ever, as to make it impossible to establish with any certainty the composition of the compound. The very flat nature of the curve in this region indicates that whatever compound is formed, it is not very stable. An eutectic was obtained at four to five mole per cent. of dimethyl dichlorosilane and about −125.5°.

The data in curve B give no indication whatever of compound formation between trimethyl chlorosilane and diethyl ether. An eutectic was obtained at twelve to thirteen mole per cent. trimethyl chlorosilane and about −126.0°.

We may thus conclude that the methyl chlorosilanes, like silicon tetrachloride, do not form very stable compounds with diethyl ether. The results of these studies are not in conflict, therefore, with the very tentative suggestion in a previous publication[2] that there isn't room about the silicon atom in silicon tetrachloride or, since the steric requirements of the methyl group are not less than those of the chlorine atom, in the methyl chlorosilanes, for the approach of the oxygen atom from the ether.

In connection with the very weak compound formed by the dimethyl dichlorosilane with diethyl ether, it is interesting to note that work with the ethyl chlorosilanes[5] indicates that dimethyl dichlorosilane would have the highest dipole moment of the three chlorosilanes studied in this work, and suggests the possibility that the weak crystalline compound between dimethyl dichlorosilane and diethyl ether may depend upon dipole interaction for its existence.

Summary

Phase studies of the systems methyl trichlorosilane–diethyl ether, dimethyl dichlorosilane–diethyl ether, and trimethyl chlorosilane–diethyl ether were carried out by the freezing point method. Weak compound formation was observed in the case of dimethyl dichlorosilane.

(5) McCusker, Witucki and Curran, Paper presented to Phys. and Inorganic Section, American Chemical Society Meeting, Sept., 1947.

COLUMBUS 10, OHIO RECEIVED JUNE 24, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

Addition Compounds of Chromic Anhydride with Some Heterocyclic Nitrogen Bases

BY HARRY H. SISLER, JACK D. BUSH AND OLIVER E. ACCOUNTIUS

The ability of pyridine to act as a base by sharing the pair of electrons on its nitrogen atom with various molecules capable of acting as Lewis acids is well known. The interest in this Laboratory in molecular addition compounds, as well as previous work on the pyridine–sulfur trioxide compound by one of the authors,[1] caused the authors to undertake a study of the reactions of pyridine and related nitrogen bases with chromic anhydride. The results of studies with pyridine, α-picoline, β-picoline, γ-picoline, quinoline and isoquinoline are reported in this paper. Reactions of this type in the case of chromic anhydride are complicated by the fact that, in addition to its acidic properties, chromic anhydride is a strong oxidizing agent. Conditions of the various reactions must, therefore, be subjected to rather more stringent requirements than in the case of such compounds as sulfur trioxide.

Experimental

Preparation of Materials.—The chromic anhydride used in this study was Mallinckrodt C.P. grade. It was dried in an electrically heated furnace under vacuum at a temperature of 140° in the presence of phosphorus pentoxide. It was then ground to a fine powder with a mortar and pestle and placed in the drier for another two-day drying period. It was stored over phosphorus pentoxide.

J. T. Baker C.P. grade pyridine was used, but all the other bases were obtained from the Eastman Kodak Company. All were fractionally distilled using a four-foot column packed with glass helices at atmospheric pressure, except quinoline and isoquinoline, which were distilled under reduced pressure. The amines were dried over barium oxide and, where necessary, were treated with activated charcoal before distillation. A middle fraction having a very narrow boiling range (<1°) and a very narrow range of refractive index (agreeing with values recorded in the literature) was collected in each case.

