A

B

The nitrite-producing reaction requires the reduction of two Cr(VI) units to Cr(III). Therefore, the absence of excess ammonia should favor the conversion of ammonia to nitrite over its conversion to nitrogen. Since the reaction of chromium-(VI) oxide with liquid ammonia is a heterogeneous reaction, chromium atoms located in the body of the solid would be most likely to react to produce nitrite, whereas surface chromium atoms which are in contact with excess ammonia would probably react to form nitrogen.

Any proposed mechanism must also explain why only 25 to 28% of the chromium is reduced and must account for the observation that the amount of nitrogen produced in this reaction is only half that expected on the basis of the chromium reduced. Reduction of chromium(VI) oxide to nitrogen and ammine chromium chromate can be represented by the overly simplified equation

$$5CrO_3 + 8NH_3 \longrightarrow$$
$$[Cr(NH_3)_3]_2(CrO_4)_3 + 3H_2O + N_2 \quad (2)$$
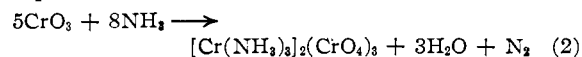
Water produced from this reaction would be formed in the vicinity of chromium(VI) oxide and would be expected to react immediately to form ammonium chromate.

$$3H_2O + 6NH_3 + 3CrO_3 \longrightarrow 3(NH_4)_2CrO_4 \quad (3)$$
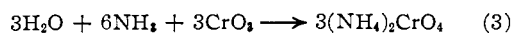
The over-all equation representing the sum of these processes would be

$$8CrO_3 + 14NH_3 \longrightarrow$$
$$[Cr(NH_3)_3]_2(CrO_4)_3 + 3(NH_4)_2CrO_4 + N_2 \quad (4)$$
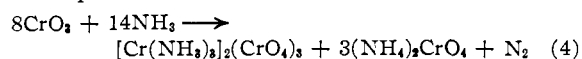
The resulting product would contain 25% of the chromium in the +3 state but the amount of nitrogen produced would be twice that reported by Sisler and Jirik.[2]

The reaction which occurs when nitrite is produced can be represented by

$$12CrO_3 + 20NH_3 \longrightarrow 2Cr(NH_3)_3NO_2CrO_4 +$$
$$[Cr(NH_3)_3]_2(CrO_4)_3 + 3(NH_4)_2CrO_4 \quad (5)$$
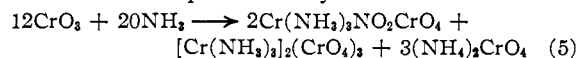
In order to explain the "missing" nitrogen quantitatively, approximately two-thirds of the reduction should follow equation 4 and one-third of the reduction should follow equation 5. Reaction 5 corresponds to reduction of 33% of the Cr(VI) to Cr(III). The combination of reactions 4 and 5 proposed above (2 to 1) would result in the reduction of 28.6% of the Cr(VI), which is only slightly greater than the experimental results previously reported.[2] Traces of water in the CrO_3 sample used (the water yields ammonium chromate which is not susceptible to reduction by liquid ammonia) as well as small variations from the 2 to 1 ratio of the two proposed reactions can easily account for the small differences.

Acknowledgment.—The authors would like to acknowledge the assistance given by Dr. M. Chamberlain in interpreting the results of the infrared study, and would like to thank Dr. John C. Bailar, Jr., and Dr. Daryle Busch for helpful discussions of this problem.

COLUMBUS, OHIO
URBANA, ILLINOIS

Reduction of Chromium(VI) Compounds by Liquid Ammonia and by Liquid Ammonia Solutions of Potassium Amide[1,2]

BY STANLEY I. TANNENBAUM, RUSSELL S. DRAGO AND HARRY H. SISLER[3]

The chemical behavior of the product of the reaction between chromium(VI) oxide and liquid ammonia is reported. This information further substantiates the presence of species proposed on the basis of an infrared and powder X-ray diffraction investigation of the product.[2] Investigations on the reactions of chromium(VI) compounds with liquid ammonia have been extended to solutions of potassium amide in liquid ammonia and reactions are proposed to explain some of the observations.

