spectively, to the stretching of terminal groups and to the stretching of interior bonds. The arguments concerning the number of stretching motions depend of course on the structure of the molecule. It must be borne in mind, however, that the spectrum was observed at moderately high temperature. Under these conditions an absorption band due merely to a single vibrational mode will be much broader than the same band at 0°K.[3,5] Consequently, absorptions due to two or more active modes of approximately equal frequencies cannot be separated readily. Thus the appearance of a single absorption at a frequency far removed from that of the diatomic monomer is evidence for the existence of a cyclic polymer.

It is impossible on the basis of the infrared spectrum described above to determine the structure of the cyclic polymer. In view of the studies of Brewer and Lofgren[1] the evidence is that the polymer is trimeric. For the purpose of estimating bond stretching force constants it will be assumed that the molecule has symmetry D_{3h}. For this structure there will be two infrared active bond stretching motions both of symmetry E′. Using the structure proposed by Schomaker and Wong[6] on the basis of electron diffraction studies, namely, a hexagon with equal bond lengths and a 90° Cu–Cl–Cu angle, and neglecting the angle bending forces and all interaction force constants, one obtains a bond stretching force constant of 1.1×10^5 dynes/cm. in the cuprous chloride trimer. This force constant is considerably smaller than 2.30×10^5 dynes/cm. which obtains for the diatomic monomer.

While the above consideration can only give a very rough picture of the forces in the trimer, qualitatively there is agreement between the force constants and bond energies, namely, weaker bonds in the trimer than in the monomer. This behavior is encountered in other systems where chlorine is bonded to two metal atoms. In the aluminum chloride dimer it is observed[2] that the bond stretching force constant for Al–Cl bonds involved in bridging the aluminum atoms is one-half the magnitude of the force constant for stretching the outer or normal Al–Cl bonds. There is, however, considerable difference between the geometry of the bridges of the two systems. In Al_2Cl_6 the Cl–Al–Cl bridge angle is small,[7] while in Cu_3Cl_3 the angle with metal atom at the vertex is open.[6] In both systems, however, the M–Cl–M bridge angle is quite similar being 90° in Cu_3Cl_3 and 100° in Al_2Cl_6. It is uncertain whether the geometry of a bridged system is determined primarily by the directional properties of the metal atom, or the constancy of the M–Cl–M angle is indicative of strong directional properties of both the metal and halogen atoms. It is probable that the $AlCl_4^-$ ion is tetrahedral and that $CuCl_2$ is linear and that the geometry of these structures is reflected in the bridge-bonded polymers. There are unfortunately, insufficient low frequency spectral data to permit evaluation of the angle bending force constants which would allow more conclusive statements concerning the directional forces present in bridged systems to be made.

Acknowledgment.—The authors wish to express their indebtedness to Professor Verner Schomaker for several important suggestions. The Research Corporation has generously aided this work. One of us (W.K.) gratefully acknowledges an Arthur B. Lamb Fellowship.

CAMBRIDGE, MASS.

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[JOINT CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORIES OF THE OHIO STATE UNIVERSITY AND THE W. A. NOYES LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

Powder X-Ray Diffraction and Infrared Investigation of the Product of the Chromium(VI) Oxide–Liquid Ammonia Reaction

BY RUSSELL S. DRAGO AND HARRY H. SISLER[1]

RECEIVED JULY 30, 1956

The infrared spectra and the X-ray powder diffraction patterns of the products of the reaction between chromium trioxide and liquid ammonia were studied and were compared with results obtained from similar investigations of several known compounds. It was concluded that the reaction product consists of ammonium chromate, an ammine chromium(III) chromate polymer of indefinite composition, a nitroammine chromium(III) chromate polymer and probably a small amount of hexammine chromium(III) chromate. Equations are suggested to account for the formation of these products and for the reported characteristics of the reaction.