Preparation of the Addition Compounds.—The general method for carrying out the reactions was to add an excess of the nitrogen base to a weighed quantity of the chromic anhydride at room temperature or below, and, after solution had been effected, to evaporate the excess amine, and to weigh the crystalline residue. The apparatus in which this operation was carried out is shown in Fig. 1. After the system was evacuated, stopcocks A and B were closed, the reaction flask disconnected from the system at J and K, and weighed. A sample of chromic anhydride was then introduced into the flask, the system again evacuated and weighed. An excess of nitrogen base was drawn into the system through stopcock B, and, in most runs, the system was shaken until solution or reaction appeared to be complete. The reaction flask was then re-attached to the system, the traps I, II and III cooled with liquid air, and the excess of nitrogen base allowed to distil off under vacuum. The reaction flask was protected against the light throughout the process of evaporation. The removal of the excess of nitrogen base was detected in three ways: (a) visually, from the physical appearance of the reaction mixture, (b) gravimetrically, by the sharp decrease in the rate of weight loss of the reaction system which was weighed from time to time as the point of complete evaporation of excess amine was approached, and (c) manometrically, by the decrease in vapor pressure in the system as measured by the thermocouple gage. It was found that conclusions based upon (a), (b) or (c) are consistent and in the latter runs (c) was used as the chief indication of solvent removal. At the end of the period of evaporation the stopcocks A and B were closed and the reaction flask again removed and weighed. Thus the weights of both the initial chromic anhydride and the solid reaction product were obtained.

Analytical Methods.—The various reaction products were analyzed for hexavalent chromium by dissolving the product in a dilute solution of phosphoric and perchloric

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(1) Sisler and Audrieth, THIS JOURNAL, **61**, 3392 (1939).

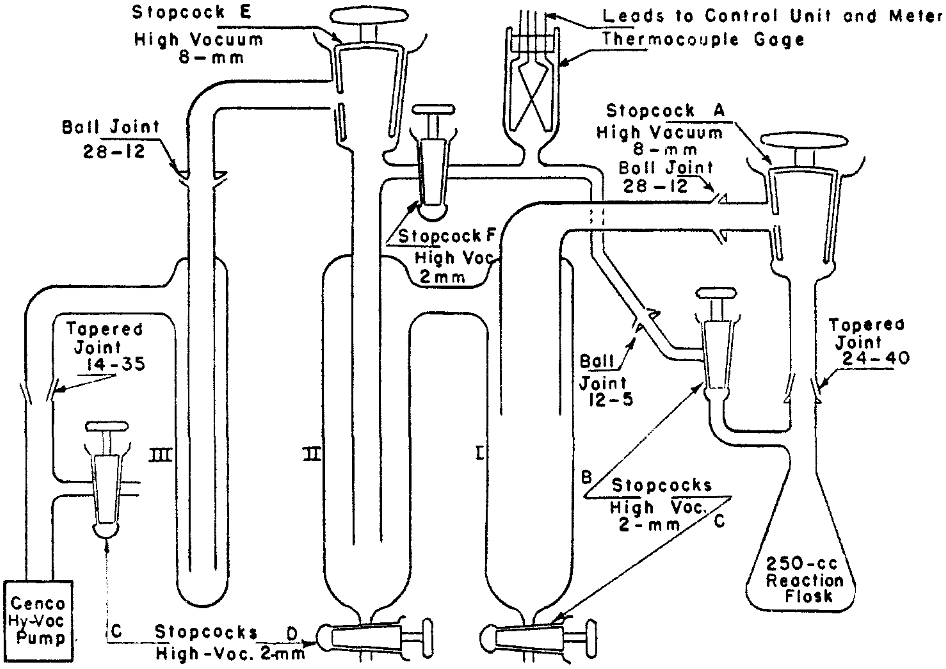

Fig. 1.

acids, warming, if necessary, to bring about complete solution, adding a slight excess of standard ferrous perchlorate solution, and back titrating with standard dichromate solution. Sodium diphenylamine sulfonate was used as indicator.

To determine total chromium, the solutions from the above titration were evaporated rapidly until heavy fumes appeared, treated with 60% perchloric acid, and allowed to simmer slowly until oxidation was complete (thirty minutes after the color changed from green to red). The solution was then diluted, phosphoric acid added, and the solutions analyzed in the same manner as for hexavalent chromium.

