port an Sn2 FS process with solvent. Clearly, in situations of this type, the use of non-aqueous solvents obscures without in any way eliminating the importance of the solvent as a catalyst for net displacement reactions.

Another type of evidence that has been cited in favor of the Sn1 mechanism is that the aquation rates of acidoammine complexes increases as the bulkiness of the ammine groups is increased through methyl or other substitution.[13] Here again, however, the same effect would be expected were the process Sn2 FS. Thus most of the arguments for an Sn1 process do not actually distinguish between it and bimolecular front side displacement. An important exception is the observation by Mathieu[14] that the solvation process is stereospecific; he found that $Coen_2NH_3Br^{++}$ underwent mutarotation to the corresponding monoaquo complex without racemization and .with retention of configuration. While this would be expected if the process were Sn2 FS, it is difficult to see why the pentacoördinated intermediate demanded by an Sn1 mechanism should retain optical activity.

Not only does the available evidence indicate that reactions considered to be Sn1 are actually Sn2 FS, but, in addition, certain reactions thought

to be normal Sn2 in type may well belong to the more special category. For example, Basolo[3] considered that the fact that the aquation rate of $Coen_2NO_2Cl^+$ was about normal rather than very slow to be evidence that the mechanism was Sn2. Actually the NO_2^- should form good hydrogen bond bridging with water, and the rate would not be expected to be abnormal if the Sn2 FS mechanism were involved.

On the other hand, those substitution reactions of type 11 whose rate is first order in Y^- are presumably not Sn2 FS. While they could be normal Sn2 in type, it probably is significant that they occur only where Y^- is basic (OH^- in water, CH_3O^- in methanol, in the case of acidopentammines and tetrammines, and CN^-, OH^- and $C_2H_3O_2^-$ in the case of KR in nitromethane containing solvents), or under circumstances such that ion pair formation between MX and Y^- is likely (see ref. 6). Such reactions may thus be Sn2 CB or Sn2 IP in nature; their detailed discussion is beyond the scope of the present paper.

Los Angeles, California

(13) R. G. Pearson, C. R. Boston and F. Basolo, This Journal, 75, 3089 (1953).

(14) J. P. Mathieu, Bull. soc. chim. France, [5] 4, 687 (1937).

# New Preparation for Chromyl Fluoride and Chromyl Chloride

By Gerald D. Flesch and Harry J. Svec

Uncontaminated chromyl fluoride and chromyl chloride have been prepared by the reaction of dry CrO_3 with CoF_3 or $AlCl_3$. The mixed halide, CrO_2FCl, was produced by the metastatic reaction of the two pure compounds. The equilibrium constant for this reaction and the infrared spectra of the mixed halide are presented.

Methods for preparing chromyl fluoride[1] and chromyl chloride,[2] as well as many of their physical properties, are well described in the literature. Many of these methods of preparation have been attempted here but have been found undesirable for various reasons. The methods often are not adaptable to small scale preparations, involve reactants difficult to handle or involve side reactions which result in mixtures difficult to purify. Simpler, more direct methods of preparation capable of producing a purer product were needed. Methods have been developed which fulfill these needs. Necessary manipulations in these methods are easy, handling of materials is reduced to a minimum, and an uncontaminated product results. The general procedure involves mixing dry CrO_3 with an appropriate dry halogenating agent, heat-

ing the mixture in a glass or an all-metal vacuum apparatus and collecting the chromyl halide in a trap cooled in a bath of solid CO_2-trichloroethylene slush.

The mixed halide, CrO_2ClF, was prepared by combining pure CrO_2F_2 with pure CrO_2Cl_2. Its infrared spectrum was determined and a tentative equilibrium constant, K_{liq}, was determined for the reaction

$$CrO_2F_2 + CrO_2Cl_2 \rightleftharpoons 2CrO_2ClF \qquad (1)$$
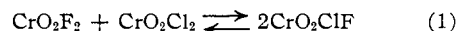
Experimental

Apparatus.—The vacuum pumping system to which the apparatus was attached consisted of a mechanical pump, mercury diffusion pump, liquid nitrogen cold trap, thermocouple vacuum gage and packless, bellows type valves (Hoke M482). Because of the corrosive nature of the reactants and products, the reaction apparatus was made of copper, nickel, monel and stainless steel. It consisted of three pieces, a monel reaction tube, a copper connecting tube and a copper U-tube fitted with Hoke valves at either end. Stainless steel or monel fittings (Hoke S24) were used to join the three pieces into a unit and connect the unit to the vacuum system. The U-tube served as the sample collector and storage vessel.

