Messrs. A. M. Busch for the heats of combustion, A. B. McKeown for the analyses, and J. F. Thompson for the determinations of physical constants.

TABLE I

PHYSICAL PROPERTIES OF 2-CYCLOPROPYL-3-METHYL-1-BUTENE AND 2-CYCLOPROPYL-3-METHYLBUTANE

		2-Cyclopropyl-3-methyl-1-butene	2-Cyclopropyl-3-methylbutane
M.p., °C.		−126.06	Glass
M.p., °C. for zero impurity		−125.98^a	
B.p., °C. at 760 mm.		116.81	115.49
$n^{20}\text{D}$		1.4337	1.4140
d^{20}, g./ml.		0.77395	0.75026
Net heat of combustion, kcal./mole		1160	1200
Carbon, %	Calcd.	87.20	85.63
	Found	87.14	85.63
Hydrogen, %	Calcd.	12.80	14.37
	Found	12.84	14.40

^{a} Determined by the geometrical construction method of W. J. Taylor and F. D. Rossini, *J. Research Natl. Bur. Standards*, **32**, 197 (1944). By assuming that for 2-cyclopropyl-3-methyl-1-butene the depression in the melting point per mole % impurity is between 0.2 and 0.3° (see footnote 12, reference 1), the purity of the hydrocarbon is better than 99.5 mole %.

Experimental

Methylisopropylcyclopropylcarbinol.—Methyl cyclopropyl ketone (120 moles, 10,100 g.) reacted with Grignard reagent from 135 moles (3280 g.) of magnesium turnings and 130 moles (15,990 g.) of isopropyl bromide in a 30-gal. glass-lined reactor to yield 7767 g. (51% yield) of crude methylisopropylcyclopropylcarbinol. The crude carbinol was refluxed with alcoholic sodium hydroxide[1] to obtain 3500 g. of halide-free product. A sample of the purified carbinol had the following properties: b.p. 160.3° (760 mm.), $n^{20}\text{D}$ 1.4465, d^{20} 0.8856 g./ml.

2-Cyclopropyl-3-methyl-1-butene.—The halide-free carbinol (13.5 moles, 1734 g.) was passed at a rate of 5 ml./min. through a 2.5- by 90-cm. Pyrex column which was packed with 8 to 14 mesh alumina and heated to 200–250°. The organic products were separated from the water layer (12 moles), dried over calcium chloride, and fractionated through a 22-mm. by 7-ft. column which was packed with 1/8-in. glass helices. The distillate consisted of 956 g. (64% yield) of 2-cyclopropyl-3-methyl-1-butene, b.p. 115–116°, $n^{20}\text{D}$ 1.4337, 130 g. of products boiling from 130–131°, $n^{20}\text{D}$ 1.4558–1.4562, and 345 g. of viscous residue.

Seven samples of the constant index distillate were selected for determination of melting points (Fig. 1). Physical properties of that sample having the highest melting point are presented in Table I.

The distillate boiling from 130–131° was not identified; the infrared spectrum of the distillate showed negligible absorption for C=C between 6.0–6.2 μ, and only moderate absorption between 9.7–9.9 μ, the region in which cyclopropane derivatives are known to absorb.[4] Strong absorption between 9.1 and 9.5 μ, observed in some tetrahydrofurans,[4a] was not present in the spectrum; the high refractive index also indicated that the unidentified distillate was not a tetrahydrofuran derivative.

Ozonolysis of 2-Cyclopropyl-3-methyl-1-butene.—A solution of 0.3 mole (33 g.) of the olefin in 100 ml. of ethanol was ozonized[5] and the products fractionated to give formaldehyde (detected only by odor and the presence of a white solid, presumably paraformaldehyde, which sublimed into the still-head) and 14 g. (42% yield) of isopropyl cyclopropyl ketone: b.p. 139–140° (atm.), $n^{20}\text{D}$ 1.4290 (lit.[6] b.p. 141.0–141.4° (761 mm.), $n^{20}\text{D}$ 1.42986). The 2,4-dinitrophenylhydrazone of the ketone was prepared, m.p. 187.5–188.0°.

