The alternate elimination of hydrogen chloride from carbon atoms 8 and 4 would have given an optically inactive product. The structure of (II) receives additional support from the properties of the carboxylic acid (III) obtained by alkaline hydrolysis of (II). In ultraviolet absorption spectrum (Fig. 1) the carboxylic acid (III) shows a peak at 248–250 mμ, which is indicative of a chromophore involving a conjugation of the carboxylic group with a double bond between carbon atoms.[4]
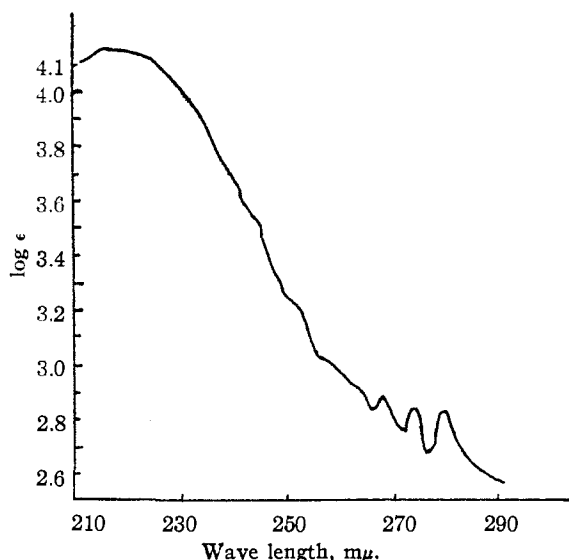

Fig. 1.—Ultraviolet absorption spectrum of 9-carboxy-1,8-(9)-p-menthadiene in 95% ethanol.

Experimental[5]

d-Limonene.—d-Limonene was obtained by fractional distillation of commercial d-limonene. The fraction used had the following constants: b.p. 171–172° (680 mm.), d^{20}_4 0.8404, $n^{20}D$ 1.4407, $[\alpha]^{20}D$ +124°.

Addition of Carbon Tetrachloride to d-Limonene.—In a three-necked, 500-cc. flask fitted with a reflux condenser, thermometer, dropping funnel and gas inlet-tube, a mixture of d-limonene (14 g., 0.1 mole) and C.P. carbon tetrachloride (154 g., 1.0 mole) was refluxed for 24 hours in a continuous stream of dry nitrogen. Benzoyl peroxide (1 g., 0.004 mole) in carbon tetrachloride (20 cc.) was added in four equal portions at intervals of six hours. During refluxing the temperature gradually rose to 88°. The brown reaction product was then washed with 10% sodium carbonate solution and with water, and dried over anhyd. sodium sulfate. From the sodium carbonate washings 0.6 g. of benzoic acid was obtained upon acidification. From the dry reaction mixture, the excess of unreacted carbon tetrachloride was removed by distillation at atmospheric pressure. The residue obtained weighed 19 g., and gave upon fractional distillation at reduced pressure 7 g. of unreacted d-limonene, 1.1 g. of intermediate and 8.7 g. of yellow oil (II), b.p. 165–170° (19 mm.), $n^{20}D$ 1.5260, $[\alpha]^{18}D$ +15.8° (ca. 10% in ethanol).

The adduct (II) represents a yield of about 30% on the basis of the d-limonene used or 60% on the basis of the d-limonene consumed.

Anal. of adduct. Calcd. for $C_{11}H_{15}Cl_3$: C, 52.4; H, 5.95; Cl, 41.6. Found: C, 51.9; H, 6.1; Cl, 41.2.

A higher yield of adduct (70% on the basis of d-limonene consumed) is obtained when the same mixture is heated in a sealed tube at 120–130° for 12 hours.

Hydrolysis of (II).—The adduct (II) is not readily hydrolyzed by aqueous, methanolic or ethanolic alkali. However,

it is hydrolyzed by aqueous alcoholic alkali when heated in a sealed tube at 140°. For the preparation of the carboxylic acid (III), a mixture of 7 g. of (II), 50 cc. of ethanol and 6.5 g. of potassium hydroxide dissolved in 15 cc. of water was heated for 15 hours at 140–150° in a sealed tube. The reaction mixture was diluted with 100 cc. of water, the ethanol removed by distillation and the alkaline residue extracted with ether. The alkaline solution was acidified with dilute sulfuric acid and again extracted with ether. After removal of the ether, 2 g. of crude acid was obtained. Recrystallization from dilute acetic acid yielded 1.5 g. (30%) of colorless long prismatic rods, m.p. 94–95°. The acid absorbs two moles of bromine (titration with 0.1 N solution of $KBr–KBrO_3$[6]).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.3; H, 8.9; neut. equiv., 180. Found: C, 73.2; H, 9.0; neut. equiv., 179.8.

