

North American Philips Company X-ray machine. The pictures were taken at 32 kilovolts and 22 milliamperes from a copper target using a nickel filter. The exposure periods were varied from one to five hours until good pictures were obtained.

CONTRIBUTION FROM THE
RESEARCH LABORATORIES OF THE
SPRAGUE ELECTRIC COMPANY
NORTH ADAMS, MASS.

RECEIVED APRIL 18, 1950

Rhenium Iodide and Chloride

BY CHARLES L. RULFS AND PHILIP J. ELVING¹

Noddack and Noddack² reported the formation of ReI_4 by the action of iodine vapor on rhenium metal. No confirmation of this compound could be found.³ Since no simple iodides of rhenium are known, it was felt worthwhile to attempt the preparation of rhenium iodide by several different methods. In no case could any evidence of reaction be found. The methods tried include the following: (1) Rhenium powder was heated with iodine in a sealed tube for six hours at 170–180°. (2) Rhenium powder suspended in carbon tetrachloride containing an excess of dissolved iodine was refluxed for seventy-two hours.

Rhenium trichloride was prepared in poor yield by an adaptation of the Ruff synthesis⁴ for iodine trichloride and monochloride.

Rhenium powder plus sulfuryl chloride, with and without traces of aluminum chloride present, were treated (a) by boiling for forty-eight hours at atmospheric pressure, (b) by heating in a sealed tube at 150° for six hours, and (c) by refluxing in excess ether for sixty hours. In every case a limited amount of reaction took place, the amount of which did not seem to be notably improved by longer treatment. Ether extraction of the reaction residues gave a red to violet solution which was filtered to remove unreacted rhenium. Vacuum evaporation of the ether left a red residue which had a high tendency to sublime or distil into the trap as a greenish vapor. Apparently, rhenium trichloride was the product of the reactions but the yield was poor under all conditions that were tried.

(1) The Pennsylvania State College, State College, Penna.

(2) I. Noddack and W. Noddack, "Das Rhenium," Voss, Leipzig, 1933.

(3) J. G. F. Druce, "Rhenium," Cambridge Univ. Press, Cambridge, 1948.

(4) O. Ruff, *Ber.*, **34**, 1749 (1901).

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

RECEIVED AUGUST 6, 1949

Solubility of Thallous Rhenide^{1a}

BY CHARLES L. RULFS^{1b} AND PHILIP J. ELVING^{1c}

The many apparent analogies of rhenide ion with the halides suggests the possible isolation

(1) (a) The work described was performed while C. L. R. was the holder of an Atomic Energy Commission Predoctoral Fellowship. (b) University of Michigan, Ann Arbor, Mich. (c) The Pennsylvania State College, State College, Pa.

of insoluble silver, lead or mercurous rhenide by precipitation. The powerful reducing action of rhenide ion, however, precludes these particular possibilities. Thallous ion, on the other hand, is not reduced by rhenide and the thallous halides are relatively insoluble.

Rhenide solution, 1 mM in rhenium and 2.4 N in hydrochloric acid, was prepared by zinc reduction under nitrogen in a water-cooled reductor as described by Lundell and Knowles.² The solution was saturated with thallous chloride at ca. 25° and then allowed to stand under nitrogen for ninety minutes at ca. 0°. The white crystals which separated from the test solution were examined microscopically and found to be isomorphous with thallous chloride. A portion of the washed precipitate was warmed and dissolved in bismuth trichloride solution, giving no evidence of any discoloration. A drop of the supernatant test solution gave an immediate black precipitate when added to the same tube, indicating the presence of rhenide in the supernatant liquid.

Contrary to expectation, it must be concluded from the failure of the compound to precipitate that thallous rhenide is considerably more soluble than is thallous iodide and at least twice as soluble as is the bromide. More specifically, the solubility of thallous rhenide (estimated from the known rhenide concentration in the presence of excess thallous ion) must be equal to or greater than 39 mg. per 100 ml. of 2.4 N hydrochloric acid at 0°. The solubilities³ of the thallous halides in mg. per 100 ml. of water at 0° are: TlCl , 161; TlBr , 22; TlI , 2.

