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The Synthesis of Oxyhalides Utilizing Fused-Salt Media

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In a molten equimolar lithium chloride–sodium chloride–potassium chloride mixture, anhydrous aluminum chloride has been found to react with several oxides or oxyanions of various nonmetals and high oxidation state transition metals to produce the corresponding acid chlorides. The compounds $VOCl_3$, $POCl_3$, NOCl, NO_2Cl, CrO_2Cl_2, $SeOCl_2$, CH_3COCl, and C_6H_5COCl were prepared. In several instances the yields or convenience of preparation exceed those realized in current synthetic methods.

Introduction

In 1939 Lux[2] presented a concept of acid–base behavior for fused salt media in which an acid was defined as an oxide ion acceptor and a base was defined as an oxide ion donor. The formal relationship between an acid and a base was represented as

$$\text{base} \rightleftharpoons \text{acid} + O^{2-}$$

In a series of articles, Lux and Flood have developed and illustrated this concept of acid–base reactions which is generally known as the Lux–Flood theory.[3-6] In contrast to extensive studies involving physical measurements in fused salts[7,8] relatively little has been reported involving syntheses in these solvents. Spectroscopy in fused salts has indicated the existence of various complex species in these melts,[9,10] and the preparation of several coordination compounds has been reported.[11] Several interesting metathesis reactions have led to convenient syntheses.[12,13] Among the more interesting reactions in fused salts is the preparation of silane in 80% yield by treating a mixture of metallic aluminum and silicon dioxide, or any of a variety of silicates, in an aluminum chloride–sodium chloride eutectic with hydrogen under a pressure of 400 atm.[14]

Duke[15,16] has reported reaction kinetics in fused salts, and the results obtained in his work have provided suggestions for synthetic work. The reactions of dichromate and of pyrosulfate in nitrate melts are of particular interest because evidence for the existence of nitryl ions has been obtained from these investigations, *e.g.*

$$S_2O_7^{2-} + NO_3^- \rightleftharpoons NO_2^+ + 2SO_4^{2-}$$

$$NO_2^+ + NO_3^- \longrightarrow 2NO_2 + {}^1/_2O_2$$

In the first step, equilibrium is established rapidly and the second step is slow. The order of the second step in nitryl ion is unity, and the order in nitrate ion cannot be determined because it is a part of the solvent. The pyrosulfate ion acts as a Lux–Flood acid in the above reaction,[15] by abstracting oxide ion from NO_3^-.

It was believed that cationic species such as the nitryl ion might be made to undergo reactions which could be utilized as preparative methods for compounds derived from this or similar cationic species. For example, the formation of nitryl ions in the presence of high concentrations of chloride ions should result in the formation of nitryl chloride. By analogy other oxychlorides could be prepared by forming oxygen-containing cations in the presence of chloride ions. In several instances, convenient, high-yield preparative methods have resulted.

Experimental Section

Reagent grade chemicals were used without further purification except as otherwise indicated. Nonhygroscopic solids were dried overnight at 110°, and hygroscopic solids were dried in a vacuum desiccator over anhydrous phosphorus(V) oxide. All transfers of chemicals were made inside a drybox.

The lithium chloride–sodium chloride–potassium chloride mixture was prepared by mixing together equimolar quantities of the anhydrous salts after the sodium chloride and potassium chloride had been dried overnight at 110°. Lithium chloride and

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[1] Abstracted in part from the Ph.D. Thesis of K. W. Whitten, University of Illinois, 1965.