It has been shown[2] that when chromium(VI) oxide reacts with liquid ammonia approximately one-fourth of the chromium is reduced to the +3 state. It was postulated that the formation of a precipitate accounted for the fact that all of the chromium is not reduced. The analytical data obtained did not permit positive identification of the product but two possibilities were considered: $Cr(NH_4)_3(CrO_4)_3 \cdot xNH_3$ and $Cr(CrO_3NH_2)_3 \cdot xNH_3$. It was also shown that the amount of nitrogen produced was only approximately one-half of the stoichiometric amount based on the amount of chromium reduced and assuming the reaction

$$2CrO_3 + 2NH_3 \longrightarrow 2Cr^{+++} + 6OH^- + N_2 \quad (1)$$

Most of the "missing" nitrogen was released when the reaction product was heated.

Further studies[3] revealed that the product gives

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[1] Department of Chemistry, University of Florida, Gainesville, Florida.

[2] H. H. Sisler and F. Jirik, THIS JOURNAL, **66**, 1344 (1944).

[3] S. Tannenbaum, Ph.D. thesis, Ohio State University, 1949.

no test for nitrate, nitrite, hyponitrite, azide or oxides of nitrogen. In view of the probability that complex formation with chromium(III) would modify the chemical characteristics of these radicals, the negative tests could not be considered conclusive. The present authors, therefore, decided to investigate the reaction product by means of infrared spectroscopy and X-ray powder diffraction. The data obtained were then compared with results from similar investigations of several known compounds. In the course of this study, several new compounds were prepared.

As a result of these investigations, we have concluded that the product of the chromium(VI) oxide–liquid NH_3 reaction consists of ammonium chromate, an ammine chromium(III) chromate polymer of variable composition, a nitroammine chromium(III) chromate polymer and probably a small amount of hexammine chromium(III) chromate. The missing nitrogen and the per cent. chromium reduced can be accounted for in terms of reactions leading to these products.

Experimental

The apparatus for the reaction between chromium(VI) oxide and liquid ammonia was essentially the same as that used in the earlier experiment[2] except that no gas analyses were made. C.P. grade chromium(VI) oxide was dried at 115° over phosphorus(V) oxide for 30 hours. Analysis indicated that the dried material was 99.5% pure. Synthetic grade anhydrous ammonia was used. Precautions were taken to keep both products and reactants out of contact with atmospheric moisture. The reaction was carried out in liquid ammonia at −33° and, after reaction was complete, the excess solvent was allowed to evaporate slowly. Analysis of a typical gross solid product showed: total Cr, 36.12%; Cr(VI), 27.18%; basic N, 22.3%. The fraction of the total chromium which had been reduced as calculated from the above analysis is 24.75%, in reasonable agreement with earlier values.[2,3] Methods of analysis employed were similar to those described in the earlier article.[2]

Initial investigations indicated that the product consisted of several substances with different solubilities in water. Samples were prepared with different amounts of washing for X-ray powder pattern and infrared analyses.

Dark brown, bulky particles and finely divided, yellow particles could be distinguished in the product. Particles of the two components were separated by filtering through a tube which had holes in it large enough to allow the fine, yellow particles to pass. The dark brown product was washed several times with liquid ammonia to remove adhering yellow particles. Both the finely divided and the bulky particles were subjected to infrared analysis.

The following compounds were prepared and their infrared spectra and X-ray powder diffraction patterns determined.

Hexammine chromium(III) chloride and hexammine chromium(III) nitrate were prepared by methods described in "Inorganic Syntheses."[4] Hexammine chromium(III) chromate was prepared by grinding a paste of hexammine chromium(III) chloride with silver chromate. The hexammine chromium(III) chromate was dissolved in water and then reprecipitated by the addition of alcohol. The product was washed with water, alcohol, acetone and ether and then vacuum dried over phosphorus(V) oxide. *Anal.* Calcd. for $[Cr(NH_3)_6]_2(CrO_4)_3$: H, 5.49; N, 25.6. Found: H, 5.43; N, 24.4.