The Reaction of Chromic Anhydride with Pyridine.—As soon as pyridine comes in contact with chromium trioxide it starts to react. Heat is evolved fairly rapidly and, if no provision for cooling is made, flame quickly appears at the surface of the solid. If cooling is provided by an ice-bath or by rapid evaporation of solvent, the reaction proceeds smoothly. The solid swells to more than twice the bulk of the original chromium trioxide before appreciable change in color occurs, and continues to swell as the solid forms a light yellow colored, fluffy product which dissolves if a sufficiently large quantity of pyridine is used. As the solution in excess pyridine becomes more concentrated, the color of the solution changes from pale yellow to an intense dark red. When the preparation of the addition compound is carried out by the method already described, but with an insufficient quantity of pyridine to dissolve completely the initial reaction product, and the excess liquid evaporated rapidly, a hard, yellow cake is obtained. On the other hand, if enough pyridine is used to dissolve the initial reaction product, and the evaporation is carried out slowly, deep red-colored crystals with partially formed faces which seem to indicate orthorhombic symmetry are obtained.

The addition compound in the presence of the saturated liquid is photosensitive and slowly turns brown on standing in the light, becoming nearly black within a week. The dry product is much less affected by light. Usually a small amount of brown material collects on the side of the flask as the level of the liquid falls during evaporation. However, if overheating during the initial reaction is avoided and, if the solution is protected from the light, only a small amount of this brown substance is obtained.

When the red crystals of the addition compound are crushed, a yellow powder is obtained which is identical in appearance with the yellow cake obtained by rapid evaporation. The two products, therefore, appear to differ only in particle size. This conclusion is supported by the analytical results. Analysis of a number of the yellow powdered and red crystalline products for total chromium and for hexavalent chromium show that very little of the chromium in these products is reduced, and that the composition of these products corresponds to the empirical formula $CrO_3 \cdot 2C_5H_5N$. Typical analytical data are: hexavalent chromium: 20.07, 20.07, 20.12, 20.13, 20.10. Total chromium: 20.53, 20.75, 20.12. Calcd. for $CrO_3 \cdot 2C_5H_5N$: chromium: 20.14. Analysis of the small amount of brown product formed on the walls of the flask shows about the same composition as the bulk of the product but with an appreciable amount of reduced chromium. Typical analytical data are: hexavalent chromium: 20.02, 20.11, 19.91, 19.50, 19.48. Total chromium: 20.44, 20.43, 20.52, 20.93, 20.64.

The formula $CrO_3 \cdot 2C_5H_5N$ for the reaction product of chromic anhydride and pyridine was further confirmed by the ratios of the weight of the original chromic anhydride to the weight of the solid product left after removal of excess of solvent. Obtained: CrO_3, 38.83, 38.52, 39.13, 38.92. Calcd. for $CrO_3 \cdot 2C_5H_5N$: CrO_3, 38.73.

$CrO_3 \cdot 2C_5H_5N$ is insoluble in carbon tetrachloride, benzene, and diethyl ether, but colors ethyl alcohol, acetone, and ethylene glycol appreciably. It is quite soluble in water (with hydrolysis) and in pyridine. On long standing in rubber-stoppered bottles, the addition compound loses a considerable portion of its pyridine content, without any significant amount of reduction of the chromium taking place (the pyridine is apparently absorbed by the rubber stoppers). This indicates that the formation of the addition compound is probably a reversible process. The compound gradually takes up moisture on standing in air. It decomposes only slowly at 100°. If a portion of the solid is warmed gently above a small Bunsen flame, it melts to a dark red liquid which does not completely recrystallize when cooled. Continued heating results in the formation of a black, tarry mass from which considerable vapor (at least part of which is pyridine) is evolved. Further heating results in a sudden deflagration, accompanied by flame, and producing a voluminous gray-green mass, presumably Cr_2O_3.

The compound $CrO_3 \cdot 2C_5H_5N$ was also prepared by adding pyridine (cooled to $-5°$) to an excess of chromic anhydride, shaking the suspension thoroughly, allowing the excess solid to settle out, and pouring the supernatant solution into approximately twice its volume of chilled, dry ether. The yellow precipitate which forms is filtered in the absence of carbon dioxide and moisture, washed with ether and dried by passing dry, carbon dioxide-free air through it. *Anal.* Found: 20.75, 20.85 hexavalent chromium. 20.80, 20.95 total chromium. Calcd. for $CrO_3 \cdot 2C_5H_5N$, 20.14.

