abundance ratio. The present accepted value on the chemical scale is slightly higher than this although it would appear that the chemical determinations should run low by from 0.00010 to 0.00015 unit due to isotopic separation in the preparation of the gas.

Summary

Deuterium free water (less than 1 D atom in 1,000,000 H atoms) has been prepared by the fractional electrolysis of 50 liters of normal water.

Density changes were determined for the light fraction in each step of the electrolysis, by means of the totally submerged float. Graphic treatment of the data yields 19.1 ± 1 p.p.m. for the influence of deuterium on the density of ordinary water. This corresponds to an abundance ratio of 5750 ± 250 for H/D, which confirms Bleakney and Gould's figure of 5000 ± 500, obtained with the mass spectrograph.

The electrolytic separation factor for O^{16} relative to O^{18} proves to be 1.008 ± 0.003. This indicates the futility of attempting to prepare pure O^{18} or pure O^{17} by electrolysis.

From the H/D ratio of 5750 the atomic weight of normal hydrogen is computed to be 1.00795 on the O^{16} scale. It is 1.00770 or 1.00775 on the chemical scale, based on O^{18} abundance ratios of Manian, Bleakney and Urey or of Mecke and Childs, respectively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Properties of Thallium Triethyl[1]

BY E. G. ROCHOW AND L. M. DENNIS

Thallium triethyl was first prepared by Groll[2] in 1930,[3] by the action of lithium ethyl upon diethyl thallic chloride in solution in petroleum ether, the apparatus being filled with nitrogen.

The authors first attempted to synthesize thallium trimethyl by the interaction of (a) mercury dimethyl and metallic thallium at elevated temperatures, (b) methyl iodide and an alloy of sodium and thallium, and (c) thallium–copper couple on methyl iodide. In each case no appreciable yield of a volatile compound of thallium was obtained.

To gain familiarity with the Groll synthesis of thallium triethyl with the view of ascertaining whether a modification of it might yield the methyl compound, his method was repeated, but the reactions were carried on in the vacuum apparatus developed in the Cornell laboratory which made possible the preparation, purification and study of the properties of thallium triethyl in the absence of air, moisture and foreign gases that might affect its behavior.

Experimental

Pulverized diethyl thallic chloride was placed in the tube H (Fig. 1), which was then evacuated and sealed. The end of the normal joint at G was closed by a curved drawn-out tip which could be broken off against a stationary indentation when H was rotated in the joint G. Granular metallic lithium was placed in the bulb C, the system attached to the vacuum apparatus by means of the joint A, and evacuated.

Purified petroleum ether and mercury diethyl were distilled into C and the stopcock B was closed. C was heated to 70° for four days, the arms being cooled to prevent loss of petroleum ether. The solution of lithium ethyl thus formed was poured into the bulb F by raising C until sufficiently tilted to allow decantation through the tube D. Some petroleum ether was distilled back into C to dissolve the remaining lithium ethyl, and again decanted. F was then sealed off at the constriction E. The bulb was cooled to −10° and the contents of the tube H added by breaking off its tip at G. The bulb was then shaken mechanically for five hours while the reaction proceeded.

The bulb was attached to the vacuum chain by means of the joint I and the volatile substances were distilled out. Petroleum ether was separated from the alkyl by fractionating *in vacuo*, leaving thallium triethyl as a bright yellow liquid.

The alkyl was analyzed by distilling a sample into a weighed bulb, condensing an excess of water in the bulb,

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[1] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] H. P. A. Groll, THIS JOURNAL, **52**, 2998 (1930).

[3] We had planned to take up, in the Cornell laboratory, the study of the normal thallium alkyls as a continuation of our investigations of the alkyls of gallium [Dennis and Patnode, *ibid.*, **54**, 182 (1932); "Gallium Trimethyl," Thesis of P. L. Brandt, 1932] and indium [Dennis, Work and Rochow, *ibid.*, **56**, 1047 (1934)], but as Dr. Groll's article established his priority in the field, we deferred doing so until word was received from him that he did not intend to carry further his researches on thallium compounds of this type.

and allowing the contents to warm slowly until the alkyl reacted smoothly with the crystals of ice. After standing at room temperature for fifteen hours to complete the hydrolysis, the evolved gas was pumped into a buret and measured. The clear solution within the bulb was transferred to a flask and was titrated with standard sulfuric acid to determine the diethyl thallic hydroxide present. The salt thus formed was removed from solution by evaporation, oxidized with fuming nitric acid, and the residue dissolved in dilute sulfuric acid. The thallium was reduced by bubbling sulfur dioxide through the warm solution, and was then precipitated as thallic oxide by the addition of dilute solutions of potassium hydroxide and potassium ferricyanide according to the method of Mach and Lepper.[4,5]

This procedure establishes the composition of both the alkyl and its hydrolysis product, diethyl thallic hydroxide.