Nitropentammine chromium(III) nitrate was prepared by a method to be described in "Inorganic Syntheses."[5]

Nitropentammine chromium(III) chromate dihydrate was produced by addition of an excess of a saturated solution of potassium chromate to a saturated solution of nitropentammine chromium(III) nitrate. Alcohol was added to complete precipitation and the precipitate was washed with water, alcohol and ether. *Anal.* Calcd. for $[Cr(NH_3)_5NO_2]CrO_4 \cdot 2H_2O$: H, 5.52; N, 25.84. Found: H, 5.51; N, 25.92. After drying *in vacuo* over phosphorus(V) oxide for 48 hours, at room temperature, analysis showed: N, 27.3; H, 4.74; calcd. for $[Cr(NH_3)_5NO_2]CrO_4$: N, 28.1; H, 5.05.

The following reaction of chromium(VI) oxide with potassium iodide in sulfuric acid solution[6]

$$8CrO_3 + 6KI \longrightarrow Cr_2(CrO_4)_3 + 3K_2CrO_4 + 3I_2$$

was used to synthesize hydrated chromium(III) chromate. Excess chromium(VI) oxide was allowed to react with a concentrated solution of potassium iodide. After removing excess chromium(VI) oxide and potassium chromate by washing with water, and iodine by washing with acetone and carbon tetrachloride, the dark brown product (chromium(VI) chromate) was washed with alcohol and ether and dried in a vacuum desiccator.

The X-ray powder patterns for ammonium chromate, the product of the reaction of chromium trioxide with liquid ammonia, and the water washed products I and II (see Table I) were obtained by using a North American Philips, X-ray diffraction unit employing an X-ray powder camera with a diameter of 11.45 cm. The patterns for the other compounds were obtained with a Hayes X-ray diffraction unit employing a 14.0 cm. powder camera. In all the X-ray investigations chromium Kα radiation and a vanadium oxide filter were employed.

The infrared investigations of the product and of the product washed with liquid ammonia were obtained with a Baird self-recording infrared spectrophotometer. All of the other spectra were obtained with a Perkin–Elmer double beam instrument. A sodium chloride prism was employed in all of these investigations.

Results

The data resulting from the infrared studies are reported in Table I. The following tentative assignments for the infrared absorption bands of the product of the CrO_3–NH_3 reaction were made by comparing spectra of the product with spectra of several known complex compounds of chromium and cobalt. To N–H stretching, 3150 cm.$^{-1}$; to N–H bending, 1630 cm.$^{-1}$; to NH_4^+ vibration, 1430 cm.$^{-1}$; to N–O vibrations in coördinated nitrite, 1305 and 1230 cm.$^{-1}$; to N–O skeletal vibration, 835 cm.$^{-1}$; to coördinated chromate, 1270 cm.$^{-1}$. The peak at 1270 cm.$^{-1}$ appears both in the product and in $Cr_2(CrO_4)_3 \cdot xH_2O$, and is believed to result from chromate ions that are coordinated to different trivalent chromium atoms thus forming the bridge for a chromium(III) chromate polymer. Results of the X-ray powder diffraction studies are compatible with the presence of such a species in the product.

Absence of absorption in the 1360–1390 cm.$^{-1}$ region indicates that there is no appreciable concentration of ionic nitrate[7] in the product. Since Nujol absorption at 1380 cm.$^{-1}$ might mask absorption by small quantities of nitrate, the absence of nitrate was substantiated by an examination of the spectrum of the product in a KBr disc.

The infrared spectrum of the product indicates, thus, that the "missing nitrogen"[2] is present as coordinated nitrite. The chemical behavior of the product[8] can also be explained by the presence of this group. Lack of absorption by the product in the 1045 to 1100 cm.$^{-1}$ region (region of skeletal vibrations) indicates that nitrite is not present in

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(4) A. L. Oppegard and J. C. Bailar, Jr., "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., New York, N.Y., p. 153.

(5) M. Mori, ref. 4, Vol. V, to be published.

(6) J. I. Aznarez and J. Vericad Raga, *Anal. real soc. espan. fis. y quim.* (*Madrid*) **50B**, 545 (1954).