Reactions of Chromic Anhydride with α-, β-, and γ-Picoline.—Each of the three isomeric picolines was allowed to react with chromic anhydride in the manner already described. On the addition of either β- or γ-picoline, solid chromic anhydride behaves in a manner similar to its reaction with pyridine and produces a yellow compound. Large crystals of these addition compounds were not readily obtained, for the operating conditions which resulted in the production of well-formed crystals of the pyridine compound produced grainy, orange particles of the γ-picoline compound, and a yellow cake of the β-picoline compound. The picoline compounds, on the basis of the intensity of the color of their saturated solutions, are less soluble in the respective picolines than is the pyridine compound in pyridine.

Analysis of the γ-picoline product gave results which agree closely with the calculated values for the formula $CrO_3 \cdot 2C_6H_7N$, and show that very little chromium is reduced. Typical results include: hexavalent chromium: 17.87, 18.16, 18.20, 18.01, 18.21, 18.21. Total chromium: 18.23, 18.25, 18.35, 18.25. Calcd. for $CrO_3 \cdot 2C_6H_7N$: chromium, 18.17. Conclusions based upon these analyses are supported by the ratios of weight of original chromic anhydride to the weight of product obtained. Obtained: CrO_3, 34.91, 35.8. Calcd. for $CrO_3 \cdot 2C_6H_7N$: CrO_3, 34.94. Some of the above analyses were carried out on samples which had stood in a desiccator in the dark for six weeks at room temperature, which indicates that the compound does not tend to undergo oxidation–reduction on standing. Analysis of the small amount of brown product obtained on the sides of the flask indicated that a considerable fraction of the chromium in this material had been reduced.

Analysis of the β-picoline product likewise showed reasonable agreement with the formula $CrO_3 \cdot 2C_6H_7N$. Typical data include: hexavalent chromium, 18.92, 18.82, 18.55. Calcd. for $CrO_3 \cdot 2C_6H_7N$: Cr, 18.17. One sample was allowed to stand in a desiccator over phosphorus pentoxide in a glass-stoppered bottle for four and one-half months, and then analyzed. Hexavalent chromium, 18.21, 18.11, 18.08. Total chromium, 18.86, 18.51, 18.23. These data indicate a definite stability toward internal oxidation–reduction at room temperature. Both the β-picoline and γ-picoline compounds undergo slow decomposition if heated in a boiling water-bath. If warmed gently over a low flame they formed a dark, tarry liquid from which considerable quantities of vapor (at least partly picoline) are evolved. Continued heating results in the production of a fluffy gray-green mass (presumably Cr_2O_3).

The reaction of chromic anhydride with α-picoline is very much different from corresponding reactions with β- and γ-picolines and with pyridine. Chromic anhydride dissolves in α-picoline at room temperature to give a dark brown, opaque mixture, from which there is deposited on the walls of the flask a brownish-red, tarry material. After this material has completely settled out, a clear, reddish-brown solution remains which is distinctly different from the solutions obtained with the previously mentioned nitrogen bases. Typical analyses on the solid remaining after removal of excess α-picoline by the method described above include: hexavalent chromium, 26.21, 29.71, 23.40, 25.35; total chromium, 32.12, 29.24, 30.10, 29.82. These data clearly show that considerable reduction of the chromic anhydride occurs and further that the composition of the solid does not approach that required by the formula $CrO_3 \cdot 2C_6H_7N$ (18.17 chromium). The analytical results are not consistent, and do not indicate any simple formula. The general appearance of the product, as well as these analytical data, indicate that the product is a mixture.