The same yield of the saponification product was obtained, when a mixture of 20 g. of (II) and 10 g. of potassium hydroxide dissolved in 75 cc. of dry ethanol was heated for 24 hours at 150–160° in a sealed tube (see, Gätzki and Stammbach,[7] Grummitt, et al.[8]).

Ethyl Ester of (III).—The ethyl ester of (III) was obtained when 1 g. of the acid was dissolved in absolute ethanol, saturated with dry hydrogen chloride, and refluxed for two hours. The ethanol was removed by distillation, and the residue was washed with water, dried and distilled at reduced pressure. A colorless oil of very pleasant odor was obtained; b.p. 125° (25 mm.), $n^{20}D$ 1.4925, yield 58%.

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 75.0; H, 9.6; sapn. equiv., 208. Found: C, 74.8; H, 9.5; sapn. equiv., 208.5.

Saponification of the ester yielded a pure specimen of the carboxylic acid, m.p. 95.5°.

Ultraviolet spectrum was obtained with a Beckman quartz spectrophotometer. The spectrum was measured in ethanol at concentration of 0.001 molar.

(4) K. W. Hausser, R. Kuhn, A. Smakula and M. Hoffer. Z. physik. Chem., B29, 371 (1935); H. Mohler and H. Lohr, Helv. Chim. Acta, 21, 485 (1938).

(5) All b.ps. and m.ps. are uncorrected.

(6) H. J. Lucas and D. Pressman, Ind. Eng. Chem., Anal. Ed., 10, 140 (1938).

(7) K. Gätzki and W. Stammbach, Helv. Chim. Acta, 29, 563 (1946).

(8) O. Grummitt, et al., This Journal, 67, 156 (1946).

Department of Organic Chemistry
The Hebrew University
Jerusalem, Israel

High Temperature Heat Contents of Magnesium Orthotitanate and Magnesium Dititanate

By R. L. Orr and J. P. Coughlin

An earlier paper[1] from this Laboratory reported high temperature heat content values for the metatitanates of calcium, iron and magnesium. The present paper contains similar data for magnesium orthotitanate and magnesium dititanate.

Materials.—The magnesium titanates were prepared from reagent-grade magnesium oxide and pure titania (99.8% TiO_2, after ignition). Stoichiometric quantities of the oxides were thoroughly mixed, compressed (15,000 lb./sq. in.) into pellets, and heated for prolonged periods at 1300 to 1500°. At intervals, the products were cooled, ground to −100 mesh, analyzed, adjusted in composition, re-formed into pellets, and reheated, until reaction was complete.

The magnesium orthotitanate analyzed 49.53% TiO_2 and 0.21% SiO_2, as compared with the theoretical 49.77% TiO_2. Tests for free magnesia showed only a negligible amount. The X-ray diffraction pattern gave no evidence of impurities.

The magnesium dititanate analyzed 79.63% TiO_2 and 0.16% SiO_2, as compared with the theoretical 79.85% TiO_2. Tests for free magnesia were negative. The X-ray diffraction pattern agreed with that of Jander and Bunde,[2] and gave no evidence of impurities.

(1) B. F. Naylor and O. A. Cook, This Journal, 68, 1003 (1946).

(2) W. Jander and K. Bunde, Z. anorg. Chem., 239, 418 (1938).

Measurements and Results.—The heat content measurements were made with previously described[3] apparatus and techniques. The substances were enclosed during the measurements in platinum –rhodium capsules. Corrections for the heat contents of these capsules were determined by separate experiments. The results are expressed in defined calories (1 cal. = 4.1833 int. joules), and molecular weights accord with the 1949 International Atomic Weights.

The measured heat content data are listed in Table I. The precision uncertainty, considering all the measurements for each substance, is less than 0.1%, although an occasional determination may deviate from a smooth curve by as much as 0.5%. Both substances show regular behavior, there being no evidence of any transformation or region of anomalous heat capacity. The heat content of the orthotitanate, the heat content of the dititanate is less than the sum for the metatitanate

TABLE I

HEAT CONTENTS ABOVE 298.16°K. (CAL./MOLE)

T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
		Mg_2TiO_4 (mol. wt. 160.54)			
392.4	3,080	1086.6	31,260	1197.9	36,420
493.9	6,780	1092.1	31,590	1286.8	40,490
592.6	10,560	1092.7	31,410	1286.8	40,550
695.3	14,640	1097.9	31,910	1295.4	41,000
789.2	18,500	1106.5	32,260	1392.1	45,650
894.8	22,910	1109.8	32,420	1490.4	50,290
999.3	27,370	1113.1	32,420	1597.2	55,400
1004.7	27,530	1113.6	32,610	1705.9	60,750
1006.0	27,550	1114.0	32,530	1792.4	64,860
1027.8	28,670	1124.6	33,050	1817.8	66,510
1074.2	30,700				
		$MgTi_2O_5$ (mol. wt. 200.12)			
396.8	3,650	901.9	26,330	1389.5	50,910
492.7	7,590	998.8	30,950	1500.5	56,920
587.8	11,750	1084.4	35,120	1601.9	62,440
695.5	16,660	1182.4	40,050	1696.2	67,790
795.0	21,190	1287.9	45,440	1812.1	74,160

TABLE II

HEAT CONTENTS (CAL./MOLE) AND ENTROPIES (CAL./DEG. MOLE) ABOVE 298.16°K.

