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The Reaction of Ammonia Compounds with
Chromyl Chloride and Chromic Anhydride.

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A thesis submitted to the
Faculty of the Graduate
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In research on the reaction between ammonium chloride and potassium dichromate when heated, the results of which were published by G.B. Frankforter, V.H. Roehrich and E.V. Manuel in the Journal of the American Chemical Society, February, 1910, the author of this thesis noted that the residue left from the above reaction gave off nitrogen upon adding water to the extent of about a third of a cubic centimeter per gram. The present thesis was undertaken in order to determine what compound yielded this nitrogen.

As stated in the above cited paper, the reaction between ammonium chloride and potassium dichromate is very complex and since the sought-for compound must exist in the residue in small amount only and can not be isolated from it, very little can be learned by examining this residue. Three things a study of it did show: First, that the material was decomposed by water

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and water-containing solvents liberating pure nitrogen and was therefore probably a new chromium compound. Second, that it was present in a mixture that had been heated to 280°C and was hence stable at this rather high temperature. Third, that the mixed residue containing it still gave off nitrogen upon adding water after boiling the material with absolute alcoholic potash until no more ammonia was liberated. This behavior with alcoholic potash indicates that the nitrogen is not evolved by the oxidation of an ammonium salt by an active oxide of chromium as the ammonia has been expelled and any free higher oxides of chromium should have been reduced by the alcohol.

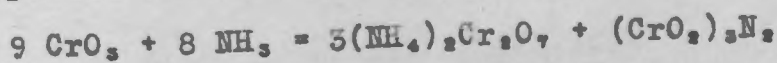
Attempts were now made to obtain the product by other reactions so as to study the reacting proportions and if possible obtain pure material. More than a year has now been spent on this work and a large number of syntheses have been attempted which can only be briefly mentioned as follows: Ammonium dichromate ignited

alone gave no gas but ignited mixed with ammonium sulphate or chloride, a small amount of gas was obtained from the residue upon adding water. Chromyl chloride and magnesium nitride yielding very little when heated in a sealed tube at 200°C. The tube exploded. The residue contained magnesium nitride and probably hypochlorite as the odor of bleaching powder appeared upon moistening it. Chromyl chloride with ammonium nitrate or carbonate, with potassium cyanate or cyanogen iodide or with various organic amines or with sulphur nitride gave no gas upon moistening the product although in each case brown chromium dioxide had been formed. Chromyl chloride or chromic anhydride did not react with boron nitride even when heated. Chromic anhydride with methyl or diphenylamine, with cyanogen iodide or urea gave no gas yielding compound although the anhydride was reduced, in some cases with ignition. Chromic anhydride and nitric oxide do not react appreciably when dry

although in solution the anhydride is reduced to brown dioxide. Chromium nitride gently heated with melted chromic anhydride gave a residue which with water yielded a little nitrogen. The original constituents do not react in water even when boiled. Magnesium nitride gently heated with a good excess of chromic anhydride gave considerable nitrogen when treated with water and left magnesium chromate and a brown precipitate. The last two reactions mentioned show that only chromium, nitrogen and oxygen need be present to form the compound which is the source of the nitrogen and like the next and most important reaction hint that it is a substitution product of chromic anhydride and ammonia.

It has been found that upon passing dry ammonia gas over rather coarse crystals of chromic anhydride at not over 100°C , the anhydride does not become incandescent and reduce to chromium sesquioxide as it does at higher temperatures or with finely powdered

crystals. but turns purple and then dark purplish-brown with some rise in temperature. No mention of this reaction has been found in the literature. The dark brown product upon treatment with water gives off nitrogen vigorously. Usually three or four but in one case nine and six-tenths and in another fourteen cubic centimeters per gram were obtained. The solution contains ammonium chromate or dichromate depending on whether the reaction took place at a high or low temperature, and a precipitate of yellowish brown chromium dioxide. In one case, analysis of material for nitrogen, chromium dioxide and ammonium dichromate supported the very plausible reaction:



thus regarding the nitrogen as liberated from trichromyl nitride which analogously to chromyl chloride would be expected to split up by the addition of water into chromic acid and ammonia and these in the nascent state might easily react to again split off water and leave

chromium dioxide and free nitrogen. Unfortunately the chromium dioxide is usually present in excess due it has been found, to the partial liberation of the nitrogen while the ammonia is reacting with the chromic anhydride. This loss of nitrogen has been detected by treating the pure dry anhydride with nearly pure dry ammonia measured over mercury and collecting and measuring the nitrogen liberated both during the reaction of the anhydride and ammonia and afterwards upon treatment of the product with hot water. The amount of nitrogen thus obtained from one hundred cubic centimeters of ammonia amounts to from two cubic centimeters to a trace liberated during the first reaction and about two and eight-tenths cubic centimeters upon adding water. It is hoped that by very careful drying of the chromic anhydride and ammonia and keeping the reaction at a low temperature the ammonia can be accurately measured, that all nitrogen will be retained in combination and that it can be measured by liberation with hot water and the amount

of reduction of the chromic anhydride then found by titration with thiosulphate and the chromium weighed as a check. Up to the present, absolutely pure dry ammonia has not been obtained as no liquid ammonia is available.

All attempts to purify the nitrogen generating chromium compound have failed because of the general insolubility of both it and ammonium chromate in anhydrous organic solvents. Such solvents as do dissolve the latter decompose the former. Of these pyridine and better still acetonitril containing 10 o/o of absolute nitric acid are good solvents of the ammonium chromate but both slowly decompose the desired compound. The one particularly promising solvent that remains to be tried is liquid ammonia.

Strangely enough, chromyl chloride pure or dissolved in carbon tetrachloride does not give a good yield of the supposed chromyl nitride even though the ammonia be diluted with air and passed in in the cold.

Flocculent chromium dioxide and ammonium chloride are formed but the material yields very little nitrogen. The reacting substances have a very strong tendency to become incandescent and the violence of the reaction probably causes all nitrogen to be freed. It might be stated that under certain conditions the chromic anhydride and ammonia react explosively, the rise in temperature probably causing ammonium chromate to break down into ammonium dichromate and the large excess of ammonia thus yielded, suddenly reacting and bringing the temperature to a point where the nitrogen is split off. Quite violent explosions have occurred several times in the course of the work.

To use up the water formed in the reaction between ammonia and chromic anhydride the anhydride was mixed with nitric anhydride and absolute nitric acid with the expectation that ammonium nitrate instead of chromate would be the impurity formed, thus allowing of purification by absolute methyl alcohol but the

material immediately ignited.

To review the work it may be stated briefly that there has been found in the various reaction products mentioned, a nitrogen yielding substance decomposed by water. It is practically impossible to isolate this by means of solvents but further analyses should give a clue to its composition. It is composed very probably of only nitrogen, chromium and oxygen but can not, as might at first be supposed, be a mixture of chromic anhydride and chromium nitride as the anhydride should be completely decomposed by the excess of ammonia used in the reaction.