

TABLE II
THERMODYNAMIC DATA FOR H₂, Zn AND Cd

<i>t</i>	H ₂	S ⁰ Zn(s)	Cd(s)	H ₂ C _p ⁰	Zn(s)
15	31.00	9.74	12.1	6.86	6.05
25	31.23	9.95	12.3	6.86	6.07
35	31.46	10.15		6.88	6.10

capacity of zinc were taken from the equations of Kelley⁵ for these elements. Entropies at 15 and 35° were computed from S_{298.1}⁰ and the specific heat equations, corrected to conform with revised C_p⁰ values at 298.1°K.⁶

The entropies of aqueous zinc and cadmium ions and the heat capacity of zinc ion are listed in Table III in calories per degree per mole. As is customary, the standard entropy and heat capacity of aqueous hydrogen ion have been considered zero at all temperatures.

TABLE III
RELATIVE ENTROPIES OF ZINC AND CADMIUM IONS.
RELATIVE HEAT CAPACITY OF ZINC ION

	Zn ⁺⁺	Cd ⁺⁺	Zn ⁺⁺ C _p ⁰
15	-25.60	-14.50	-9.05
25	-25.89	-14.82	-9.32
35	-26.21		-9.60

It is probable that the accuracy of the entropy of zinc ion is of the order of ± 0.5 cal./deg. mole. The value for the entropy of cadmium ion is subject to the combined uncertainties inherent in the work of the author and of Parks and La Mer, but it is thought to be correct to about ± 1 cal./deg. mole.

Latimer, Pitzer and Smith,⁷ in their recent review of ionic entropies, list -25.7 ± 1 and -16.4 ± 1.5 for zinc and cadmium ions, respectively. The value for the standard entropy of cadmium ion computed from equation (4) lies just outside the limit of accuracy estimated by these authors. For zinc ion the agreement is excellent.

(5) Kelley, Bureau of Mines, Bull. 371, 1934.

(6) See footnote 23 of the paper by Owen and Brinkley, THIS JOURNAL, 60, 2233 (1938).

(7) Latimer, Pitzer and Smith, *ibid.*, 60, 1829 (1938).

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The Aldehydic Constituents from the Ethanolysis of Spruce and Maple Woods

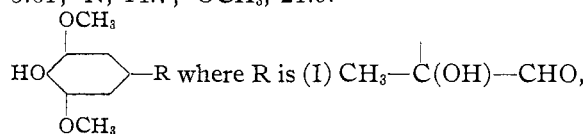
By LEO BRICKMAN, JAMES J. PYLE AND HAROLD HIBBERT

In accompanying communications¹ from these Laboratories the occurrence has been reported of

(1) Cramer, Hunter and Hibbert, THIS JOURNAL, 61, 509 (1939); Hunter, Cramer and Hibbert, *ibid.*, 61, 516 (1939).

aldehydic constituents among the ethanolysis products of spruce and maple woods. The aldehyde fraction of the latter readily yields a crystalline semicarbazone, m. p. 210–210.5°, analysis of which points to a structural formula for the aldehyde corresponding to either I, II, III, IV or V.

Anal. Calcd. for C₁₂H₁₇O₅N₃ (I, II, III): C, 50.87; H, 6.05; N, 14.8; OCH₃, 21.9. Calcd. for C₁₂H₁₅O₅N₃ (IV and V): C, 51.24; H, 5.37; N, 14.9; OCH₃, 22.0. Found: C, 51.61; H, 5.61; N, 14.7; OCH₃, 21.9.



where R is (I) CH₃—C(OH)—CHO, (II)—CH(OH)CH₂CHO, (III)—CH₂CH(OH)CHO, (IV)—COCH₂CHO and (V)—CH₂COCHO. The experimental data are somewhat in favor of IV or V but nevertheless in good agreement with all five structures.

A similar semicarbazone has also been isolated from the ethanolysis aldehyde fraction of spruce wood and the investigation of both products is in progress.

The relation of both to the structure of lignin is discussed in the accompanying *communication* by one of us (H. H.)

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The Phosphorescence of Tetraphenylmethane and Certain Related Substances

By DANIEL B. CLAPP

Upon irradiation of solid crystalline tetraphenylmethane and certain of its derivatives with ultraviolet light from a Hanovia quartz mercury vapor cold-discharge lamp, it was noted that the substances exhibit marked luminescence after extinction of the exciting light. Tetraphenylmethane,¹ m. p. 281.5–282°, which was purified by distillation, sublimation, and recrystallization, shows a brilliant blue-green after-glow, with a visible duration at room temperature of about twenty-three seconds. The duration of the phosphorescence is dependent upon temperature; at 130° the duration is so short that no after-glow is visible; at 125° it persists for about two seconds, at 80°

(1) Prepared both according to Ullmann and Münzhuber, *Ber.*, 36, 404 (1903), and to Schoepfle and Trepp, THIS JOURNAL, 58, 794 (1936).

for four seconds, at 40° for nine seconds, and at -20° for thirty-five seconds.

