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 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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[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).

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORIES OF THE OHIO STATE UNIVERSITY]

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]

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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 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 ±

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[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.

27.4, in good agreement with the theoretical value of 455.56 for monomeric $TiBr_4 \cdot O(CH_2CH_2)O$. It should be noted that the red color of the solutions of the addition compound in 1,4-dioxane remained unchanged, and that no noticeable increase in pressure in the cell occurred during the course of the experiment. At the termination of one experiment, solvent 1,4-dioxane was removed by evaporation at reduced pressure, leaving a red fluffy powder which appeared to be the original solute. The fact that the X-ray diffraction pattern of this powder was identical with that of the original addition compound, $TiBr_4 \cdot$1,4-dioxane, substantiated this conclusion.

X-Ray Diffraction Analysis.—The Kα radiation (λ = 1.5418 Å.) of copper, using a nickel filter to remove β-radiation, was supplied by a Phillips Model 5100 X-ray diffraction unit. The extremely hygroscopic addition compounds were contained in 0.5 mm. i.d. Lindemann glass capillary tubes that were filled in a dry-box and then hermetically sealed. Different preparations of the addition compounds were checked in order to establish the reproducibility of the preparative method as well as to ensure the absence of hydrolysis before and/or during the six-hour irradiation by X-rays. Results of X-ray analyses are given in Table I. Intensities were determined visually. The data were corrected for film shrinkage with the aid of fiducial points (notched film) since no back reflections were obtained.

TABLE I

X-RAY RESULTS FOR THE ADDITION COMPOUNDS

$TiBr_4 \cdot$1,4-Dioxane		$TiBr_4 \cdot$2 Tetrahydropyran		$TiBr_4 \cdot$2 Tetrahydropyran	
d, Spacing, Å.	I/I_0	d, Spacing, Å.	I/I_0	d, Spacing, Å.	I/I_0
5.67	90	8.41	100	7.84	100
5.30	50	6.36	90	6.28	60
4.72	10	5.87	80	5.46	10
4.47	10	5.63	70	4.59	40
4.32	10	4.27	50	3.53	40
3.75	50	3.90	50	3.46	20
3.56	40	3.66	70	3.18	10
3.44	20	3.50	70	3.07	80
3.25	100	3.24	90	2.85	30
3.11	40	3.02	10	2.73	30
2.95	60	2.94	50	2.64	10
2.83	30	2.83	50	2.56	10
2.78	40	2.66	20	2.49	30
2.62	80	2.60	40	2.41	10
2.57	10	2.55	20	2.27	10
2.44	10	2.45	20	2.13	10
2.33	10	2.39	10	2.02	10
2.29	20	2.34	40	1.85	10
2.23	20	2.27	10	1.76	10
2.16	10	2.22	10	1.72	10
2.12	20	2.15	50	1.67	10
2.10	20	2.12	10	1.59	10
2.07	30	2.09	10	1.50	10
1.97	10	2.06	10	1.45	10
1.93	10	2.03	10	1.32	10
1.85	10	1.99	20	1.23	10
1.78	10	1.95	40		
1.75	10	1.82	50		
1.71	10	1.78	50		
1.58	10	1.69	10		
1.50	10	1.64	20		
1.44	10	1.58	10		
		1.55	20		
		1.52	10		
		1.49	10		
		1.45	10		
		1.41	10		
		1.39	10		
		1.35	10		

The observed d-spacings were corrected for sample absorption effects by the method of Taylor and Floyd[4] and indexed with the use of Hull–Davey Charts.[5] The results of this indexing indicate that the crystal form of the three addition compounds may be tetragonal with the tentative lattice parameters:

	a_0, Å.	a_0/c_0
$TiBr_4 \cdot$1,4-dioxane	18.45	2.46
$TiBr_4 \cdot$2 tetrahydropyran	12.26	1.76
$TiBr_4 \cdot$2 tetrahydrofuran	13.88	2.41

Infrared Measurements.—Emulsions of the solid addition compounds in "Nujol" were prepared in a dry-box and examined immediately after preparation with a Baird Infrared Spectrometer. The data listed in Tables II, III and IV were obtained from samples sandwiched between sodium chloride crystals. Relative intensities were not tabulated because of sample scattering.

TABLE II

INFRARED ABSORPTION BANDS FOR $TiBr_4 \cdot$1,4-DIOXANE

Microns	Cm.$^{-1}$	Microns	Cm.$^{-1}$
6.92	1445	9.57	1045
7.25	1379	11.27	887
7.55	1325	11.74	852
7.71	1297	12.00	833
7.96	1256	13.86	722
9.14	1094		

TABLE III

INFRARED ABSORPTION BANDS FOR $TiBr_4 \cdot$2 TETRAHYDROFURAN

Microns	Cm.$^{-1}$	Microns	Cm.$^{-1}$
6.82	1466	9.58	1044
7.24	1381	10.07	993
7.44	1344	10.57	946
8.04	1244	10.88	919
8.17	1224	12.30	813
8.55	1170	13.87	721
9.25	1081		

TABLE IV

INFRARED ABSORPTION BANDS FOR $TiBr_4 \cdot$2 TETRAHYDROPYRAN

Microns	Cm.$^{-1}$	Microns	Cm.$^{-1}$
6.81	1468	9.86	1014
7.21	1387	10.06	994
7.33	1364	10.57	946
7.62	1312	11.29	886
7.80	1282	11.53	867
8.37	1195	11.64	859
8.62	1160	12.54	797
9.07	1103	12.80	781
9.27	1079	13.80	725
9.76	1025		

Discussion and Conclusions

The fact that the C–O–C ring stretching frequency (1122 cm.$^{-1}$) present in the infrared spectrum of dioxane is completely absent from the spectrum of $TiBr_4 \cdot$1,4-dioxane indicates that both ether oxygens are involved in bonding to the $TiBr_4$. A similar conclusion can be reached with respect to $TiBr_4 \cdot 2C_4H_8O$ since the intense C–O–C ring stretching frequency of tetrahydrofuran (1076

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(4) A. Taylor and R. W. Floyd, *Acta Cryst.*, **3**, 385 (1950).