(1) (a) K. Fredenhagen, Z. anorg. allgem. Chem., 242, 23 (1939); (b) H. V. Wartenburg, ibid., 247, 135 (1941); (c) K. Wiechert, ibid., 261, 315 (1950); (d) A. Engelbrecht and A. V. Grosse, This Journal, 74, 5262 (1952).

(2) H. H. Sisler, "Inorganic Syntheses," W. C. Fernelius, ed., Vol. II, 1st Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 205.
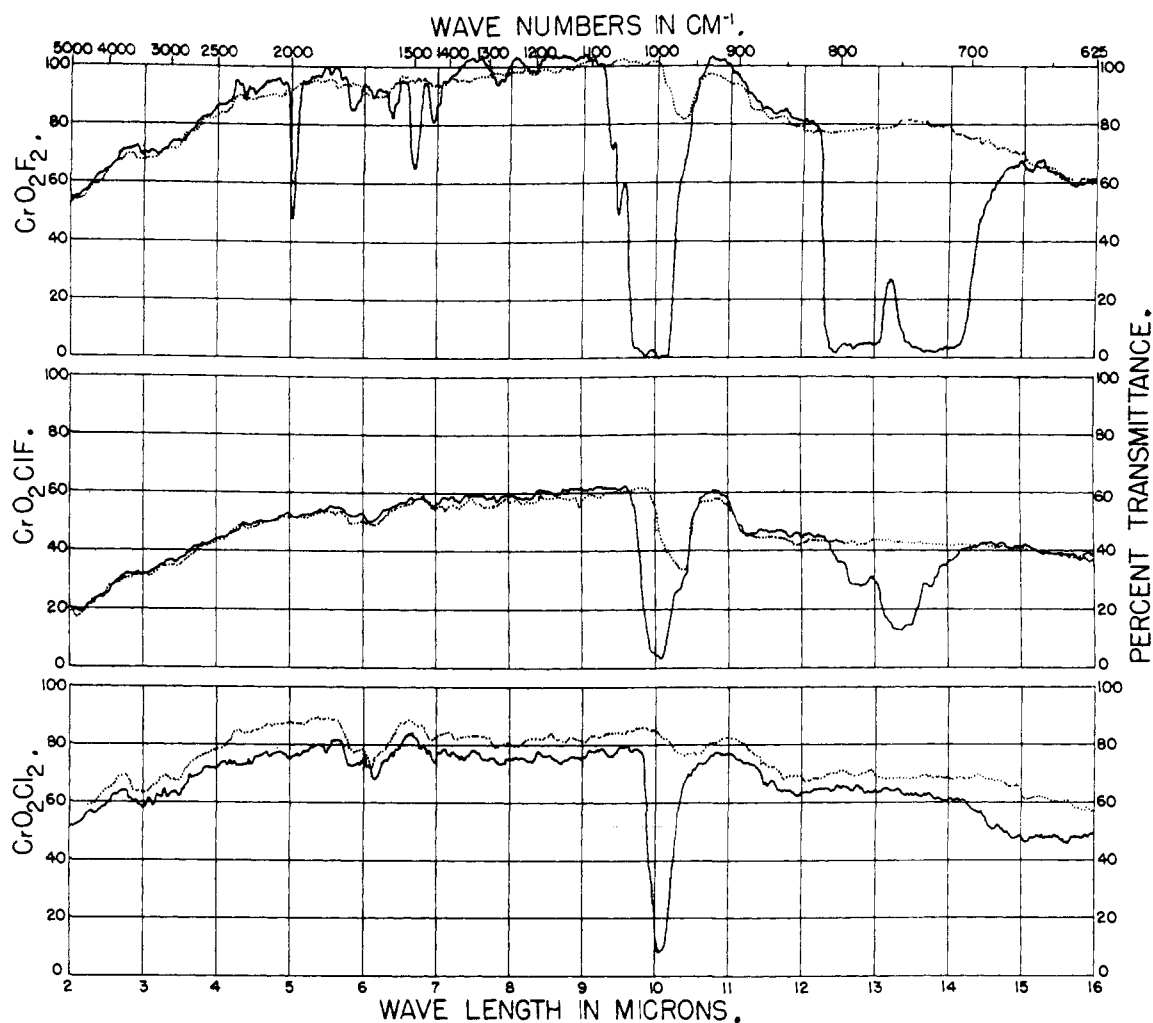
Fig. 1.—Infrared spectra of chromyl fluoride, chromyl chlorofluoride and chromyl chloride.