In a preceding paper[1] in this series it was reported that chromium(VI) oxide, potassium chlorochromate and ammonium dichromate react with liquid ammonia at $-33°$ in such a manner that a maximum of approximately $1/4$, $1/4$ and $1/8$, respectively, of the chromium which they contain is

(1) Preceding paper in this series H. H. Sisler and F. Jirik, THIS JOURNAL, 66, 1344 (1944).

(2) R. S. Drago and H. H. Sisler, ibid., 79, 1811 (1957).

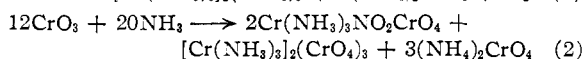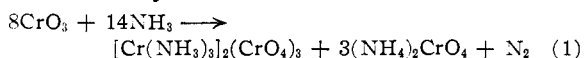(3) Department of Chemistry, University of Florida, Gainesville, Florida.

reduced to Cr(III). The fraction of chromium reduced is increased by the presence of ammonium nitrate in liquid ammonia and is decreased by the presence of water. Gaseous nitrogen corresponding to only about one-half the equivalent of the reduced chromium is produced by the reaction.

An X-ray powder diffraction and infrared study[2] of the reaction has established the presence of ammonium chromate and indicated the formation of a polymeric ammine chromium(III) chromate of indefinite composition, a polymeric material containing nitrite coördinated to some of the trivalent chromium atoms and possibly some hexammine chromium(III) chromate. Two general formulas were proposed to describe the polymers

$$[Cr(NH_3)_3]_{2n}(CrO_4)_{3n} \text{ and } (Cr(NH_3)_3NO_2CrO_4)_n$$
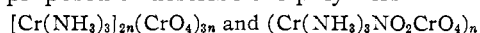
where $n = 1, 2, 3, 4$.

Idealized equations (1) and (2) represent the stoichiometry of the individual reactions

$$8CrO_3 + 14NH_3 \longrightarrow$$
$$[Cr(NH_3)_3]_2(CrO_4)_3 + 3(NH_4)_2CrO_4 + N_2 \quad (1)$$
$$12CrO_3 + 20NH_3 \longrightarrow 2Cr(NH_3)_3NO_2CrO_4 +$$
$$[Cr(NH_3)_3]_2(CrO_4)_3 + 3(NH_4)_2CrO_4 \quad (2)$$

It is believed that solid chromium(VI) oxide is the reactant and the two processes occur simultaneously producing mixed polymers which are composed of the two simpler units, viz., ammine chromium(III) chromate and nitro ammine chromium(III) chromate. In order to account for the per cent. chromium reduced and reported[1] values for the amount of nitrogen produced in this reaction, it was proposed that two-thirds of the reduction occurs in accordance with equation 1 and the remainder proceeds in accordance with equation 2. The ratio of trivalent chromium to coördinated nitrite resulting from the above scheme is four to one.

This effect of ammonium salts on the oxidation-reduction processes involving chromium(VI) compounds with liquid ammonia was postulated[1] to be analogous to the effect of hydronium ions on similar processes in aqueous systems. We were interested, therefore, in determining whether amide ions in liquid ammonia would have an opposite effect. The results of these investigations, along with other chemical observations concerning the reaction product of chromium(VI) oxide with liquid ammonia, also are reported in this article.

Experimental Methods

Materials.—Synthetic, anhydrous ammonia with a stated purity of 99.95% was distilled from the tank and used in this study.

Chromium(VI) oxide (C.P. grade) was dried under vacuum at a temperature of 150° for 24 hours before use. Its purity was checked by analysis for Cr(VI): found Cr(VI), 51.88; 51.75; calcd. for CrO_3, 52.00.

Potassium chlorochromate was prepared by the reaction of chromyl chloride with potassium chromate.[4] The product was dried by standing over calcium chloride for several weeks and was analyzed for chlorine and for Cr(VI). Calcd. for $KCrO_3Cl$: Cr(VI), 29.79; Cl, 20.31. Found: Cr(VI), 29.98, 29.85; Cl, 20.48, 20.66.

