of the argument favors C_2O if one considers only the major products.

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RECEIVED MAY 8, 1962

TUNGSTEN TRIBROMIDE AND TUNGSTEN TETRABROMIDE

Sir:

The preparations of tungsten dibromide,[1,2,3] tungsten pentabromide,[1,4,5,6,7] and tungsten hexabromide[2,7] are well known. However, conspicuous for their absence among the known halides of tungsten are those of tungsten(III). Others[3] have attempted to prepare anhydrous tungsten trihalides but were unsuccessful. We wish to report the preparation of the first simple trihalide of tungsten, tungsten tribromide, and the preparation of tungsten tetrabromide.

Tungsten tribromide was prepared by the reaction between WBr_2 and excess liquid bromine in a sealed tube at 50° for two weeks. On removal of the excess bromine *in vacuo*, a black powder remained. An X-ray diffraction powder pattern of the resulting compound did not indicate the presence of any of the known tungsten bromides. Chemical analyses on several samples of the product indicated the formula WBr_3 (calcd. for WBr_3: W, 43.40; Br, 56.60. Found: W, 43.22 ± 0.07; Br, 56.30 ± 0.56). The preparation of other trihalides of tungsten by similar methods or by using WBr_3 as a starting material is being investigated.

From the available information on the tungsten halides Brewer, *et al.*,[8] estimated that the tungsten trihalides should not be thermally stable compounds. An examination of the effect of heat on WBr_3 confirmed this estimate. At about 80° *in vacuo* decomposition into WBr_2 and bromine became noticeable. The decomposition at this temperature was very slow, but accelerated with increasing temperature. At 300° the decomposition was rapid and complete; only at the latter temperature was a relatively small amount of a volatile higher bromide formed. X-Ray diffraction powder patterns of this volatile fraction showed that the major constituent was WBr_5.

In its inertness to water, concentrated hydrochloric acid, and air WBr_3 closely resembles $MoBr_3$. Attempts to prepare chloride or bromide complexes from WBr_3 and the aqueous hydrogen halides were unsuccessful because of the low solubility of the solid. This apparent low solubility in water and relative stability in air suggests that the solid WBr_3 exists in a polymerized form rather than a form of simple structure. The solid is slightly soluble in some polar organic solvents, *e.g.*, nitroethane, nitrobenzene and acetonitrile, producing wine-red solutions. Molecular weight determinations and identification of the species in these solutions are in progress.

An examination also is being made of the oxidation state of tungsten in WBr_3. The possibility of WBr_3 containing trivalent tungsten is of special interest since the only trivalent tungsten compounds known at the present time are confined to the anion complexes of tungsten(III), *e.g.*, $W_2Cl_9^{3-}$. The latter ion has been shown to have a dimeric structure[9,10] and is considered to be a derivative of the hypothetical dimer W_2Cl_6.

Although the tungsten tetrahalides WF_4, WCl_4, and WI_4 are known, the preparation of WBr_4 has not been reported. This compound was prepared by reducing WBr_5 with tungsten metal. The starting materials were placed in opposite ends of a Vycor tube along which a uniform temperature gradient was maintained: 630° at the tungsten end and 340° at the WBr_5 end. Upon cooling the tube after ten days a crystalline deposit was observed near the center of the tube. Analysis of this deposit indicated a compound having the formula WBr_4 (calcd. for WBr_4: W, 36.52; Br, 63.48. Found: W, 36.63; Br, 63.45). The X-ray diffraction powder pattern of this compound was similar to those[11] of $MoBr_4$, $NbBr_4$, and $TaBr_4$. The available data indicate the existence of an isomorphous series for these tetrabromides.

The magnetic susceptibilities and structural relationships of WBr_3 and WBr_4 with other tri- and tetrahalides of niobium, tantalum, and molybdenum are presently under consideration. In addition, a study is being made on the stability relations among the complete series of tungsten bromides, WBr_2 through WBr_6.

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(1) H. E. Roscoe, *Liebigs Ann. Chem.*, **162**, 349 (1872); *Chem. News*, **25**, 73 (1872).

(2) H. A. Schaffer and E. F. Smith, *J. Am. Chem. Soc.*, **18**, 1098 (1896).

(3) H. J. Emeleus and V. Gutmann, *J. Chem. Soc.*, 2116 (1950).

(4) C. W. Bloomstrand, *J. prakt. Chem.*, **82**, 430 (1861).

(5) M. A. Riche, *Ann. chim. et phys.*, [3] **50**, 24 (1857).

(6) M. E. Defacqz, *Compt. rend.*, **128**, 1233 (1899); *Ann. chim. et phys.*, [7] **22**, 249 (1901).

(7) S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, *Zhur. Neorg. Khim.*, **4**, 2185 (1959).

(8) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, "The Chemistry and Metallurgy of Miscellaneous Materials," L. L. Quill, Ed., McGraw-Hill Book Co., New York, N. Y., 1950, pp. 294–297.

(9) C. Brosset, *Nature*, **135**, 874 (1935).

(10) L. Pauling, *Chem. Eng. News*, **25**, 2970 (1947).

(11) R. E. McCarley, P. J. H. Carnell, B. A. Torp and J. C. Boatman, to be published.

(12) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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RECEIVED JUNE 2, 1962

CHEMISTRY OF THE NEOMYCINS. XI.[1] N.M.R. ASSIGNMENT OF THE GLYCOSIDIC LINKAGES

Sir:

In the accompanying communication[1] the gross structures of neomycins B and C were completed. In the present report the stereochemistry of the ribose-neamine linkage is established by n.m.r. spectroscopy, thus completing the stereochemistry of neomycin C (except for the absolute stereochemistry of the substituted deoxystreptamine)[2]

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(1) Paper X in this series: K. L. Rinehart, Jr., M. Hichens, A. D. Argoudelis, W. S. Chilton, H. E. Carter, M. Georgiadis, C. P. Schaffner and R. T. Schillings, *J. Am. Chem. Soc.*, **84**, 3218 (1962).