[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Action of Bromine on Some Complex Chlorides of Molybdenum and Tungsten: Preparation of $WBrCl_3$

BY RALPH C. YOUNG AND ROBERT A. LAUDISE

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Tungsten monobromotrichloride has been prepared by the action of bromine on both $K_3W_2Cl_9$ and $K_5W_3Cl_{14}$ at 450°. Molybdenum trichloride has been obtained by the bromination of K_3MoCl_6 at 450°. At 45° a mixture of KBr and K_2MoCl_6 was produced.

A mixed halide, $WBrCl_3$, has been obtained by the bromination of the complex salts $K_3W_2Cl_9$ and $K_5W_3Cl_{14}$.

$$K_3W_2Cl_9 + Br_2 = 3KCl + 2WBrCl_3$$

$$2K_5W_3Cl_{15} + 3Br_2 = 10KCl + 6WBrCl_3$$

Under the conditions of the experiments the KCl was gradually changed to KBr.

Method.—A stream of nitrogen, freed from oxygen and water, was passed through a "bubbler" containing bromine and into a Pyrex tube which held about **1** g. of $K_3W_2Cl_9$ or $K_5W_3Cl_{14}$.[1] The tube was heated with an electric hinge furnace at 450 ± 10°. The exit end of the tube, which extended 2 ft. beyond the furnace, was fitted with U tubes containing Drierite.

A dark crystalline substance, which proved to be $WBrCl_3$, collected at the end of the furnace. This was contaminated by a very small amount of a red material which was separated from the dark crystals by fractional sublimation. For this purpose a movable electric sleeve heater was used, the temperature of which was controlled to ±0.5° by a W. S. Macdonald temperature controller Type 18B.

After sufficient product had collected and the bromine had been expelled from the system by the nitrogen, the hinge furnace was cooled to room temperature and the sleeve heater put over the product and brought up to about 135°, at which the bromochloride sublimed. Since the red substance volatilized at about 110° in the current of nitrogen, after 3 or 4 sublimations separation was complete.

Analysis.—Appropriate measures were taken to prevent hydrolysis and oxidation in obtaining and weighing a sample. The tungsten was precipitated as the cinchonate after oxidation to the +6 state. The bromide and chloride were determined as silver salts and the total equivalents of halide by the Volhard method. The agreement of the analyses made both on the residues and on the sublimed portions indicated the substance to be a true compound.

Anal. Calcd. for $WBrCl_3$: W, 49.7; Br, 21.6; Cl, 28.7. Found: W, 49.5; Br, 20.9; Cl, 29.3.

Properties.—Tungsten monobromotrichloride, which deposited in dark needle-like crystals, is very reactive toward moist air, undergoing hydrolysis and oxidation. The water solution is dark green. It is insoluble in such organic solvents as benzene and carbon tetrachloride, but shows some solubility in certain ethers. An attempt was made to determine the molecular weight of the halide in dioxane by the freezing point depression. Although the dioxane was carefully dried, enough moisture was present to react with the bromochloride, and a low result was obtained. More of the compound was added and a second freezing point depression obtained based on the difference in the freezing point of the two solutions. This process was continued until no more of the substance would dissolve, the solubility being only about 1 g. per liter. The final molecular weight obtained was 320.

Bromination of K_3MoCl_6.[2]—A red-brown heterogeneous material collected at the end of the furnace when tripotassium hexachloromolybdate (III) was brominated at temperatures varying from 200 to 450° as described above. The mixture could not be separated by fractional sublimation. A fairly homogeneous product could be obtained by use of the Saint Claire Deville principle, runs being made at 450°. The cold finger[3] was tried at various distances from the molybdate and the substance was analyzed without further purification. The molybdenum was removed and determined as lead molybdate and the chloride and bromide as described before. The atomic ratios, varying between $Mo_{1.00}Cl_{3.07}Br_{0.00}$ and $Mo_{1.00}Cl_{2.95}Br_{0.18}$, showed that the red-brown substance was, in the main, $MoCl_3$.

The reaction was not a simple decomposition into KCl and $MoCl_3$, because the chloromolybdate was found not to decompose in a current of nitrogen at 450°, even when heated for 96 hours; Senderoff and Brenner[4] state that it is stable *in vacuo* at 650°. Bromine vapor and liquid bromine attack K_3MoCl_6 at room temperature, and the color changes from red to dark green. To effect complete change, of about 1 g., however, it was necessary to keep the substance in contact with liquid bromine at 45° in a loosely capped tube for one week. After the excess bromine had been evaporated and the residue heated *in vacuo* at 40° for 24 hours, the gain in weight accounted for the addition of 0.96 ± 0.02 atoms of bromine per one mole of K_3MoCl_6. X-Ray powder photographs obtained with a North American Philips Powder Camera showed no lines of K_3MoCl_6 nor of KCl, but strong lines of KBr and lines that could be assigned to a new compound, K_2MoCl_6. (The authors wish to thank Professor David P. Shoemaker and Mr. Norman E. Weston for their aid in the X-ray work.) The reaction postulated is

$$K_3MoCl_6 + {}^1/_2Br_2 = KBr + K_2MoCl_6$$

Extraction with dry ethyl acetate gave a residue of KBr and a yellow-green solution. Treatment with 1 *N* HCl (to prevent hydrolysis) produced a green aqueous solution. To show that the molybdenum was in an oxidation state of 4, some of the solid was added to a saturated solution of KCN at 5° and the familiar yellow solution and yellow crystals of $K_4Mo(CN)_8$ were formed.[5]

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(1) R. A. Laudise and R. C. Young, THIS JOURNAL, **77**, 5288 (1955).