Reagent grade potassium dichromate was dried in an oven at 110° for 24 hours and was analyzed for Cr(VI). Calcd. for $K_2Cr_2O_7$: Cr(VI), 35.36. Found: Cr(VI), 35.36, 35.34.

(4) H. H. Sisler, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 208.

Reagent grade potassium chromate was dried at 110° for five hours and analyzed for Cr(VI). Calcd. for K_2CrO_4: Cr(VI), 26.78. Found: Cr(VI), 26.88.

Platinum black was prepared according to the directions of McDermott.[5]

Apparatus and Procedure.—The procedure for the reaction with liquid ammonia was the same as that previously described by Sisler and Jirik.[1] Where filtration was required, the inverse process using a small fritted glass disk was employed. Reactions with potassium amide solutions were carried out by adding to the liquid ammonia a weighed quantity of potassium followed by a small amount of platinum black to catalyze its conversion to potassium amide. These operations were accomplished under a positive pressure of nitrogen gas to avoid introduction of air or moisture to the system.

Analytical Methods.—Cr(VI) was determined by dissolving the reaction product in dilute (15%) sulfuric acid, then treating one aliquot with an excess of an acidified standard ferrous sulfate solution. Sodium diphenylamine sulfonate was the indicator and some sirupy phosphoric acid was added to improve the end point by complexing the ferric ion formed.

Total chromium was determined by boiling another aliquot of the same solution with ammonium persulfate in the presence of two drops of silver nitrate solution as catalyst. This treatment oxidized the Cr(III) to Cr(VI). The analysis for Cr(VI) was made as before and Cr(III) was determined as the difference between final and original chromium titrations.

Chloride was determined by the Mohr method.

Nitrogen present as NH_4^+, NH_3, NH_2^- or NH^- was determined by the Kjeldahl method.

Results

CrO₃ in Liquid Ammonia.—A vigorous reaction occurs when chromium(VI) oxide is dropped into liquid ammonia. A heterogeneous brown and yellow precipitate forms, in which approximately $1/4$ of the chromium is present as Cr(III). The yellow precipitate which forms is finely divided but the dark brown particles are very large. In spite of the apparent heterogeneity of the initial product of reaction, reduction is complete in less than five minutes. This was shown by dropping a sample of chromium(VI) oxide into liquid ammonia, stirring the mixture for four minutes, filtering the excess ammonia and then quenching the reaction product with a large amount of acidified water. When analysis was made, it was found that 25.3% of the chromium was present as Cr(III).

When the product of the reaction between chromium(VI) oxide and liquid ammonia was dissolved in dilute acid and analyzed by methods described in the Experimental section, constant values for Cr(VI) were obtained only when the amount of phosphoric acid used in the titration was kept constant. As the amount of concentrated phosphoric acid used in the analysis of a series of 25-ml. aliquots of the product was increased from three to ten milliliters the amount of Cr(VI) found also increased. Values obtained for Cr(VI) in concentrated phosphoric acid solution agree with those reported in the earlier publication. If concentrated sulfuric acid is added to an aliquot of the solution being analyzed, lower values are obtained for Cr(VI) even in the presence of large amounts of phosphoric acid. The behavior in sulfuric acid solution can be explained by assuming that nitrite, which is coördinated to Cr(III), is dissociated in the sulfuric acid and then reduces some of the Cr(VI) to Cr(III).

(5) McDermott, THIS JOURNAL, 32, 336 (1910).

In view of the effect of acid on solutions of the product, it was decided that analysis for Cr(VI) should be carried out by another method. Polarographic analysis in basic solution was tried. The values obtained for Cr(VI) by polarographic analysis in 0.1 M sodium hydroxide solution were in agreement with the higher values for Cr(VI) obtained by analysis in concentrated phosphoric acid solution.