Anal. Subs. 0.56985 gram or 1.955 millimoles. Ethane: calcd. 43.74 cc., found 43.79 cc. (at standard conditions). Diethyl thallic hydroxide: calcd. 0.4910 gram requiring 17.68 cc. of 0.1105 *N* acid; found 0.4939 gram requiring 17.78 cc. of acid. Thallium: calcd. 0.39957 gram or 70.113%, found 0.39958 gram or 70.115%. Molar ratio of sample : ethane : $(C_2H_5)_2TlOH$: Tl = 1.955: 1.956:1.964:1.955.

Pure thallium triethyl is an oily, yellow liquid, readily decomposed into metallic thallium by exposure to diffused daylight and more slowly upon standing in evacuated containers screened from the light. It has a distinctive pungent odor, fumes strongly in air, but does not spontaneously ignite. Like the alkyls of gallium and indium, it hydrolyzes rapidly, yielding an alkyl metallic hydroxide, but differs from them in that only one alkyl group can be removed by boiling with acids.

The density was determined by condensing a sample in a weighed bulb having a graduated, closed tube at the base, and subsequently weighing the bulb containing the same volume of mercury: d^{23}_{23} 1.957.

The melting point was determined by the dropping-ring method,[6] surrounding the tube with a pentane bath whose temperature was read with a calibrated thermocouple: melting point −63.0°. The alkyl is very viscous at its melting point.

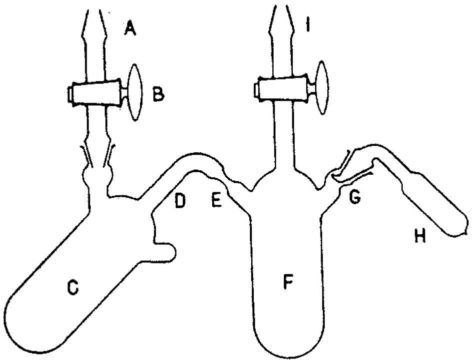

Fig. 1.—Apparatus for the preparation of thallium triethyl.

The vapor pressures from 0 to 80° were measured by means of an apparatus having a small bulb and differential manometer completely immersed in the heating bath, the vapor pressure of the substance being balanced by a measured pressure of dry air in the chain.[7] The results may be plotted as a linear function of log *P* and 1/*T*, the equation of the line being

$$\log P = -1.032 \times 10^6 (1/T) + 2224$$

The vapor pressure is 1 mm. at 9° and 25 mm. at 74°. Extrapolation of the curve gives 192.1° as the normal boiling point, but decomposition is rapid at this temperature.

Thallium triethyl dissolves in ether, but no indications of an etherate stable at room temperature were found. No reaction was observed in liquid ammonia. Carefully dried air is without action, but small amounts of moisture cause hydrolysis.

The authors intend to apply the same method to the synthesis of thallium trimethyl.

Summary

Thallium triethyl has been prepared in an evacuated apparatus by the action of lithium ethyl upon diethyl thallic chloride. Some of the chemical properties are described, and physical constants are given.

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(4) Mach and Lepper, *Z. anal. Chem.*, **68**, 41 (1926).

(5) The determination of thallium in organic compounds is discussed by Goddard and Goddard in *J. Chem. Soc.*, **121**, 488 (1922), and in the other extensive studies of A. E. Goddard. Of the many methods that were tried in the course of the present investigation, the one here described proved to be the most satisfactory. It was found necessary accurately to control the volumes and concentrations at every stage of the analysis, and to standardize this established procedure with a sample of carefully purified, fused thallous sulfate.

(6) Dennis, Corey and Moore, THIS JOURNAL, **46**, 666 (1924) .

(7) Laubengayer and Corey, *J. Phys. Chem.*, **30**, 1045 (1926).