride

BY RALPH C. YOUNG AND CARL H. BRUBAKER, JR.

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Hydrogen Chloride and Tantalum.—When hydrogen chloride gas is passed over tantalum metal at 410° and above, white tantalum pentachloride is formed and can be collected upon a cold-finger condenser. When the temperature is elevated to 600–750°, a thin film of metal, containing dissolved hydrogen, is formed on the heated tube walls. This metal is probably formed by the reduction or thermal decomposition of the pentachloride or some lower chloride, which may begin to form and immediately disproportionate (*cf.* Ruff and Thomas,^{1,2} on $TaCl_3$) at the higher temperature. After the reaction has proceeded (600–750°) for a few hours, it is slowed markedly and an olive colored powder forms on the surface of the unreacted metal. Chemical properties and analyses indicate that the olive powder is tantalum dichloride as described by Ruff and Thomas.^{1,2}

The tantalum dichloride powder (mixed with metal) was treated with 1 *M* potassium hydroxide and the residual tantalum was filtered away. When the solution was heated, hydrogen bubbled off and a dark flocculent precipitate (presumably $TaO_2 \cdot xH_2O$) formed. The tantalum was oxidized with nitric acid, the pentoxide thus formed was filtered off and chlorine was determined as silver chloride in the filtrate (*Anal.* Cl/Ta = 1.97).

The metallic tantalum films were fused with sodium carbonate and, during the fusion, considerable adsorbed hydrogen gas escaped and burned. The cooled melts were dissolved in water and the solutions were acidified with nitric acid. The weights of pentoxide thus formed indicated the metallic films were tantalum (99.9% Ta or higher.)

Hydrogen Bromide and Tantalum.—If hydrogen bromide is passed over metallic tantalum at 375°, tantalum pentabromide is formed and if the temperature is maintained at 550° or above, some tribromide begins to form, apparently mixed with a still lower bromide or perhaps the metal. *Anal.* Calcd. for $TaBr_3$: Ta, 43.0; Br, 57.0. Found: Ta, 44.7; Br, 55.5.

At higher temperatures (up to 800°) tantalum

metal is deposited in the apparatus, probably as the result of reduction or thermal decomposition of the penta- or tribromide. This reaction is also slowed by the formation of a green powder (tantalum tribromide) on the surface of the unreacted metal.

Tantalum Pentachloride and Tantalum.—Schäfer and Pietruck³ have shown that tantalum pentachloride is not reduced by the metal at 350–400° in an evacuated tube, an observation which was also made in the course of the present work. In the range 475–500°, however, a small amount of a green chloride is formed. If the unreacted pentachloride is sublimed away *in vacuo* and the green material is dissolved in water, one obtains a green solution in which the chlorine to tantalum ratio is 3.35 and the average oxidation state of the tantalum is 3.29. This latter value was obtained electrometrically by use of platinum and saturated calomel electrodes and a potassium nitrate–agar salt bridge. Ceric sulfate was the oxidant. When the inflection in the plot of e.m.f. *vs.* volume of titrant was noted, a brown flocculent precipitate (*cf.* $TaO_2 \cdot xH_2O$) was present in the solution. It was assumed that the tantalum was then in oxidation state (IV). These analyses would indicate the presence of some tantalum in a lower oxidation state (probably III) and possibly a compound such as Ta_3Cl_{10} .

Hydrogen and Tantalum Pentachloride.—Although niobium pentachloride is readily reduced with hydrogen to form the trichloride,⁴ Schäfer and Pietruck³ have shown that tantalum pentachloride is not affected at temperatures up to 400°. Studies in the course of the present work resulted in the same conclusions. However, if the reaction is carried out at 500°, some reduction of the pentachloride does occur and a film of the product, tantalum metal, containing dissolved hydrogen, is deposited on the heated walls of the reduction tube. No lower chlorides could be detected. This is in contrast to the reduction of the pentabromide by hydrogen. The formation of tantalum tribromide has been reported by Van Haagen⁵ and by Young and Hastings.⁶

(3) H. Schäfer and C. Pietruck, *Z. anorg. allgem. Chem.*, **266**, 151 (1951).

(4) C. H. Brubaker, Jr., and R. C. Young, *THIS JOURNAL*, **73**, 4179 (1951).

(5) W. K. Van Haagen, Thesis, University of Pennsylvania, 1909 (from Friend, "Textbook of Inorganic Chemistry," Vol. VI, p. 195).

(6) R. C. Young and T. H. Hastings, Jr., *THIS JOURNAL*, **64**, 1740 (1942).

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O^3, O^4, N -Triacetyl-(–)-epinephrine

BY LLEWELLYN H. WELSH

RECEIVED MARCH 21, 1952

The action of excess acetic anhydride on an aqueous solution of ephedrine in the presence of bicarbonate yields the N-monoacetyl derivative.¹ When essentially the same procedure is applied to (–)-epinephrine (Ia), there is obtained a quantitative yield of a crystalline, levorotatory triacetyl

(1) O. Ruff and F. Thomas, *Ber.*, **55**, 1466 (1922).

(2) O. Ruff and F. Thomas, *Z. anorg. allgem. Chem.*, **148**, 1 (1925).

(1) L. H. Welsh, *J. Am. Pharm. Assoc.*, **36**, 373 (1947).