(2) Lundell and Knowles, *J. Research Nat. Bur Standards*, **18**, 629 (1937).

(3) A. Seidell, "Solubilities of Inorganic Compounds," ed. 3, D. Van Nostrand Co., New York, N. Y., 1940, pp. 1538 ff.

PURDUE UNIVERSITY AND
PURDUE RESEARCH FOUNDATION
LAFAYETTE, INDIANA

RECEIVED AUGUST 6, 1949

Some Physical Constants of α -Tocopherylhydroquinone¹

BY HARRIS ROSENKRANTZ AND A. T. MILHORAT

Recent reports from this Laboratory have demonstrated that α -tocopherylhydroquinone has vitamin E activity.^{2,3} Since other workers undoubtedly will study this compound, a report on certain of its physical constants appears to be desirable. The substance may exist either as a waxy solid⁴ or an oil at room temperatures. Fieser, Tishler and Wendler⁵ prepared 2,3,5-trimethyl-6-phytyl-1,4-benzohydroquinone in crystalline form, and Tishler and Wendler⁴ obtained tocopherylhydroquinone as a white waxy solid. We have succeeded in crystallizing tocopherylhydroquinone as short thin needles. Solutions containing 250 mg. α -tocopherylhydroquinone per cc. of absolute ethanol were placed in a desiccator immediately after hydrogenation and removal of the catalyst. The desiccator was evacuated at the water-pump for twenty-four hours; after the solution had stood for an additional period of twenty-four

(1) Aided by the Armour Fund for Research in Muscular Disease and by a grant from The Nutrition Foundation, Inc.

(2) Ulick and Milhorat, *Science*, **110**, 531 (1949).

(3) Milhorat, Mackenzie, Ulick, Rosenkrantz and Bartels, *Annals N. Y. Acad. Sci.*, **52**, Art. 3, 334 (1949).

(4) Tishler and Wendler, *Texts Journal*, **63**, 1532 (1941).

(5) Fieser, Tishler and Wendler, *ibid.*, **63**, 2865 (1940).

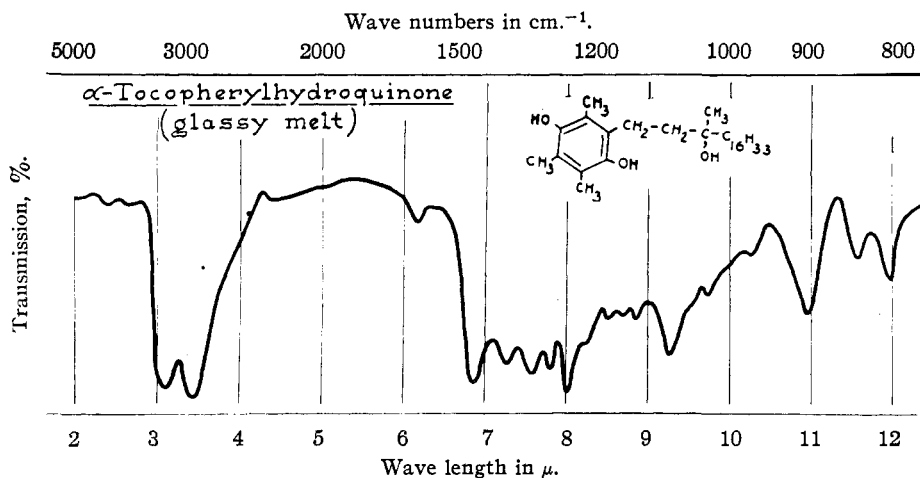


Fig. 1.—Infrared spectrum of α -tocopheryhydroquinone.

hours, formation of crystals occurred and continued slowly over the next three days. Melting point determinations of the white solid gave values of 59.5–61.4°. The infrared absorption spectrum (Fig. 1) may be distinguished readily from that of either α -tocopherol or α -tocopherylquinone. Hydrogen bonding is indicated by the broadening of the hydroxyl absorption band and the location of this band near 3.1 μ ; unbonded phenolic hydroxyl groups usually absorb near 2.8 μ . Infrared absorption spectra of the corresponding tocopherol and tocopherylquinone⁶ and data on the ultraviolet absorption spectrum of α -tocopheryhydroquinone² were published previously.