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

(8) To be published, This Journal.

TABLE I[a]

Product	$(NH_4)_2CrO_4$	$Cr(NH_3)_6(NO_3)_3$	$[Cr(NH_3)_6]_2(CrO_4)_3$	$Cr_2(CrO_4)_3\cdot XH_2O$	$Cr(NH_3)_5NO_2(NO_3)_2$	$Cr(NH_3)_5NO_2CrO_4\cdot 2H_2O$	$Cr(NH_3)_5NO_2CrO_4$
3150s, i	3120m, i	3265s, i	3140m, i	3200b	3300		
		3200sh			3240s, i		
		3150sh			3180sh		
1660sh		2380s, wk				3160v, b, i	3150v, b, i
		1755m, wk			2350s, v. wk		
1630m, m	1650m, m	1630s, m	1625m, m	1615m, m	1625s, m		
					1482s, i	1640m, m	1637s, m
1450s	1460sh			1445sh			1630s, m
1430s, i	1420s, i			1430sh		1445s, i	
1415sh	1417b, i			1420sh			1425s, wk
		1360v, b, i	1370sh		1380m, i	1420s, m	
			1327s, m				
1350sh			1320sh		1340sh		
1305s, m			1290sh		1300s, m	1345s, m	1332s, m
1270s, m				1275s, i		1300s, i; 1317s, i	1312sh
1230s, wk					1227s, m	1287sh	1285m, i
1005m, wk		1050s, v. wk			1017s, i		1250sh, v. wk; 1272sh
982s, m						1100sh	1080sh
	947sh			950–700b, i		1075s, i	1045s, i
	920sh					882sh	950s, v. wk
900–860 b, i	875b, v. i.		890m, i				
845sh	845sh					867s, i	875s, i
835sh		830s, m	838s, i		833s, m	843s, i	855s, i
828sh			810s, i			790s, m	837s, i
775m, v. wk.	742m, m	767s, i			770s, m		800s, m
		712s, wk					

[a] The letters immediately following the values for the frequency denote the band width. The letter after the comma indicates the intensity of absorption. The following symbols have been used to indicate band width: s = sharp; b = broad; m = medium. The following abbreviations refer to the intensity: i = intense; wk = weak; m = medium; v. before any symbol refers to very; sh = shoulder.

the product as the compound nitropentammine chromium(III) chromate. Since skeletal vibrations vary considerably with crystal structure, nitrite may be coördinated to trivalent chromium which is present as a chromium(III) chromate polymer or in either of the compounds chromato nitrotriammine chromium(III) $[Cr(NH_3)_3NO_2CrO_4]$ or chromato nitrotetrammine chromium(III) $[Cr(NH_3)_4NO_2CrO_4]$. Evidence to be discussed shortly substantiates the presence of polymeric species. The absorptions at 1005 and 982 cm.$^{-1}$ are tentatively assigned to skeletal vibrations produced by the polymers.

By washing the product with ammonia (as described in the Experimental section) a dark brown bulky material can be separated from the rest of the reaction mixture. The infrared spectrum of this substance contains only lines which were present in the spectrum of the product but changes in intensities of some of these lines and the disappearance of other lines support the assignments previously made. There is a considerable decrease in intensity of the absorption at 3150 cm.$^{-1}$, and a complete disappearance of absorption attributed to ammonium ion vibration at 1430 cm.$^{-1}$. The intensity of the peak assigned to coördinated chromate at 1270 cm.$^{-1}$ is increased, indicating an increase in the concentration of polymer in the dark brown material. It is believed that most of the simple compounds are washed out of the product as finely divided material and the residue consists mostly of polymeric substances. Absorptions which were assigned to nitrite (1305, 1230 and 835 cm.$^{-1}$) are present in the residue, supporting the proposal that nitrite is coördinated to some of the trivalent chromium atoms in the chromium(III) chromate polymer. The peak at 1630 cm.$^{-1}$ is still present at approximately the same intensity in this part of the product. This absorption is probably caused by ammonia coördinated to trivalent chromium. The peaks at 1005 and 982 cm.$^{-1}$ which were originally assigned to the chromium(III) chromate species are also present in the dark brown substance. There is an intensification in the 1005 cm.$^{-1}$ peak but very little change in the peak at 982 cm.$^{-1}$.