The apparent stability of the product in phosphoric acid solution was investigated further by detecting the end-point in the Cr(VI) analysis of the product by potentiometric means. Similar results were obtained when potentiometric analyses were carried out on solutions which were concentrated in both phosphoric and sulfuric acids and also on solutions which contained only phosphoric acid. The values found are in agreement with the low results obtained for Cr(VI) when the analysis was carried out on solutions which contain concentrated sulfuric and phosphoric acids, and an indicator was used to detect the end-point. Since the potentiometric titrations were carried out very slowly in well stirred solutions, the behavior of phosphoric acid in the analyses in which an indicator was employed can be explained by assuming the phosphoric acid either slows down the rate at which nitrite is dissociated from the coördination sphere of Cr(III) or slows down the rate of the oxidation–reduction reaction between nitrite and chromate.

If the explanation for the behavior of the product in sulfuric acid solution is correct, then a quantitative estimate of the amount of nitrite present can be obtained by considering the difference between Cr(VI) determinations in concentrated phosphoric acid solutions and in solutions to which concentrated sulfuric acid has been added. This difference represents Cr(VI) which has been reduced by nitrite, and considering the stoichiometry of the reaction of nitrite with chromate, the number of moles of nitrite can be determined. Since Cr(III) can be calculated from the difference in the results of the analyses for total chromium and the value obtained for Cr(VI) in concentrated phosphoric acid solution, the ratio of Cr(III) to nitrite can be calculated. Table I contains the results of these analyses on the product.

TABLE I

Analysis performed	Mmoles of Cr	Cr, %
Total chromium	0.385	36.12
Cr(VI), H_3PO_4, indicator	.293	27.58
Cr(VI), 0.1 M NaOH, polarograph	.290	27.18
Cr(VI), H_3PO_4 and H_2SO_4, indicator	.279	26.17

The value for total chromium agrees within ±0.3% with analyses from several other products. The value for Cr(VI) is an average value of many determinations which agree with the one reported here within ±1.0%. Within the limit of error of the Cr(VI) determination, the ratio of Cr(III) to nitrite agrees with the value of four to one previously proposed. The evidence obtained from the above analyses, the analyses of the gaseous products of the reaction and the infrared studies previously reported indicate that coördinated nitrite is produced in small quantities in the reaction of chromium(VI) oxide with liquid ammonia.

The theoretical composition of the mixed product formed by the proposed reaction scheme was calculated by assuming that each chromate has one molecule of ammonia attached to it. *Anal.* Calcd.: N, 23.2; Cr(VI), 28.6; Cr(total), 37.2. Found: N, 22; Cr(VI), 27.6; Cr(total, 36.1).

The analytical results which were found are all slightly low but agree reasonably well with the calculated values for the combined products.

Ammonium chromate produced in this reaction can be removed from the polymeric material by washing with water. Attempts were made to do analyses on the water-insoluble material but it was found that the values obtained depended upon the extent of water washing. Increased amounts of washing resulted in smaller values for Cr(VI) in the insoluble residue. It is believed that the product probably reacts with excess water by breaking up the polymers and replacing the terminal chromate groups with hydroxide. No Cr(III) is found in the wash solution. The amount of ammonia present in the polymer also decreases with increased washing.

Attempts were made to obtain a pure polymeric material for analyses by separating the polymer, consisting mainly of large particles, from the rest of the product by washing with liquid ammonia and filtering through a tube designed to remove the smaller particles. Results of analyses of several products prepared in this manner also appeared to be a function of the extent of liquid ammonia washing.

$KCrO_3Cl$ in Liquid Ammonia.—The reaction of potassium chlorochromate with liquid ammonia is similar to the reaction of chromium(VI) oxide with liquid ammonia but somewhat milder. The dried product is colored the same as the chromium(VI) oxide–liquid ammonia product and contains approximately 29% of the chromium in the +3 state. When the product is washed with liquid ammonia and filtered, the color of the final precipitate is orange and almost all of the chloride ion appears in the filtrate. As in the case of chromic oxide the amount of nitrogen obtained in this reaction is approximately only 50% of that expected on the basis of the chromium reduced. Analysis of the orange-brown product gave: Cr(III), 9.76; Cr(VI), 22.55; N, 13.1. It is believed that the reactions involved are of a type similar to those which chromium(VI) oxide undergoes.