(2) K. H. Lohmann and R. C. Young, *Inorg. Syntheses*, **IV**, 97 (1953).

(3) C. H. Brubaker, Jr., and R. C. Young, THIS JOURNAL, **73**, 4179 (1951).

(4) Senderoff and Brenner, *J. Electrochem. Soc.*, **101**, 28 (1954).

(5) R. C. Young, THIS JOURNAL, **54**, 1402 (1932).

It was found that the KBr–K_2MoCl_6 mixture decomposed at 450° in a current of nitrogen, and $MoCl_3$ was deposited at the end of the reaction tube. Since excess bromine at 450° can change KCl to KBr, the equation for the over-all reaction of K_3MoCl_6 and Br_2 at 450° can be expressed as

$$K_3MoCl_6 + 1.5Br_2 = 3KBr + MoCl_3 + 1.5Cl_2$$

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Chromium–Diphenylcarbazide Reaction[1]

BY RONALD T. PFLAUM AND LESTER C. HOWICK[2]

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A study of the nature of the chromium–diphenylcarbazide reaction was carried out. Absorptimetric data for the reactions of chromium(VI), chromium(III) and chromium(II) ions with diphenylcarbazide and diphenylcarbazone were compared. The stoichiometry of the various systems was determined together with the effects of *p*H and the extractability of the colored reaction product into non-aqueous media. The behavior of the colored complex under the influence of an electric field was observed. The nature of the highly absorbing complex formed in the reaction of chromium and the organic reagents was postulated.

Introduction

The color reaction between diphenylcarbazide and chromium(VI) has long been used for the colorimetric determination of chromium.[3] Today it is one of the most widely used reactions for this particular analysis.[4] The colored system enjoys this popularity due to the sensitivity, selectivity, and simplicity inherent in the reaction. In addition, the organic reagent is readily available in a state of purity sufficient for analytical work.

In spite of the above situation, little is known of the actual nature of the red-violet species formed in the reaction. A survey of the literature reveals many inconsistent and contradictory statements, as well as many unexplained observations. The present investigation was undertaken in order to resolve certain of these factors and to gain a better insight into the nature of the color reaction.

Various formulations for the colored species formed in the reaction have been advanced in the 50-odd years since Cazeneuve first reported his observations.[5,6] He proposed that an organo-metallic compound was formed in the reaction of diphenylcarbazide and chromium. Babko and Paulii[7] and Feigl[8] have concluded, however, that the colored material is merely an oxidation product of the reagent. Moreover, the oxidation must be very selective since none of the other common oxidizing agents, *i.e.*, ceric salts, permanganate, persulfate, etc., give similar results. The most recent work was carried out by Bose[9] who postulated that it is highly unlikely that chromium(VI) should possess a unique oxidizing ability but that, however, some type of oxidation–reduction with subsequent coordination must be involved in the reaction. He performed absorption, migration, extraction and magnetic susceptibility studies and concluded that the colored species was a neutral monodiphenylcarbazone–chromium(II) complex. This conclusion was based in part upon the observation that chromium(III) ion did not react with the reagent.

The present investigation became imperative when it was learned that the diphenylcarbazone used in the above study was in reality a 1:1 mixture of diphenylcarbazide and diphenylcarbazone[10,11] and when it was observed that chromium(III) did react with the reagents. The work described herein is intended to clarify some of the unresolved factors in the chromium–diphenylcarbazide reaction.

Experimental Part

Materials Used.—Diphenylcarbazide was prepared by the condensation of urea and phenylhydrazine at 155°.[12] The pure white compound with a melting point of 170° (on repeated recrystallization from ethanol) was used as the pure reagent. Diphenylcarbazone was prepared by the oxidation of crude diphenylcarbazide with 3% hydrogen peroxide in alcoholic potassium hydroxide.[10] On neutralization and recrystallization, the red-orange mixture of the two reagents was obtained. Treatment of this product with sodium carbonate in hot ethanol, extraction of the diphenylcarbazide with ether and acidification of the aqueous solution with hydrochloric acid yielded a red powder melting at 127°. This material is pure diphenylcarbazone.[11]

Dimethylformamide was obtained from the Rohm and Haas Company. Purification was effected by treatment with barium oxide for a period of 24 hr. with subsequent rectification in an all glass system. The fraction boiling at 151 ± 1° was used as the purified solvent. All other technical grade solvents were distilled before use.

Solutions of chromium(II) ion were prepared according to the method of Hatfield[13] and stored under nitrogen. Standardization was carried out titrimetrically with standard ceric and ferrous sulfates. All other chemicals used were of reagent grade quality.

Spectrophotometric Measurements.—A Cary Model 11 recording spectrophotometer and a Beckman Model B spectrophotometer were used to obtain absorptimetric data. All measurements were made in matched 1.00 ± 0.01 cm. cells at room temperature of approximately 25°.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio.

[2] An Abstract of a thesis submitted by Lester C. Howick to the Graduate College of the State University of Iowa, 1955, in partial fulfillment of the requirements for the Degree of Master of Science.

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