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TABLE I

PREPARATIVE CONDITIONS FOR THE SYNTHESIS OF VARIOUS OXYHALIDES

Starting materials[a]	Yield,[b] %	Identification[c]
		$VOCl_3$
V_2O_5 (45 g, 0.247 mole) $AlCl_3$ (65 g, 0.487 mole)	72 (V_2O_5)	Calcd. for $VOCl_3$ V, 29.40. Found: V, 29.37. Bp 127–128.5° (127)[d]
$NaVO_3$ (50 g, 0.410 mole, Fisher Scientific) $AlCl_3$ (74 g, 0.555 mole)	99 ($NaVO_3$)	Boiling point (see above). Calcd for $VOCl_3$: V, 29.40. Found: V, 29.80
		$POCl_3$
P_4O_{10} (75 g, 0.264 mole) $AlCl_3$ (53 g, 0.397 mole)	98 ($AlCl_3$)	Bp 105–106° (105.3°).[e] Calcd for $POCl_3$: P, 20.20; Cl, 69.36. Found: P, 19.92; Cl, 69.03
		NOCl
KNO_2 (30 g, 0.353 mole) $AlCl_3$ (35 g, 0.262 mole)	52 (KNO_2)	Calcd for NOCl: Cl, 54.16. Found: Cl, 54.20
		NO_2Cl
KNO_3 (40 g, 0.396 mole) $AlCl_3$ (35 g, 0.263 mole)	56 ($AlCl_3$)	Calcd for NO_2Cl: Cl, 43.52; N, 17.19. Found: Cl, 42.87; N, 18.10
		CrO_2Cl_2
CrO_3 (90 g, 0.90 mole) $AlCl_3$ (85 g, 0.637 mole)	57 (CrO_3)	Calcd for CrO_2Cl_2: Cr, 33.55. Found: Cr, 33.26. Bp 114–115° (117)[f]
		$SeOCl_2$
SeO_2 (59 g, 0.532 mole) $AlCl_3$ (43 g, 0.322 mole)	82 ($AlCl_3$) 74 (SeO_2)	Calcd for $SeOCl_2$: Se, 47.60. Found: Se, 47.16. Bp 176–177° (177°)[g]
		$C_6H_5C(O)Cl$
$NaOC(O)C_6H_5$ (90 g, 0.625 mole) $AlCl_3$ (71 g, 0.532 mole) "Chloride mixture" (350 g)	57 ($AlCl_3$)	Bp 196–197° (197°)[h]

[a] Unless indicated otherwise, 300 g of "chloride mixture" was used in each reaction. [b] Parentheses contain the materials on which the yield is based. [c] Parentheses contain the reported boiling point and the superscript indicates the reference [d] F. E. Brown and F. A. Griffiths, *Inorg. Syn.*, **1**, 106 (1939). [e] K. Arii, *Inst. Phys. Chem. Res.* (Tokyo), **8**, 545 (1929). [f] H. H. Sisler, *Inorg. Syn.*, **2**, 205 (1946). [g] G. B. L. Smith and J. Jackson, *ibid.*, **3**, 130 (1950). [h] R. L. Schriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 274.

anhydrous aluminum chloride were used without additional drying and were never exposed to atmospheric moisture. We did not investigate other chloride mixtures but there is no a priori reason to suspect they will not work.

The reaction vessels were 7.5 × 35 cm Pyrex or Vycor cylinders fitted with standard taper 24/40 outer joints. A standard taper 24/40 connecting tube was used to connect the reaction vessel to a vacuum distillation assembly. The receiving vessels were 3.5 × 20 cm cylinders fitted with standard taper 24/40 outer joints. Vacuum adapters with long delivery tubes connected the water-cooled condenser to the receiving vessels. The dried apparatus was flushed with nitrogen after assembly and the exit tube connected to drying traps. In collecting those compounds that were solids at the temperature of the baths in which the receiving vessels were immersed, a 1.2 × 8 cm piece of glass tubing was sealed to the short delivery tube of a vacuum adapter. This arrangement prevented obstructions in the adapter delivery tubes caused by the formation of solids. The receiving cylinders were immersed in dewars which were filled with water–ice–salt, Dry Ice–acetone, or liquid nitrogen depending on the melting point and boiling point of the compound being collected. In some preparations a series of two or three receivers immersed in different cooling baths was employed.

The reaction mixtures were heated with a Hevi-Duty Electric Co. Type M-3012 furnace mounted vertically. Temperatures were measured with a chromel–alumel thermocouple and a Thermo Electric Manufacturing Co. Model PM-1K50 Temco portable pyrometer.

Previously dried solid reactants and the lithium chloride–sodium chloride–potassium chloride mixture (hereafter referred to as the "chloride mixture") were placed in dry reaction vessels inside the controlled atmosphere box and shaken vigorously for at least 5 min. The quantities of materials employed in most of the experiments are indicated in Table I. The reaction vessel was then placed in the furnace under the vacuum distillation apparatus, and the temperature of the reaction mixture was increased slowly. The heating period for each preparation is indicated under the individual reactions together with any special precautions or unusual observations. In some of the preparations it was found that better results were obtained if the reactions were run under reduced pressures, and such conditions are indicated appropriately.

The compounds prepared in this investigation were liquid or gaseous at room temperature, and purifications were effected by fractional distillation. Yields of purified products are reported in Table I. Most analyses were conveniently performed by classical volumetric or gravimetric methods.