$K_2Cr_2O_7$ and K_2CrO_4 in Liquid Ammonia.— When potassium dichromate is added to liquid ammonia, no immediate visible reaction occurs. However, on standing, the supernatant liquid takes on a yellow color and the solid changes from orange to yellow. The rate of the reaction is very slow and only 12.5% of the chromium is reduced to Cr(III).

No visible reaction whatever occurs when potassium chromate is added to liquid ammonia. Analyses of the material after prolonged exposure to liquid ammonia show that no reduction of Cr(VI) has occurred.

CrO₃ in KNH₂ Solution in Liquid Ammonia.—
When chromium(VI) oxide is dropped into solutions of potassium amide in liquid ammonia, the amount of Cr(III) which is formed varies with the mole ratio of KNH₂ to Cr(VI) as shown in Fig. 1.
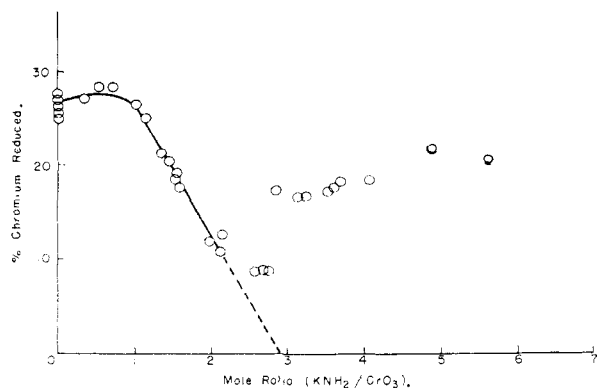

Fig. 1.—Reaction of CrO₃ with solutions of KNH₂ in liquid NH₃.

The amount of platinum black used was shown, by several blank runs, to have no influence on the amount of reduction of CrO₃. It is interesting to note that decreasing the mole ratio KNH₂/Cr(VI) causes a regular decrease in the amount of reduction at mole ratios between 1 and 2.5 but at mole ratios greater than this value an increase in per cent. reduction begins to take place. There appears to be no simple, detectable relationship between molar amide concentration in the liquid ammonia solution and the amount of reduction.

The color of the product obtained by the reaction likewise depends on the mole ratio of potassium amide to chromium(VI) oxide as indicated below.

TABLE II

Mole ratio (KNH₂/Cr(VI))

	0	1	2	3	4	5	6
Color of product	yellow	orange	red	light brown		5	dark brown

KCrO₃Cl in KNH₂ Solution in Liquid Ammonia.—The same type of dependence on mole ratio was noted in the reaction of potassium chlorochromate with a solution of potassium amide in liquid ammonia as was found for the analogous chromium(VI) oxide reaction. The results are shown in Fig. 2.

K₂Cr₂O₇ and K₂CrO₄ in KNH₂ Solutions in Liquid Ammonia.—The presence of potassium amide in the liquid ammonia showed essentially no effect on the degree of reduction of Cr(VI) to Cr(III) in potassium dichromate. Throughout the range of mole ratios used (up to 17.1) the per cent. of chromium reduced remained at 12.5 ± 1.0, which is essentially the same as for the reaction in pure ammonia.

Although liquid ammonia alone has no effect on potassium chromate, some reduction is effected in the presence of large amounts of potassium amide. At a KNH₂/Cr(VI) mole ratio of 6.7, 9.3% of the chromium is reduced.
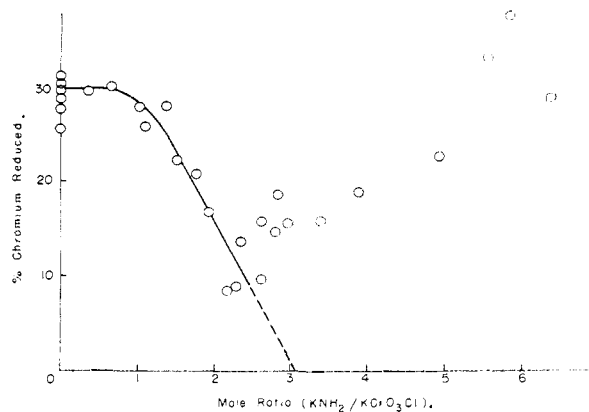

Fig. 2.—Reaction of KCrO₃Cl with solutions of KNH₂ in liquid NH₃.