When the chloride preparation was to be used immediately, a modified apparatus was used. The three-piece metal unit was replaced by a corresponding one-piece unit of glass attached to a valve with a glass-to-metal seal.

CrO_2F_2.—Technical trade CrO_3 was vacuum dried overnight at 110°, then placed in a dry-box where all the handling of the reactants took place. Equal amounts of CrO_3 and CoF_3 were finely ground and intimately mixed. The mixture was placed in the monel reaction tube, removed from the dry-box, placed on the vacuum system and evacuated. A furnace was then placed around the reaction tube and the tube initially heated to 200°. This served to outgas the reactants and reaction tube but was not sufficient to start the reaction. The tube was kept at that temperature for ten minutes, or until the pressure returned to normal or near normal for the all-metal vacuum apparatus. Solid CO_2-TCE slush was placed around the U-tube and the temperature of the furnace raised to 450°. The reaction took place rapidly with an over-all increase in pressure due to a product not retained in the liquid nitrogen cold trap of the vacuum pumping system. When the pressure returned to near normal, the reaction was essentially completed. The product contained impurities estimated to be less than one per cent., with the principal impurity being HF.

CrO_2Cl_2.—The procedure for preparing the chloride was the same as that for the fluoride up to the point at which the reaction tube was placed on the vacuum system, except that anhydrous $AlCl_3$, as received, was used as the halogenating agent. Because the reaction producing the CrO_2-Cl_2 is quite rapid even at room temperature and under atmospheric pressure, the product forms as soon as the reactants are mixed. Therefore, some loss of the product occurs during the initial evacuation of the apparatus. To avoid

further loss, no outgassing of the apparatus or reactants was attempted, the solid CO_2-TCE slush being placed about the U-tube immediately after evacuation for collection of the product. Although the rate of the reaction was greater at temperatures above room temperature, contamination of the product also was greater. In addition, care had to be exercised because too high a temperature caused melting of the solid reactants. The purest product was obtained when the reaction was run at room temperature. The primary product was 99+% pure as determined mass spectrometrically, the principal impurity being HCl.

CrO_2ClF.—Pure CrO_2F_2 and pure CrO_2Cl_2 were vacuum distilled into a common U-tube and the mixture allowed to stand for several days. The products were examined mass spectrometrically and identified as CrO_2Cl_2, CrO_2F_2 and CrO_2ClF. The total ion current was measured and the current due to each species calculated. The relative ionization sensitivity of each species was estimated by the method of Otvos and Stevenson.[3] From the sensitivity, the relative concentration of each species in the vapor phase was computed. From the known vapor pressure of pure chloride[4] and pure fluoride,[1d] and on the assumption that the vapor pressure of the mixed halide was the geometric mean of those of the pure halides, the relative concentrations of each species in the liquid phase was estimated. On this basis, the equilibrium constant of the liquid phase was calculated to be 2.0.

The infrared spectra of the pure fluoride, pure chloride and the mixture indicated in (1) are shown in Fig. 1. These were obtained with a 10 cm. gas cell at the room temperature

(3) J. W. Otvos and D. P. Stevenson, This Journal, 78, 546 (1956).

(4) E. Moles and L. Gomez, Z. physik. Chem., 80, 513 (1912).

vapor pressure of the compounds in question. (Model B Infra-Red Spectrophotometer, Baird Associates Inc., Cambridge, Mass.) The spectra of the pure compounds compare favorably with those found by Hobbs.[5] They indicate

(5) W. E. Hobbs, "The Infrared Spectrum of Chromyl Fluoride," U. S. A.E.C. Report No. K-1325, July, 1957.

that the absorption band at 750 cm.$^{-1}$ is characteristic of the mixed halide.

The mass spectra of these compounds will be reported in another publication.