Results of X-ray diffraction investigations are reported in Table II. The first column of figures contains values calculated for the *d*-spacings whereas the second column (I/I_0) contains estimated values of the relative intensities of these spacings.

Data reported in Table II show conclusively that ammonium chromate is one of the principal substances produced in the chromium(VI) oxide–liquid ammonia reaction. The product of this reaction gives the same principal lines, in the same order or relative intensity, as does ammonium chromate, and also gives several lines in addition to those attributed to ammonium chromate. The presence of hexammine chromium(III) chromate

TABLE II

POWDER X-RAY DIFFRACTION DATA

$(NH_4)_2CrO_4$		Product		Washed prod. I		Washed prod. II		$Cr(NH_3)_3NO_2$-$CrO_4\cdot 2H_2O$		$Cr(NH_3)_5NO_2$-CrO_4		$Cr(NH_3)_5NO_2$-$(NO_3)_2$		$[Cr(NH_3)_6]_2$-$(CrO_4)_3$		$Cr(NH_3)_6$-$(NO_3)_3$	
d (Å.)	I/I_0	d (Å.)j	I/I_0	d (Å.)	I/I_1	d (Å.)	I/I_0	d (Å.)	I/I_0	d (Å.)	I/I_0	d (Å.)	I/I_0	d (Å).	I/I_0	d (Å.)	I/I_0
6.96	5	6.90	4					6.67	3			6.85	2	6.94	3		
		6.19	1	6.23	1			6.07	4			6.17	10	6.40	4	6.33	4
5.65	6	5.64	5	5.61	1									5.62	5	5.53	3
5.43	6	5.44	4														
		5.25	4	5.28	5	5.20	1	5.20	1	5.11	2			5.30	5		
4.80	10	4.78	10	4.80	5			4.91	10	4.98	10			4.93	2		
		4.53	5	4.55	5	4.52	3	4.43	8	4.64	5			4.56	2	4.59	1
		4.38	7	4.37	9	4.40	10	4.31	2	4.15	2			4.33	10	4.24	1
3.89	5	3.90	6	3.90	4			4.06	2					3.98	2	3.96	2
3.73	5	3.70	4			3.71	2	3.92	5	3.76	2	3.76	10	3.71	2	3.89	10
3.62	5	3.64	3	3.64	1			3.59	5								
3.45	6	3.46	6	3.46	6	3.44	1	3.52	5	3.52	6						
3.37	1							3.47	6								
3.17	7	3.18	9	3.17	8	3.19	5	3.29	4	3.25	1	3.22	6			3.30	2
3.12	6	3.12	6													3.14	2
3.04	1	3.00	4	3.02	2	3.00	2	3.05	2	3.07	1	3.08	6				
2.93	5	2.93	4					2.98	5							2.95	2
2.84	3	2.84	2					2.89	3	2.90	4						
2.81	3							2.82	3	2.84	1					2.85	2
2.75	3							2.72	5	2.75	1			2.77	4	2.78	2
2.54	2	2.54	3					2.66	5	2.65	1	2.66	6	2.71	4	2.74	5
2.49	1							2.52	5	2.56	4			2.62	4	2.55	1
2.31	8	2.32	6	2.32	2			2.51	6								
2.22	1							2.45	2	2.47	2	2.45	$^1/_2$			2.45	2
2.18	1	2.19	2					2.40	4			2.39	2				
1.99	4	2.02	1					2.10	3			2.18	1			2.11	1
1.97	2							2.07	3			2.05	2				
1.92	2							2.02	3							1.95	1
1.88	2							1.97	3	1.90	1	1.88	2				
1.86	2							1.93	5	1.83	1	1.80	3			1.85	2
1.84	2							1.85	5	1.78	1	1.68	1			1.73	1

would be compatible with infrared determinations and would also account for *d*-spacings in the product at 4.38, 5.25 and 6.19 Å. The other lines of the product cannot be assigned definitely at this time.