Tetraphenylmethane derivatives containing the following substituents also show phosphorescence, although less marked: 4-hydroxy, 2,4-dihydroxy, 4-methoxy, 2,4-dimethoxy, 4-ethoxy, 4-amino, 4-methylamino, 4-ethylamino, 4-*n*-butylamino, 4-dimethylamino, 4-diethylamino, 4-di-*n*-butylamino, 4-amino-3-methyl, 4-amino-3,5-dimethyl. The color of the after-glow varies from green to blue, with visible durations of two to twelve seconds.

α -Triphenylmethylpyrrole, in which one of the phenyl groups of tetraphenylmethane has been replaced by a pyrrol group, gives a green after-glow with a duration of nine seconds. Compounds of silicon, tin, and lead, which are structurally analogous to tetraphenylmethane, also show phosphorescence. Tetraphenylsilane² and tetra-*p*-tolylsilane² show bright green phosphorescence lasting about twenty seconds. Tetra-*p*-xenylsilane,² on the other hand, does not phosphoresce under these conditions. Tetraphenyltin and tetraphenyllead both show phosphorescence, that of the latter substance being very weak at room temperature.

Kirchoff³ has reported that fluorene and benzoin on irradiation with light from a mercury vapor lamp show phosphorescence with a visible duration of several seconds. Both these substances, however, under conditions used in these experiments, give no visible after-glow. Nevertheless, several organic substances unrelated to tetraphenylmethane, as succinic acid, resorcinol, and sucrose, which do show phosphorescence, were encountered. It is known⁴ that very small traces of impurities, particularly triphenylmethane dyes, are responsible for the phosphorescence of many solid organic compounds. If this is the case with tetraphenylmethane and related substances, it would seem that this series of compounds provides a favorable "grundmaterial" for organic phosphors. The presence of traces of triphenylmethane dyes in the tetraphenylmethanes themselves seems quite possible, although such impurities would not be expected in the silicon, tin, and lead analogs.

The following tetraphenylmethane derivatives were prepared by a modification of the method used by Fischer⁵

(2) These substances were kindly furnished by Mr. C. M. Saffer, Jr., cf. Schumb, Ackermann and Saffer, *THIS JOURNAL*, **60**, 2486 (1938).

(3) Kirchoff, *Physik. Z.*, **30**, 240 (1929).

(4) Lenard, Schmidt and Tomaschek, "Handbuch der Experimentalphysik," Vol. XXIII, part 1, "Phosphoreszenz-Fluoreszenz," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1928, p. 561.

(5) Fischer, *Z. physiol. Chem.*, **115**, 92 (1921).

for the preparation of 4-dimethylaminotetraphenylmethane.

4 - Ethylaminotetraphenylmethane.—Triphenylcarbinol (3.5 g.), and ethylaniline (5 g.) were added to a solution prepared from glacial acetic acid (20 cc.), hydrochloric acid (sp. gr. 1.19) (4 g.), and acetic anhydride (4 g.), and the mixture refluxed for one hour. On pouring into 100 cc. of 25% alcohol containing 10 g. of sodium hydroxide, a brown oil separated, and gradually solidified. The solid was washed thoroughly with water, dried, and purified by crystallization from ligroin (b. p. 70-80°), with the use of decolorizing carbon: yield 2 g.; m. p. 172-173°.

Anal. Calcd. for C₂₇H₂₅N: C, 89.22; H, 6.93; N, 3.85. Found: C, 89.16; H, 6.97; N, 3.76, 3.85.

4 - *n* - Butylaminotetraphenylmethane was prepared similarly from *n*-butylaniline. Purified by several recrystallizations from absolute alcohol, the yield was 2 g.; m. p. 135-136°.

Anal. Calcd. for C₂₉H₂₉N: C, 88.96; H, 7.46; N, 3.58. Found: C, 88.96; H, 7.50; N, 3.63.

4-Diethylaminotetraphenylmethane.—From diethylaniline; recrystallized from ligroin (b. p. 90-120°); yield 2.6 g.; m. p. 177.5-178.5°. *Anal.* Calcd. for C₂₉H₂₉N: C, 88.96; H, 7.46; N, 3.58. Found: C, 88.92; H, 7.51; N, 3.62, 3.63.

4 - Di - *n* - butylaminotetraphenylmethane.—From di-*n*-butylaniline; recrystallized from ligroin (b. p. 90-120°); yield 2.6 g.; m. p. 177-178°. *Anal.* Calcd. for C₃₃H₃₇N: C, 88.54; H, 8.33; N, 3.13. Found: C, 88.56; H, 8.35; N, 3.18, 3.14.

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RESEARCH LABORATORY OF ORGANIC CHEMISTRY
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The Determination of Water in Organic Liquid Mixtures

BY R. A. DAY, JR., AND ROBERT N. PEASE

We have wished to determine water in a complex mixture of alcohols, aldehydes, acids and peroxides resulting from the oxidation of hydrocarbons. A simple method which gives promise of some usefulness is the following.

The sample of liquid is added to a weighed sample of powdered anhydrous copper sulfate. After thorough mixing, the solid is filtered off, washed with liquid butane, and again weighed. The gain in weight is taken as the water content of the sample.

Use is made of a Jena sintered glass Gooch crucible of 15 cc. capacity. A sample of powdered anhydrous copper sulfate equal to two to three times that required for the formation of the trihydrate is weighed into the crucible. This is then set up in a filter flask, which stands in a