AMES, IOWA

The Complexes of Pyridinaldazine with Iron(II) and Nickel(II). II

BY WILMER J. STRATTON AND DARYLE H. BUSCH

Pyridinaldazine (PAA) has been shown to react with iron(II) and nickel(II) to form compounds of the type $[M_2(PAA)_3]X_4$ which are believed to involve a dinuclear cation, with each ligand coördinated in a tetrafunctional manner. In solution the iron(II) compound has been shown to dissociate one metal ion, approaching an equilibrium according to the equation $[Fe_2(PAA)_3]^{+4} \rightleftarrows [Fe(PAA)_3]^{+2} + Fe^{+2}(aq)$. Each ligand is then coördinated in a difunctional manner. Evidence for the $[Fe(PAA)_3]^{+2}$ ion has been obtained from a continuous variations study of the absorption spectrum and from a mole ratio study of the magnetic susceptibility. Preliminary kinetic data for the above reaction were obtained from both absorption spectra and magnetic susceptibility data, and the equilibrium constant has been evaluated. A further equilibrium has been shown to exist according to the equation $2[Fe(PAA)_3]^{+2} + Fe^{+2}(aq) \rightleftarrows 3[Fe(PAA)_2]^{+2}$. The rate at which this second process occurs is much slower than that associated with the first reaction.

Introduction

The preparations of the complexes of iron(II) and nickel(II) with 2-pyridinaldazine (structure I) have been described in an earlier paper.[1] Com-

I
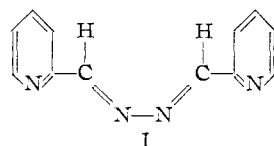
pounds of the type $[M(PAA)_2]X_2$ can be prepared by the addition of pyridinaldazine (PAA) to an aqueous solution of the metal salt, followed by heating on a steam-bath for a few minutes. Compounds were prepared in which M was iron(II) or nickel(II) and X was the iodide, perchlorate or fluoroborate ion. These compounds were of the expected type in which each ligand is presumed to coordinate in a tridentate manner, with one of the azine nitrogens being used in coördination (structure II). The iron compounds were found to be essentially diamagnetic, and conductivity data were

II
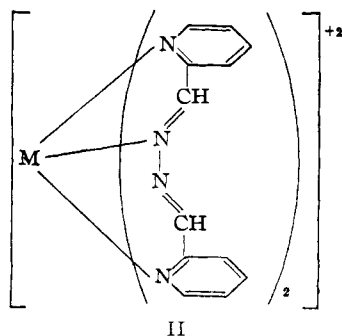
in agreement with the formulation of the compounds as electrolytes of the MX_2 type.

If, however, solutions of ligand and metal ion are kept at room temperature and crystallized by cooling fairly rapidly, compounds with the empirical formula $M_2(PAA)_3X_4$ are obtained. The iron com-

(1) W. J. Stratton and D. H. Busch, THIS JOURNAL, 80, 1286 (1958).

pounds were found to be diamagnetic in the solid state, indicating that both metal ions are involved in coördination. The structure of these $M_2(PAA)_3X_4$ compounds presents an intriguing problem, and this paper is devoted to some studies which have been undertaken in an effort to elucidate their nature. The authors have previously suggested that the structures of these substances probably involve a dinuclear cation, $[M_2(PAA)_3]^{+4}$. Magnetic susceptibilities of the iron compounds, conductivity data and the existence of salts with anions of poor coördinating ability all support this hypothesis. Conductivity data in 10^{-3} M solutions were interpreted as representing the MX_4 electrolyte type with a large unsymmetrical cation, but it was pointed out that the same data would also support a structure involving free metal salt, $[M(PAA)_3]X_2 \cdot MX_2$. The diamagnetism of the crystalline iron compounds seemed to rule out the latter structure, however.

Experimental

Spectrophotometric Measurements.—All measurements of spectra in the visible region were carried out with a Cary Recording Spectrophotometer, Model 10, using matched one centimeter quartz cells.

Magnetic Measurements.—The magnetic measurements were carried out with a Gouy type balance, using a Consolidated Engineering Corporation magnet and power supply which were operated at a field strength of approximately 8000 gauss. The study of susceptibility as a function of mole ratio was made using a balance of 0.1 mg. sensitivity, while the study of susceptibility as a function of time was carried out with a balance of 0.01 mg. sensitivity. Both studies used 25 ml. of solution in a tube of 19 mm. diameter fitted with a standard taper cap.

Results

Visible spectra are shown in Fig. 1 for $Fe_2(PAA)_3$-I_4 (curve A, 1 × 10^{-4} M), and $[Fe(PAA)_2]I_2$ (curve B, 2 × 10^{-4} M). Curve C was obtained using the solution of $Fe_2(PAA)_3I_4$ (10^{-4} M) after it had stood for 70 hr. and is assumed to represent an equilibrium mixture of complexes. A spectrum similar to C may be obtained by allowing a dilute solution of $Fe(PAA)_2I_2$ to reach equilibrium.