Results

(A) The Preparation of Vanadium Oxytrichloride from Vanadium(V) Oxide and Sodium Metavanadate.—The vessel containing the reaction mixture of vanadium(V) oxide, anhydrous aluminum chloride, and "chloride mixture" was evacuated and heated to 450° over a period of 4 hr. Most of the reaction mixture was molten at this temperature, but a small amount of solid material remained undissolved. Evolution of $VOCl_3$ began at approximately 100° and the reaction was essentially complete when the temperature reached 250°, even though the reaction mixture was only partially molten at this temperature. The product, $VOCl_3$, is a yellow liquid. The reaction of vanadium(V) oxide with aluminum chloride in the "chloride mixture" may be represented as

$$V_2O_5 + 2AlCl_3 \longrightarrow 2VOCl_3 + Al_2O_3$$

The Vycor reaction vessel containing the sodium metavanadate, anhydrous aluminum chloride, and "chloride mixture" was evacuated and heated to 600° over a period of 6 hr. At approximately 200° vanadium oxytrichloride began to distil out and evolution continued until the temperature reached 400°. At this temperature the reaction mixture was completely molten except for a small amount of green solid on the bottom of the vessel.

The reaction of sodium metavandate with aluminum chloride in the chloride eutectic may be formulated as

$$3NaVO_3 + 4AlCl_3 \longrightarrow 3VOCl_3 + 3NaCl + 2Al_2O_3$$

(B) The Preparation of Phosphorus Oxytrichloride from Phosphorus(V) Oxide.—A reaction mixture of phosphorus(V) oxide, anhydrous aluminum chloride, and "chloride mixture" was heated over a period of 6 hr to 600° (Vycor vessel). Evolution of $POCl_3$ began at approximately 350° and continued until the temperature of the reaction mixture reached approximately 500°. The reaction of phosphorus(V) oxide with anhydrous aluminum chloride may be represented as

$$P_4O_{10} + 4AlCl_3 \longrightarrow 4POCl_3 + 2Al_2O_3$$

It is of interest to note that when phosphorus(V) oxide was heated with the "chloride mixture" with no anhydrous aluminum chloride present some phosphorus oxytrichloride was produced together with some free chlorine. This observation may be interpreted by assuming that the lithium ion acts as a Lux-Flood acid and forms the corresponding oxide, resulting in the formation of phosphorus oxytrichloride.

Phosphorus oxytrichloride was obtained in lower yield when sodium metaphosphate was employed instead of phosphorus(V) oxide. No volatile compounds were obtained when potassium orthophosphate or sodium pyrophosphate were employed.

(C) The Preparation of Nitrosyl Chloride from Potassium Nitrite.—A reaction mixture of potassium nitrite, anhydrous aluminum chloride, and "chloride mixture" was heated slowly.

Two receivers in series were cooled in an ice–salt bath and a Dry Ice–acetone bath. When the temperature reached 150° evolution of a yellow-brown gas began. Over a period of 15 hr the temperature of the reaction mixture was cautiously increased to 375°. The red liquid which collected in the ice–salt cooled receiver was discarded. The Dry Ice–acetone cooled receiver contained a bright red solid which was allowed to melt and evaporate and then pass through a series of three drying tubes which contained (1) sodium nitrate, (2) potassium chloride plus 2.4% water, and (3) anhydrous calcium chloride. This was followed by refluxing in a Dry Ice–acetone cooled condenser.[17] The product, a blood-red solid, was then condensed in a flask cooled in a Dry Ice–acetone bath. Too rapid a heating rate resulted in a product which contained such large amounts of oxides of nitrogen impurities that purification was impractical. None of the reported preparations and purifications of nitrosyl chloride is quite so simple as may be commonly believed. By careful work, reasonable quantities of nitrosyl chloride of a high degree of purity can be prepared conveniently by this molten salt reaction.

The reaction of potassium nitrite with anhydrous aluminum chloride to produce nitrosyl chloride may be formulated as

$$3KNO_2 + 2AlCl_3 \longrightarrow 3NOCl + 3KCl + Al_2O_3$$

(D) The Preparation of Nitryl Chloride from Potassium Nitrate.—The reaction mixture of potassium nitrate, anhydrous aluminum chloride, and "chloride mixture" was heated to 400° over a period of 16 hr. A series of two receivers, the first cooled in an ice–salt bath and the second in a Dry Ice–acetone bath, was used to collect the product. The apparatus was tightly wrapped in aluminum foil to exclude light. At approximately 150° the evolution of brown vapors began. As the temperature of the reaction mixture was increased to 400° large amounts of brown gas were evolved. Several milliliters of red liquid collected in the receiver cooled in the ice–salt bath, and this material was discarded. The bright red liquid in the receiver which was cooled in the Dry Ice–acetone bath was slowly distilled twice through a series of three receivers immersed in an ice–salt bath and then collected in a Dry Ice–acetone bath as a yellow liquid. Again, the entire apparatus was tightly wrapped with aluminum foil to exclude light.