Anal. Calcd. for $C_{13}H_{16}N_4O_4$: N, 19.17. Found: N, 19.29.

2-Cyclopropyl-3-methylbutane.—A solution of 6.6 moles (727 g.) of 2-cyclopropyl-3-methyl-1-butene ($n^{20}\text{D}$ 1.4337) in 500 ml. of ethanol and 73 g. of barium-promoted copper chromite catalyst[7] were charged to a 4.4-l. rocker-type autoclave under an initial hydrogen pressure of 1850 p.s.i. The rocking mechanism was started and the temperature gradually increased to 100°; hydrogenation began within 30 min., and was completed within 6 hours. Maximum temperature and pressure reached were 140° and 2480 p.s.i., respectively. The products were removed from the autoclave when cooled to room temperature, filtered through Celite to remove the catalyst, washed with water to remove the ethanol, dried over calcium chloride, and then fractionated through a 6-ft. Podbielniak column. Part of the product was lost midway through the distillation because of insufficient cooling water in the still head; however, the 487 g. of distillate that was obtained had a constant refractive index, $n^{20}\text{D}$ 1.4138, and, omitting the first and last fractions, varied in density from 0.7498 to 0.7501. Fractions taken near the end of the distillation varied in density only 0.00005 unit, so these fractions were combined and the physical properties of the sample were determined: m.p., glass; b.p. 115.45° (760 mm.), $n^{20}\text{D}$ 1.4140, d^{20} 0.75001.

In order to obtain the hydrocarbon in higher purity, the constant index fractions were combined and azeotropically fractionated with propanol through a 6-ft. Podbielniak column. Each fraction of distillate was washed with water to remove the propanol and the hydrocarbon layer was dried over calcium chloride. The refractive index and density of the hydrocarbon portions of the distillate are plotted in Fig. 2. The distillate collected between the points of 20 to 80% distilled was of constant refractive index and density within the limits of accuracy of measurement, 0.0002 and 0.00005 unit, respectively. Since none of the fractions could be induced to crystallize and methods of determining purity based on melting points could not be applied, the distillate between the points of 25 to 50% distilled was selected for the determination of physical properties (Table I).

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(4) (a) Unpublished work from this Laboratory and (b) J. M. Derfer, E. E. Pickett and C. E. Boord, THIS JOURNAL, **71**, 2482 (1949).

(5) A. L. Henne and W. L. Perilstein, *ibid.*, **65**, 2183 (1943).

(6) P. Bruylants, *Bull. soc. chim. Belg.*, **36**, 519 (1927).

(7) Purchased from E. I. du Pont de Nemours and Co., Ammonia Division, Wilmington, Delaware.

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The Vapor Pressures of Rhenium Heptoxide and Perrhenic Acid

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RECEIVED APRIL 17, 1952

Although the vapor pressure of rhenium heptoxide has been reported[2] a check on the work seemed desirable since the data are essential to the calculation of the thermodynamic properties of perrhenic acid.

Experimental

Since the heptoxide vapor reacts with mercury and also with stopcock lubricants, but not with glass, it was decided to make the measurements in an all-glass container. A sickle gage of the type designed by Jackson[3] was used as a null instrument. The air pressure necessary to counterbalance the pressure of the system within the sickle was measured to ±0.05 mm. with a cathetometer on a closed mercury manometer. The temperatures from 30 to 70° used in measurements on perrhenic acid were controlled to within ±0.1° using a water-bath. The higher temperatures, 220 to 350°, necessary for measuring the vapor pressures of solid and liquid rhenium heptoxide were controlled to within ±0.5° in a molten salt-bath containing 53% potassium nitrate,

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[1] This paper is based in part on a thesis presented by Lloyd E. Line, Jr., to the University of Tennessee as a part of the requirements for the M.S. degree, August, 1941.

[2] E. Ogawa, *Bull. Chem. Soc. Japan*, **7**, 265 (1932).