Reactions of Chromic Anhydride with Quinoline and Isoquinoline.—The reactions of chromic anhydride with quinoline and isoquinoline were carried out in the manner already described. Somewhat surprisingly, quinoline was found to behave in a manner more closely resembling that of β-picoline than that of α-picoline. On addition of quinoline to solid chromic anhydride, the solid swells and acquires an appearance similar to that observed in the case of pyridine. However, the reaction of quinoline with chromic anhydride is very slow, requiring hours instead of minutes, and the product of the reaction has a relatively low solubility in an excess of quinoline. The reaction takes place so slowly that no noticeable heat effect is observed. A slow evolution of bubbles from the solid material presumably results from an appreciable, though low, rate of oxidation.

Because of the relatively low solubility of the reaction product in excess quinoline, complete solution of the reaction product requires a large excess of the amine. On the other hand, because of the relatively low volatility of quinoline this large excess of the solvent leads to an inconveniently long evaporating period. Therefore, in the quinoline reaction, complete solution was not attained and the reaction was thus carried out in a heterogeneous system. Even so, roughly two weeks elapsed between the addition of the reagents and the recovery of the dry product. The product consisted of a yellow cake covered with a thin surface layer of black, tarry material which was also present on the walls of the flask. Analyses of the yellow product correspond roughly to the formula $CrO_3 \cdot 2C_9H_7N$, but indicate more reduced chromium than in the case of pyridine. For example: Hexavalent chromium, 15.37, 15.48, 15.39. Total chromium, 16.42, 16.16, 16.03. Calcd. for $CrO_3 \cdot 2C_9H_7N$: hexavalent and total chromium, 14.51. The wall residue showed a considerably greater proportion of reduced chromium.

The reaction of chromic anhydride with isoquinoline was carried out, but it was found that virtually all the chromium present in the product of this reaction had been reduced.

Reaction of $CrO_3 \cdot 2C_5H_5N$, $CrO_3 \cdot 2C_6H_7N(\beta)$, and $CrO_3 \cdot 2C_6H_7N(\gamma)$ with Liquid Ammonia at $-33°$.—It was reported in a previous publication[2] that when chromic anhydride reacts with liquid ammonia at $-33°$, approximately 25% of the chromium is reduced to the trivalent state by the ammonia. Possible explanations for the fact that the reduction proceeds only to the extent of about 25% were advanced, but no conclusive answer to the question could be given. It was, therefore, considered desirable to investigate the reactions of the addition compounds described with liquid ammonia, with the hope that some light might be shed on this problem.

The technique used in carrying out the reactions of the chromic anhydride addition compounds with liquid ammonia was the same as that previously described in detail,[2] and consisted briefly in the addition of weighed samples of the various addition compounds to a large excess of synthetic, anhydrous, liquid ammonia at $-33°$ in the absence of air and moisture, allowing the excess ammonia to evaporate (this usually required about twenty-four hours), and analyzing the dry residue for hexavalent and total chromium. As in the CrO_3–NH_3 reaction, the reactant does not dissolve to any large extent in the liquid ammonia, nor does the reaction product appear to have any high degree of solubility. The system remained heterogeneous

TABLE I

Addition compound	% Cr reduced		
$CrO_3 . 2C_5H_5N$	25.5	22.8	26.2
$CrO_3 . 2C_6H_7N$ (β)	26.2	24.2	23.1
$CrO_3 . 2C_6H_7N$ (γ)	24.5	24.7	24.2

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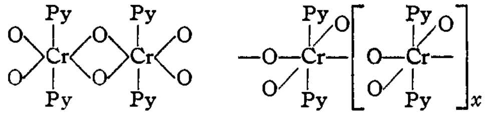
(2) Sisler and Jirik, THIS JOURNAL, **66**, 1344 (1944).

throughout the reaction. The analytical methods have already been described.[2] The percentages of chromium reduced in the various reactions are listed in Table I.