(6) Rosenkrantz, *J. Biol. Chem.*, **173**, 439 (1948).

DEPARTMENTS OF MEDICINE AND PSYCHIATRY
CORNELL UNIVERSITY MEDICAL COLLEGE
RUSSELL SAGE INSTITUTE OF PATHOLOGY, AND
THE NEW YORK HOSPITAL
NEW YORK, N. Y.

RECEIVED JANUARY 12, 1950

Studies of Non-aqueous Solvates. V. The Preparation of Anhydrous Magnesium Bromide in Diethyl Ether¹

BY H. H. ROWLEY

The reaction of free bromine with magnesium in anhydrous diethyl ether to form the magnesium bromide–diethyl ether system has been known and studied for some time.^{2–6} The present work describes the preparation of pure anhydrous magnesium bromide from this system.

Experimental

Apparatus.—The preparation of 2–3-g. samples of anhydrous magnesium bromide can be carried out in an Erlenmeyer flask with addition of liquid bromine from a dropping bottle. By slow addition of bromine and care-

ful control of temperature a very pure product can be obtained with only a trace of impurities. For larger amounts of material an apparatus following the general design of Fig. 1 was found to be most suitable. To control the speed of the reaction, a bromine vaporizer (A) was used. Passage of dry nitrogen gas (15 ml./min.) through the bromine, which was heated to 50–55°, served to introduce bromine directly into the ether and also to provide the inert atmosphere which was found necessary. The bromine could be stopped at any time by manipulation of stopcocks (S₁, S₂, S₃) without halting nitrogen flow. The reaction vessel (B) was fitted with ground joints (M), a mercury seal (T) and spiral stirrer (N). In later runs, a 500-ml. round-bottom, three-necked standard taper flask was used with satisfactory results.

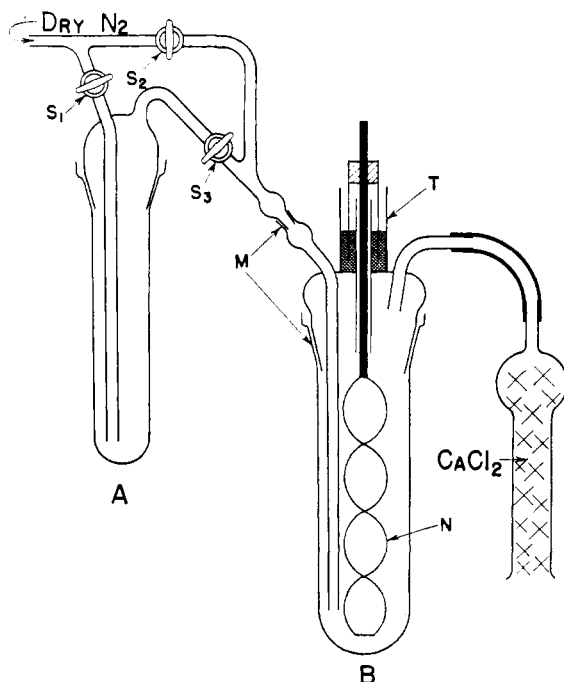


Fig. 1.

Procedure.—A typical run consisted of about 10 g. of magnesium turnings, Grignard quality, in 150 ml. of freshly distilled anhydrous diethyl ether. Excess mag-

(1) Presented at the Fifth Southwest Regional American Chemical Society meeting, Oklahoma City, Okla., December 9, 1949.

(2) Zelinsky, *Chem. Zentr.*, **74**, II, 277 (1903).

(3) Menshutkin, *Z. anorg. Chem.*, **49**, 34 (1906).

(4) Evans and Rowley, *This Journal*, **52**, 3523 (1930).

(5) Rowley, *ibid.*, **58**, 1337 (1936).

(6) Rowley, *ibid.*, **59**, 621 (1937).