[3] C. G. Jackson, *J. Chem. Soc.*, **99**, 1066 (1911).

40% sodium nitrite and 7% sodium nitrate. All temperatures were measured with thermometers calibrated by the Bureau of Standards and the appropriate corrections were made. The pressures as read on the mercury manometer were corrected to mercury at 0°.

The following procedure was followed for preparing samples and measuring vapor pressures for both the oxide and the acid. The entire assembly was flushed out several times with oxygen which was dried over phosphorus pentoxide. The rhenium metal sample which was within a tube which had been sealed to the sample chamber was flamed under vacuum during the flushing process. Oxygen was then introduced to a pressure of about one atmosphere and the sample of rhenium burned by bringing a tube furnace up over the sample tube and heating to approximately 400°. The oxide which condensed in the cooler tube just beyond the furnace was resublimed several times by successively moving the furnace up farther on the sample tube. That part of the sample tube containing the residues from burning and resublimations was then sealed off from the assembly. The entire apparatus was then evacuated with an oil pump and a mercury diffusion pump equipped with a cold trap. The sample compartment, within the sickle, was then sealed off from the vacuum line. The vapor pressure of the heptoxide was measured using several different samples in as many different gages. Measurements were made both after the successive increases and after successive decreases of the temperature.

In order to keep the system being examined in contact with nothing but glass while known weights of water were introduced in a stepwise manner, another tube was sealed onto the sample chamber before the rhenium sample was burned. This tube was equipped with several teats into which water samples, sealed in glass capillaries, were introduced, one sample in each teat. These capillary samples were prepared by filling a small, thin-walled glass capillary of known weight with water, degassing the water in a vacuum and then sealing off the two end segments of the capillary. The weight of water in each sample was obtained by difference since the weight of the glass itself was known. These capillary samples were checked for leaks by reweighing after they had been stored in a vacuum. These water samples were successively released into the system by breaking the capillaries. This was accomplished by freezing the water by bringing a freezing mixture up on the teat containing the capillary. Several samples which could not be released in this manner were broken by heating the capillary, through the glass wall of the teat, with a flame. When this was necessary the gage was protected from shock by cooling the tube between the capillary to be broken and the glass diaphragm with a mixture of solid carbon dioxide and acetone.

After the introduction of each water sample the vapor pressures were measured at 10° intervals over the range from 30 to 70°. Equilibrium was assured by checking pressure measurements obtained after increases against those obtained after decreases in the temperature.

Results

The plot of the logarithm of the vapor pressure of the heptoxide against the reciprocal of the absolute temperature revealed no trend toward deviation from linear relation in the case of either the liquid or the solid. Consequently the best straight line relation was obtained for each equilibrium using the method of least squares. The equation obtained for the sublimation of the solid is

$$\log p\ (\text{mm.}) = -\frac{7320}{T} + 15.010.$$

From this equation $\Delta H_{(\text{subl})} = 33.5 \pm 0.1$ kcal. mole^{-1} and $\Delta S_{(\text{subl at the f.p.})} = 58.4 \pm 0.2$ e.u. mole^{-1}. The relation obtained for the vapor pressure of the liquid is

$$\log p\ (\text{mm.}) = -\frac{3868}{T} + 8.989$$

From this equation $\Delta H_{(\text{vap})} = 17.7 \pm 0.1$ kcal. mole^{-1} and $\Delta S_{(\text{vap at the b.p.})} = 28.0 \pm 0.1$ e.u. mole^{-1}. The melting point calculated by the simultaneous solution of the two vapor pressure equations is 300.3 ± 0.3°. This value agrees with a direct observation of the melting point in a sealed tube although it is somewhat lower than 301.5° previously reported.[4] The normal boiling point calculated using the vapor pressure equation for the liquid is 360.3 ± 0.3°. Since vapor pressure measurements were made up to 354° this boiling point calculation does not require much of an extrapolation. The heat of fusion from these data is $\Delta H = 15.81 \pm 0.1$ kcal. mole^{-1} and $\Delta S_{(\text{fus at the m.p.})} = 27.6 \pm 0.2$ e.u. mole^{-1}. The data obtained by Ogawa[2] agree within 2% of the values presented in this paper. The fact that Ogawa's value for the freezing point is lower (297–298°) and the boiling point higher (363°) together with the fact that his temperatures were controlled with an air-bath having a fluctuation of ±2° is an indication that the data presented in this paper may be more reliable.