T, °K.	Mg_2TiO_4		$MgTi_2O_5$	
	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$
400	3,340	9.61	3,780	10.87
500	6,990	17.74	7,910	20.08
600	10,850	24.77	12,290	28.06
700	14,840	30.92	16,830	35.06
800	18,930	36.38	21,470	41.25
900	23,120	41.31	26,200	46.82
1000	27,430	45.86	31,010	51.89
1100	31,910	50.13	35,910	56.56
1200	36,510	54.13	40,930	60.92
1300	41,200	57.88	46,090	65.05
1400	45,960	61.41	51,410	69.00
1500	50,760	64.72	56,850	72.75
1600	55,600	67.84	62,370	76.31
1700	60,470	70.79	67,940	79.68
1800	65,370	73.59	73,530	82.88

(3) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper, 686 (1946).

and rutile by 6.4% at 400°K., and greater than this sum by 1.7% at 1800°K. No previous high temperature heat content data for either the orthotitanate or dititanate were found in the literature.

Table II contains heat content and entropy increments above 298.16°K. at even 100° intervals, for use by those who prefer the tabular method of thermodynamic calculations. The entropy increments have been calculated to match the heat contents by the method of Kelley.[4]

The heat contents are represented, to within the average deviation indicated in parentheses, by the equations

Mg_2TiO_4: $H_T - H_{298.16} = 35.96T + 4.27 \times 10^{-3}T^2 + 6.89 \times 10^5 T^{-1} - 13,412$; (298 − 1800°K.; 0.3%)

$MgTi_2O_5$: $H_T - H_{298.16} = 40.68T + 4.60 \times 10^{-3}T^2 + 7.35 \times 10^5 T^{-1} - 15,003$; (298 − 1800°K.; 0.3%)

(4) K. K. Kelley, U. S. Bur. Mines Bull., 476 (1949).

MINERALS THERMODYNAMIC BRANCH
REGION III, BUREAU OF MINES
UNITED STATES DEPARTMENT OF THE INTERIOR
BERKELEY 4, CALIFORNIA

The Identity of Neamine and Neomycin A

By BYRON E. LEACH AND CHARLOTTE M. TEETERS

The hydrolysis of the antibiotic neomycin with mineral acid yields a crystalline biologically active base which has been named neamine.[1] Peck and co-workers[2] had previously reported the isolation of neomycin A hydrochloride from the fermentation broths of Streptomyces fradiae. An exchange of samples with Dr. R. L. Peck[3] has revealed that neamine is identical with neomycin A.

Neomycin A hydrochloride was converted to the free base and crystallized from ammoniacal methanol. The melting point was 256° (dec.), and showed no depression in melting point when mixed with neamine. The infrared absorption spectra, measured in liquid petrolatum (Nujol) suspension, of the hydrochloride and the crystalline free base of neomycin A were identical with neamine hydrochloride and its crystalline free base, respectively. Paper chromatograms using wet n-butanol containing 2% p-toluenesulfonic acid monohydrate[4] and also n-butanol–acetic acid–water (2:1:1) systems showed no differences in R_f values for these two substances; the slopes of the B. subtilis bioassay curves were also identical.

Hydrolysis of neamine with boiling 48% hydrobromic acid yielded the hydrobromide of an optically inactive base. The analytical data obtained for this compound are in good agreement with those calculated for the dihydrobromide of 1,3-diamino-4,5,6-trihydroxycyclohexane which Kuehl, et al.,[5]

(1) B. E. Leach and C. M. Teeters, THIS JOURNAL, 73, 2794 (1951).

(2) R. L. Peck, C. E. Hoffhine, Jr., P. Gale and K. Folkers, ibid., 71, 2590 (1949).

(3) We are grateful to Dr. R. L. Peck, Research Laboratories, Merck and Co., Rahway, N. J., for the sample of neomycin A hydrochloride.

(4) D. H. Peterson and L. M. Reineke, THIS JOURNAL, 72, 3598 (1950).

(5) F. A. Kuehl, Jr., M. N. Bishop and K. Folkers, ibid., 73, 881 (1951).