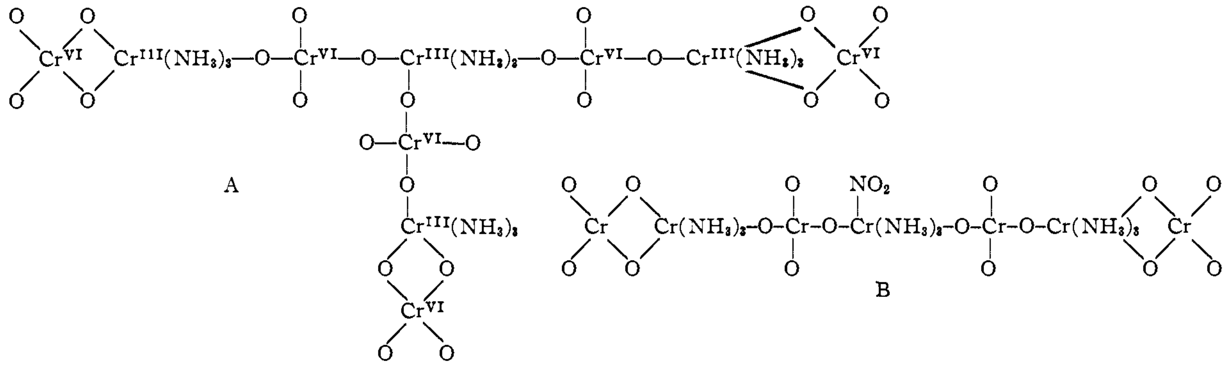
Washing the reaction product with water removes ammonium chromate and leaves as a residue a dark brown solid which is almost amorphous to X-rays. Intensities reported for the washed products I and II are relative intensities for that pattern. Actually all of the lines are very weak on these two films and the strongest line would probably be assigned an intensity of 3 relative to the intensity of the 4.80 line of the ammonium chromate pattern. Attempts to increase the intensity of lines in the washed product by increasing exposure time resulted only in an increased background on the film. X-Ray powder analysis of hydrated chromium(III) chromate showed that this material is also amorphous to X-rays. These findings indicate that both hydrated chromium(III) chromate and ammine chromium(III) chromate consist of a series of polymeric materials of variable composition. The polymers are quite probably three dimensional and have highly irregular structures. If simple units were present these compounds would be expected to have characteristic diffraction patterns. The weak lines in the diffraction pattern of the washed product can be attributed to small concentrations of these simpler units.

Discussion

The results of these investigations indicate that the product of the chromium (VI) oxide–liquid ammonia reaction contains ammonium chromate, an ammine chromium(III) chromate polymer of indefinite composition, a nitroammine chromium(III) chromate polymer and some hexammine chromium(III) chromate.

Ammine chromium(III) chromate is probably a three-dimensional polymer, which can be represented by the general formula $[Cr(NH_3)_3]_{2n}(CrO_4)_{3n}$ where n = 1, 2, 3 and 4. For n = 2 the structure (A) would represent a possibility. This type of material could be produced by direct attack of ammonia on the solid chromium(VI) oxide without prior conversion of the oxide to CrO_3 monomers.

The oxidation–reduction reaction may be presumed to follow either of two paths; one leading to the formation of nitrogen, the other leading to the formation of nitrite coördinated to Cr(III). The general formula for the latter product can be represented by $[Cr(NH_3)_3NO_2CrO_4]_n$. It is quite likely that the product species include many different combinations of the two general formulas proposed. One simple example is represented by the structure (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.

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[JOINT CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORIES OF THE OHIO STATE UNIVERSITY AND THE W. A. NOYES LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF 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]

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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

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[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).

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