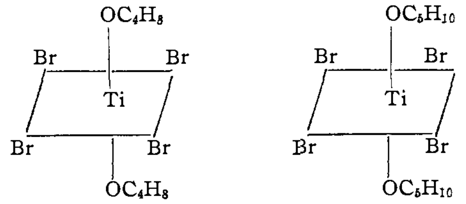
(5) J. C. Bell and A. E. Austin, "Battelle Indexing Charts for Diffraction Patterns of Tetragonal, Hexagonal and Orthorhombic Crystals."

cm.$^{-1}$) is almost completely absent in the spectrum of $TiBr_4 \cdot 2C_4H_8O$. Likewise the C–O–C ring stretching frequency in the tetrahydropyran spectrum is greatly reduced in the spectrum of $TiBr_4 \cdot 2C_5H_{10}O$. No evidence for a C–Br bond was found in the range of 2 to 16 μ.

Cryoscopic measurements on solutions of $TiBr_4 \cdot$ 1,4-dioxane indicate that the compound is monomeric in dioxane solution.

The results of the X-ray diffraction analyses indicate that the three solids are composed of tetragonal crystals. It must be pointed out that there is probably some error in the value for the lattice constants due to the absence of *d*-spacings with θ values between 50 and 85°. Also, the broad diffraction lines reduced the accuracy in the evaluation of the observed *d*-spacings. The very large surface area of the powder samples did not permit accurate pycnometric density measurements in "Ultrasene." Therefore, the precise X-ray evaluation of the addition compounds cannot be made without investigation of single crystals.

On the basis of the above information, one may tentatively propose the following structures for the tetrahydrofuran and tetrahydropyran complexes



The corresponding *cis* forms are also a possibility.

It might be proposed that the bonding could take place between the bromine atoms and ether oxygens instead of between the titanium atoms and oxygen atoms. However, the known lability of complexes formed by halogen to oxygen binding[6] serve to remove any reasonable consideration of such a possibility for these rather stable compounds.

If we assume that the dioxane complex is monomeric in the solid state as well as in dioxane solution the structure in which the two oxygens of dioxane are attached to adjacent positions on the titanium octahedron suggests itself.

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[6] Hassel and Hvoself, *Acta Chem. Scand.*, **8**, 873 (1954).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

Isopiestic Studies on Aqueous Gallium(III) Perchlorate Solutions[1]

BY C. S. PATTERSON[2] AND S. Y. TYREE, JR.

RECEIVED NOVEMBER 3, 1956

Vapor pressures of gallium perchlorate solutions with from zero to 2.5 hydroxide ions per gallium(III) ion added and over the concentration range from 0.1 to 1.2 *m* were determined by the isopiestic method. The data are interpreted in terms of cationic polymerization with degrees of polymerization ranging from 1.3 at $r = 0.5$ to 84 at $r = 2.0$. The values are in reasonable agreement with those predicted by the oxygen bridging mechanism of Granner and Sillen.

On the basis of potentiometric titrations, Moeller and King,[3] in 1950, proposed that either peptization or polymerization occurs when hydroxide ions are added to gallium(III) salt solutions. In 1952 these same workers reported polarographic data[4] which indicated that polymerization is the important process. Insufficient data were taken to allow any quantitative interpretation of the mechanism.

Experimental

In an attempt to gain some knowledge of the species formed in these solutions, the vapor pressures of aqueous $Ga(ClO_4)_3$ solutions were determined by the isopiestic equilibration technique over a range of concentrations and base-to-gallium ratios. (This is the quantity *r* in Table I and will be subsequently referred to simply as "the ratio.") The apparatus and reagents used have been described previously.[5]

A total of 95 equilibrations were made of KCl or $CaCl_2$ (the reference standard solutions) with seven series of solutions of $Ga(ClO_4)_3$ having from zero to 2.5 moles of OH^- added per mole of Ga^{+3}. Several runs were made at each ratio, the gallium concentration being varied from 0.1 *m* up to about 1.2 *m*. The base was added as NaOH to some solutions and as Na_2CO_3 to others without detectably altering the results.

Results

A large-scale plot was made of the isopiestic ratio *R vs* the gallium concentration *m* for each series of solutions. From them the molalities of KCl isopiestic with round molalities of $Ga(ClO_4)_3$ were calculated. Then from a plot of the relative vapor pressure lowering *vs.* KCl concentration, vapor pressures for the gallium solutions could be read.

The smoothed experimental data, given as equilibrium molalities, isopiestic ratio and the relative vapor pressure lowering, are recorded in Table I for each series of solutions.

The average agreement between duplicate determinations was within about 0.2% and, in most cases, the agreement was within 0.1%. A few runs at the lowest concentrations gave larger deviations.

Some of the significant features of the results are summarized below.

(i) At high concentrations addition of OH^- decreases the vapor pressure lowering of the solution although no precipitation occurs. However, at low concentrations the reverse is true.

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[1] Based on a dissertation submitted by C. S. Patterson in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of North Carolina in Chapel Hill.

[2] Du Pont Research Fellow, 1953–1954.

[3] T. Moeller and G. L. King, *J. Phys. Colloid Chem.*, **54**, 999 (1950).

[4] T. Moeller and G. L. King, THIS JOURNAL, **74**, 1355 (1952).

[5] C. S. Patterson, S. Y. Tyree and Kerro Knox, *ibid.*, **77**, 2195 (1955).