Discussion

If we were to consider the addition compounds of the type $CrO_3{\cdot}2\beta$ (β = pyridine or some similar nitrogen base) prepared in this study to be monomeric, and to be formed by the sharing of electrons between the nitrogen and chromium atoms, it must be assumed that the chromium atom has the unusual coördination number of five. Such an assumption is not necessary, however, if we consider the possibility of molecules containing more than one molecule of chromic anhydride. Two possibilities which immediately suggest themselves are



To obtain additional information as to the molecular structure of these complexes, X-ray diffraction studies of these compounds are contemplated. Cryoscopic studies on solutions of the various addition compounds in an excess of the corresponding nitrogen base are also indicated, and it is expected that such studies will be carried out in this Laboratory.

The percentages of chromium reduced in the reactions of the chromium anhydride addition compounds of pyridine, β-picoline, and γ-picoline, with liquid ammonia do not differ greatly from those obtained in the reaction of chromic anhydride itself.[2] These results may be taken to indicate in a rough way that the reduction of only about 25% of the chromium is not explainable in terms of the arrangement of the CrO_3 units in the crystal lattice.

It is interesting to note the marked difference in the behavior of α-picoline toward chromic anhydride and that of β- and γ-picoline. The former amine apparently has a much less tendency to coördinate with chromic anhydride and a much greater tendency to be oxidized by that substance than do the β- and γ-picolines. The latter effect is to be expected for it is a well known fact that an α-methyl group on a pyridine ring is of the activated type and is, therefore, more susceptible to oxidation than are β- or γ-methyl groups. The lesser tendency of α-picoline toward coördination with chromic anhydride may result, in part at least, from the steric interference of the methyl group with a CrO_3 molecule approaching the neighboring nitrogen atom.

Summary

The reactions of chromic anhydride with pyridine, α-picoline, β-picoline, γ-picoline, quinoline and isoquinoline have been studied. The compounds $CrO_3{\cdot}2C_5H_5N$, $CrO_3{\cdot}2C_6H_7N(\beta)$, $CrO_3{\cdot}2C_6H_7N(\gamma)$ and $CrO_3{\cdot}2$ quinoline have been prepared.

Chromic anhydride is almost completely reduced by isoquinoline at room temperature. α-Picoline is more easily oxidized by chromic anhydride than is β- or γ-picoline or pyridine, and has a lesser tendency to coördinate with chromic anhydride than the latter substances.

The reactions of $CrO_3{\cdot}2C_5H_5N$, $CrO_3{\cdot}2C_6H_7N(\beta)$ and $CrO_3{\cdot}2C_6H_7N(\gamma)$ with liquid ammonia at $-33°$ were carried out. These substances react with liquid ammonia in a manner similar to chromic anhydride itself and give a similar percentage of reduced chromium (about 25%).

COLUMBUS 10, OHIO

RECEIVED JUNE 24, 1948

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

On Physical Adsorption.[1] II. A Comparison of Methods of Estimating Surface Areas of Crystalline Solids by Gas Adsorption[2]

BY SYDNEY ROSS[3]

Introduction

The adsorption isotherms of ethane at −183° on cube crystals of sodium chloride and potassium chloride have been reported.[4] The results obtained were interpreted as indicative of a two-dimensional phase transition of ethane. The nature of these isotherms makes it possible to compare some of the methods that have been proposed for estimating the surface area of crystalline solids by means of gas adsorption. The great practical utility of the methods involved is proffered as justification for the subject of this report.

The BET[5] method of obtaining the surface area

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(1) The first paper of this series (see ref. 4) will be published within the next few months.

(2) This document is based on work performed under Contract No. W-35-058, eng 71 for the Atomic Energy Project at the Clinton Laboratories (now Oak Ridge National Laboratory). Presented before the Division of Colloid Chemistry at the 113th national meeting of the American Chemical Society, Chicago, Illinois, April 19–23, 1948.

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(4) S. Ross and G. E. Boyd, "New Observations on Two-Dimensional Condensation Phenomena." Presented at the 111th meeting of the American Chemical Society, Atlantic City, N. J., April 14–18, 1947. See Abstracts of Papers, p. 33P, No. 52. Also see MDDC 864 (Office of Technical Services, Department of Commerce, Washington, D. C.).

(5) S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938); P. H. Emmett, "Advances in Colloid Science," Vol. I, New York, 1942, pp. 1–36.