Discussion

The heterogeneity of the reacting systems and the complex nature of the reaction products here studied make the application of the usual sort of methods for kinetic studies and determination of mechanism exceedingly difficult if not impossible. The following mechanisms, must, therefore, be regarded as speculative. They do, however, account for many of the observed phenomena in terms of reasonable assumptions.

Chromium(VI) oxide undergoes reaction with liquid ammonia to produce ammonium chromate plus polymeric chromium(III) chromate species which have nitrite coördinated to some of the trivalent chromium atoms. The separate reactions occurring can be described by equations 1 and 2, while the over-all stoichiometry can be represented by the equation

$$28CrO_3 + 48NH_3 \longrightarrow 3[Cr(NH_3)_3]_2(CrO_4)_3 +$$
$$2Cr(NH_3)_3NO_2CrO_4 + 9(NH_4)_2CrO_4 + 2N_2 \quad (3)$$
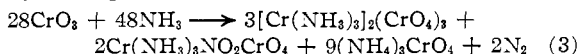
This stoichiometry quantitatively accounts for the observed nitrogen evolution, the per cent. chromium reduced and the behavior of the product toward sulfuric acid solutions. The proposed products are also compatible with the results obtained in the infrared and X-ray powder diffraction studies.[2]

When potassium amide is added to liquid ammonia solutions which are subsequently reacted with chromium(VI) oxide the reactions occurring become much more complex. Since there is no apparent correlation between amide ion concentrations and per cent. of chromium reduced it is clear that the effect of potassium amide on the reaction is not simply dependent on raising the basicity of the solution. Rather the effect depends upon mole ratio. From Figs. 1 and 2 it is seen that in the region of mole ratio of KNH₂/Cr(VI) = 0.0 to 1.0 no significant change occurs in the amount of chromium reduced over that in pure liquid ammonia. However, the per cent. of chromium reduced varies inversely with the mole ratio in the region from 1.0 to 2.3. Zero reduction is never actually attained, for at a mole ratio of about 2.5 the reduction begins to increase sharply.

In solutions containing a mole ratio of KNH₂ to Cr(VI) of less than 1.0, most of the potassium amide is probably used to neutralize the ammo-

nium ion produced by the reduction of chromium-(VI) oxide and thus has no effect on the amount of chromium reduced. When the mole ratio of potassium amide to Cr(VI) is increased to values larger than 1.0, the amide evidently reacts in another manner.

O. Schmitz and co-workers[6] have shown that hexammine chromium(III) nitrate reacts with potassium amide to produce polymeric chromamide. The pink colored chromamide which is produced is amphoteric and reacts with more potassium amide as described by equation 4

$$[Cr(NH_2)_3]_n + n\ KNH_2 \longrightarrow K_n[Cr(NH_2)_4]_n \longrightarrow$$
$$K_n[Cr(NH)(NH_2)_2]_n + nNH_3$$
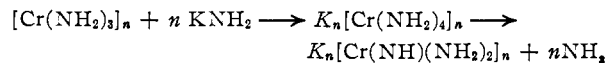
The authors report that color of the product changes during the above reaction from pink to brownish red to a violet black. Reactions of this type could account for the color changes observed when the reaction of chromium(VI) compounds with ammonia is carried out at the higher mole ratios of potassium amide to chromium(VI). If the product of the chromium(VI) oxide–liquid ammonia reaction reacted in this manner toward amide, one would expect that nitrite would be reduced by potassium amide. Indication of this is obtained, for quantitative measurements of the amount of gas produced in this reaction show that as the mole ratio of $KNH_2/Cr(VI)$ is increased the amount of nitrogen produced in the reaction is correspondingly increased. Water which would be

(6) O. Schmitz, et al., Z. anorg. allgem. Chem., 248, 175 (1941); Chem. Zentr., 113, I, 594 (1942); Z. anorg. allgem. Chem., 280, 180 (1955).

produced in the reduction of nitrite by the potassium amide would react with ammonia and result in a slight decrease in the per cent. chromium reduced. The results of the nitrogen analyses could equally well be accounted for by assuming that amide inhibits the nitrite forming reaction 2 and favors reaction 1. However, neither of these possibilities accounts for the small amounts of Cr(III) that are found in the product and this result cannot be explained at present. An X-ray powder diffraction and infrared study of the product formed in amide solution is anticipated.