A preliminary examination of the rhenium heptoxide–water system indicated that the vapor phase is principally water in the temperature range used.

The vapor pressure of a sample of rhenium heptoxide prepared in a gage was measured at 10° intervals from 30 to 70° after each of seven additions of water. The amount of rhenium heptoxide in the sample was determined at the end of the run.[5] A plot of the data (Fig. 1) indicates a break at a mole fraction of 0.5 which corresponds to a formula of $HReO_4$ or $Re_2O_7 \cdot H_2O$.

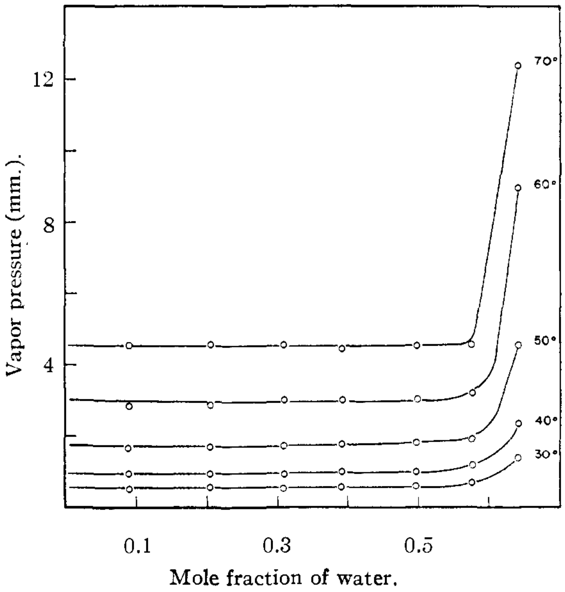

Fig. 1.—Plot of the vapor pressure *vs.* the mole fraction of water for the system Re_2O_7–H_2O at several temperatures.

From the values for the vapor pressure of the acid at the five different temperatures the equation relating vapor pressure and temperature was determined to be

$$\log p\ (\text{mm.}) = -\frac{2409}{T} + 7.680$$

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[4] W. Biltz, G. A. Lehrer and K. Meisel, *Nachr. Ges. Wiss. Gottingen, Math-physik. Klasse, Fachgruppen,* 191 (1931).

[5] H. H. Willard and G. W. Smith, *Ind. Eng. Chem., Anal. Ed.,* **11**, 305 (1939).

The slope of this curve gives the heat of the reaction

$$^{1}/_{2}Re_2O_7(s) + {}^{1}/_{2}H_2O(v) \longrightarrow HReO_4(s),\ \Delta H = -5.50 \pm 0.05 \text{ kcal.}$$

Using the value $\Delta H = -295.5 \pm 2$ kcal. mole^{-1}, determined by Roth and Becker[6] for the heat of formation of rhenium heptoxide the heat of formation of solid $HReO_4$ 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 Formaldehyde[1]

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

RECEIVED MAY 5, 1952

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 $C_{11}H_{14}O_6H_2$: 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 Å^3. 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.

TABLE 1

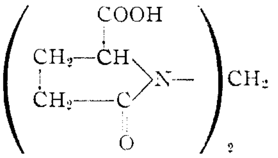
X-RAY POWDER DATA FOR METHYLENE BIS-(N-PYRROLIDONE-2-CARBOXYLIC ACID)

$CuK\alpha = 15418$ Å.

d	*I*[a]	*d*	*I*[a]	*d*	*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
3.55	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 $C_{12}H_{12}O_5N_2$: 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.*

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[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.

[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).