

pentachloride compounds. van Arkel and De Boer assigned the formula  $2\text{ZrCl}_4\cdot\text{POCl}_3$  on the basis of zirconium and chlorine analyses. However, analyses for phosphorus, a more sensitive criterion of composition, indicate a more probable formula  $3\text{ZrCl}_4\cdot 2\text{POCl}_3$  (phosphorus: Calcd. 6.17%; found, 6.27, 6.12, 6.10%).

The vapor pressures of pure  $3\text{ZrCl}_4\cdot 2\text{POCl}_3$  and  $3\text{HfCl}_4\cdot 2\text{POCl}_3$  have been determined in the range 0.1–1.0 atmosphere and are represented graphically in Fig. 1. The boiling points are 360 and 355° for the zirconium and hafnium compounds, respectively; the 5° difference in boiling points (which we feel is accurate to  $\pm 1^\circ$ ) leads to a calculated value of  $\alpha_0 = 1.14$  for the ratio of the vapor pressures at the boiling points. The heat of vaporization for both complexes is  $20.5 \pm 0.5$  kcal.

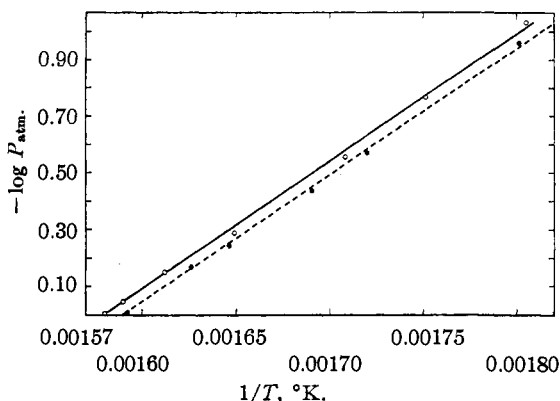


Fig. 1.—Vapor pressure of  $\text{HfCl}_4\text{-POCl}_3$  and  $\text{ZrCl}_4\text{-POCl}_3$  complexes: —, Zr complex; - - -, Hf complex.

A glass perforated plate column<sup>3</sup> with 50 physical plates was used in the distillation. In a typical experiment  $3\text{ZrCl}_4\cdot 2\text{POCl}_3$  containing 2.5% hafnium (on the weight of zirconium) yielded a first fraction (5%) containing 16% hafnium. The residue, after distilling 40% away, contained  $< 0.2\%$  hafnium.

Calculation shows the column can also be operated to yield essentially pure hafnium. This aspect, as well as further studies of the chemical and physical properties of these interesting compounds, is presently being investigated.

(3) C. F. Oldershaw, *Ind. Eng. Chem., Anal. Ed.*, **13**, 265 (1941).

CHEMISTRY DIVISION  
ARGONNE NATIONAL LABORATORY  
CHICAGO, ILLINOIS

RECEIVED MAY 19, 1949

### Sodium Testosterone Sulfate

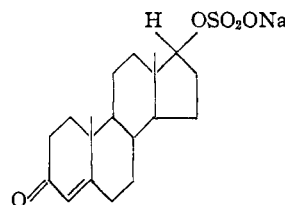
BY G. W. HOLDEN, I. LEVI AND R. BROMLEY

Sodium testosterone sulfate has been prepared with the object of comparing its androgenic activity with that of testosterone and other of its

derivatives. The results of the biological tests will be reported later.

With the exception of the use of charcoal in the purification procedure, the method followed was that described by Butenandt and Hofstetter<sup>1</sup> for the preparation of sodium estrone sulfate.

In alcohol, sodium testosterone sulfate exhibits an absorption maximum at 241  $m\mu$ , characteristic of testosterone. In water the maximum is shifted to 248–249  $m\mu$ .



A solution of chlorosulfonic acid, prepared by dissolving chlorosulfonic acid (1 ml.) in dry chloroform (30 ml.), cooling to 0° and adding pyridine (15 ml.), was added to a solution of testosterone (1.5 g.) in dry pyridine (20 ml.) and dry chloroform (50 ml.). After forty-eight hours at room temperature the solvent was removed *in vacuo* with a water-bath temperature of 40–50°. The solid residue was dissolved in methanol and the acidic solution almost neutralized (litmus) by the addition of methanolic sodium hydroxide. Aqueous sodium bicarbonate was then added to make the solution alkaline and the methanol removed *in vacuo* in the presence of water. The final volume of about 50 ml. was quite clear. This solution was shaken occasionally with Nuchar C (3 g.) at room temperature during one day. The Nuchar was filtered, washed several times with water (negative test for chloride) and eluted by suspending in methanol while still moist. Sodium testosterone sulfate (714.8 mg., 35%) was obtained by concentrating the methanol to small volume, clarifying by filtration using a little Nuchar to remove some yellow color, and precipitating with several volumes of ether. The product, thus obtained, is almost colorless. The m. p. (Fisher-Johns) is quite sharp at 215° with a green color changing to a clear brown at practically the same temperature;  $[\alpha]^{25}_D + 74.5^\circ$  (1% in water),  $+68^\circ$  (1% in ethanol);  $\epsilon_{(248-249)} 20,300$  (in water);  $\epsilon_{(240.5-241)} 17,700$  (in ethanol). *Anal.* Calcd. for  $\text{C}_{19}\text{H}_{27}\text{O}_6\text{SNa}$ : C, 58.43; H, 6.97; Na, 5.88. Found: C, 58.54; H, 6.38; Na, 6.03. The semicarbazone precipitated at once on addition of semicarbazide hydrochloride to an aqueous solution of sodium testosterone sulfate. It does not melt up to 300° but starts to darken at 240° becoming slate-gray and finally chocolate-brown. For the determination of testosterone, 53.4 mg. of sodium testosterone sulfate was added to the barium chloride sodium acetate solution described by Talbot<sup>2</sup> for the hydrolysis of sodium dehydroisoandrosterone sulfate. After four hours heating on the steam-bath the solution was extracted with ether. Only 6.5% of the theoretical weight of residue was obtained. Fifty milligrams of sodium testosterone sulfate was then hydrolyzed by refluxing one hour with a mixture of 100 ml. of water and 15 ml. of concd. hydrochloric acid in the presence of 75 ml. of toluene. The toluene was separated, the aqueous solution further extracted with ether and the combined extracts distilled after washing with sodium bicarbonate and water. The yellowish gummy residue weighed 26.8 mg. (68%). It was crystallized by means of aqueous acetone to yield 9.3 mg. (25.3%) of testosterone m. p. 153.5° and mixed m. p. with pure testosterone undepressed.

RESEARCH LABORATORIES  
CHARLES E. FROSST & CO.  
MONTREAL, CANADA

RECEIVED JULY 11, 1949

- (1) Butenandt and Hofstetter, *Z. physiol. Chem.*, **239**, 222 (1939).  
(2) Talbot, Ryan and Wolfe, *J. Biol. Chem.*, **148**, 598 (1945).