When the mole ratio of KNH_2/CrO_3 is larger than 2.5 to 1, it appears that another oxidation–reduction reaction, apparently between potassium amide and hexavalent chromium becomes important. This reaction leads to an increase in the amount of reduction of chromium. In view of the known ability of amides to act as reducing agents, this behavior is not too surprising. The reaction which occurs is probably similar to the one between potassium chromate and solutions of potassium amide in liquid ammonia.

Before definite conclusions can be drawn regarding the reactions of potassium chlorochromate with ammonia and with potassium amide solutions of ammonia the products of these reactions should be investigated by infrared and X-ray powder diffraction analysis. However, the observations concerning these reactions qualitatively indicate that the processes occurring are similar to those that occur with chromium(VI) oxide.

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X-Ray and Infrared Studies of the Addition Compounds of Titanium Tetrabromide with 1,4-Dioxane, Tetrahydrofuran and Tetrahydropyran

By Robert F. Rolsten and Harry H. Sisler[1]

Received September 7, 1956

The addition compounds of titanium tetrabromide with 1,4-dioxane, tetrahydrofuran and tetrahydropyran were examined by X-ray diffraction and infrared spectroscopy. The infrared spectra show that the ether oxygens are involved in the bonding; in the case of the dioxane compound both ether oxygens probably are involved. Cryoscopic studies of solutions of $TiBr_4 \cdot O(CH_2CH_2)_2O$ in 1,4-dioxane indicate that the solute of this solution is monomeric. Structural implications of these data are briefly discussed.

Introduction

In a previous publication from this Laboratory,[2] the formation of addition compounds $TiBr_4 \cdot 1,4$-dioxane, $TiBr_4 \cdot 2C_4H_8O$ and $TiBr_4 \cdot 2C_5H_{10}O$ by the direct combination of the tetrabromide with the corresponding ether was announced. The present communication deals with the results of infrared, X-ray and cryoscopic studies of these three compounds.

Experimental

Purification of Materials.—The 1,4-dioxane, purified by the method of Fieser,[3] was distilled over sodium under an

(1) Department of Chemistry, University of Florida, Gainesville, Florida.

(2) R. F. Rolsten and H. H. Sisler, This Journal, 79, 1068 (1957).

(3) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath & Company, Boston, Mass., 1941, Part II, p. 368.

atmosphere of dry argon using a five-foot fractionation column. The constant boiling middle fraction, 100.3–100.7° at 744 mm., was taken and used immediately after distillation. The three addition compounds, $TiBr_4 \cdot 1,4$-dioxane, $TiBr_4 \cdot 2$ tetrahydrofuran and $TiBr_4 \cdot 2$ tetrahydropyran were prepared as previously reported.[2]

Molecular Weight Determination.—Cryoscopic measurements on $TiBr_4 \cdot 1,4$-dioxane in 1,4-dioxane were carried out. A freezing point cell, isolated from the atmosphere and provided with continuous stirring, was used. Temperatures for the freezing point curves were measured with a platinum resistance thermometer in conjunction with a G-2 Mueller Bridge. In every experiment the freezing point cell was first charged with carefully purified 1,4-dioxane, the freezing point determined, a sample of the addition compound added, the mixture stirred until complete solution had been obtained and the freezing point of the solution determined. Dry argon was maintained in the cell at all times. Results of four determinations in the concentration range of 0.0005 to 0.0394 m gave values of 453, 472, 421 and 496 for the molecular weight. The average of these results is 460.5 ±