Pure nitryl chloride is a colorless liquid at −78°. The analysis of the yellow material prepared by the above procedure indicated that the nitryl chloride was relatively pure, and no attempt was made to remove the remaining impurities. The low chloride content, high nitrogen content, and yellow color of the nitryl chloride indicated that the impurities were probably oxides of nitrogen.

Extreme caution must be exercised in slowly raising the temperature of the reaction mixture to obtain significant yields of nitryl chloride. A large excess of aluminum chloride must also be avoided to prevent the formation of unduly large amounts of nitrogen(IV) oxide.

The equation for the reaction of potassium nitrate with anhydrous aluminum chloride may be represented as

$$3KNO_3 + 2AlCl_3 \longrightarrow 3NO_2Cl + 3KCl + Al_2O_3$$

(E) The Preparation of Chromyl Chloride from Chromium(VI) Oxide.—The reaction mixture of chromium(VI) oxide, anhydrous aluminum chloride, and "chloride mixture" was prepared. Evolution of chromyl chloride began as soon as the reactants were shaken together, hence the reaction flask had to be placed under the vacuum distillation apparatus immediately. The receiving vessel was cooled in a Dry Ice–acetone bath, and the reaction system was evacuated throughout the course of the reaction. The entire reaction system was tightly wrapped with several layers

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[17] J. R. Morton and H. W. Wilcox, *Inorg. Syn.*, **4**, 48 (1953).

of aluminum foil to protect the chromyl chloride from light.

The temperature of the reaction mixture was increased to 400° over a period of 6 hr. The mixture was only partially molten with a large amount of green solid, probably Cr_2O_3, remaining in the reaction vessel. The product was a deep red liquid which contained some free chlorine. The free chlorine was allowed to evaporate as the product warmed to room temperature prior to distillation through a 12-in. Vigreux column. The distillation apparatus was tightly wrapped with several layers of aluminum foil to exclude light.

The reaction of chromium(VI) oxide with aluminum chloride may be represented as

$$3CrO_3 + 2AlCl_3 \longrightarrow 3CrO_2Cl_2 + Al_2O_3$$

In this preparation of chromyl chloride the temperature of the reaction mixture must be increased slowly to prevent the formation of large quantities of chlorine and Cr_2O_3 with correspondingly reduced yields of chromyl chloride. Failure to evacuate the reaction system resulted in reduced yields of the desired product.

(F) The Preparation of Selenium(IV) Oxychloride from Selenium(IV) Oxide.—An intimate mixture of selenium(IV) oxide and anhydrous aluminum chloride was placed in a Vycor reaction vessel, and 300 g of the "chloride mixture" was placed on top of the selenium(IV) oxide–aluminum chloride mixture. The reaction flask was placed under the vacuum distillation apparatus and the receiver was immersed in an ice–salt bath. The reaction mixture was heated slowly at atmospheric pressure until vapors of selenium(IV) oxychloride were observed condensing in the top of the reaction vessel (approximately 200°). This procedure was necessary to prevent the sublimation of selenium(IV) oxide before the reaction began. The reaction mixture was increased to 500° over a period of 3 hr.

The product was a yellow liquid which contained some suspended solid material. The solid material was removed by filtration through glass wool inside the drybox and purified by three successive distillations through an 8-in. Vigreux column.

The preparation of selenium(IV) oxychloride by the reaction of selenium(IV) oxide with aluminum chloride may be formulated as

$$3SeO_2 + 2AlCl_3 \longrightarrow 3SeOCl_2 + Al_2O_3$$

Throughout the preparation and purification of selenium(IV) oxychloride necessary precautions must be taken to exclude moisture because the compound is quite sensitive to even traces of water. Smith and Jackson[18] have included specific instructions for handling this compound and all of these precautions were observed.

(G) The Preparation of Phosphorus(V) Sulfochloride from Phosphorus(V) Sulfide.—A reaction vessel containing a mixture of 113 g of anhydrous iron(III) chloride (0.698 mole), 100 g of phosphorus(V) sulfide (0.227 mole), and 300 g of "chloride mixture" was evacuated, heated to 400° over a period of 4 hr, and then maintained at this temperature for an additional 2 hr. Two receiving vessels, the first cooled in an ice–salt bath and the second in a Dry Ice–acetone bath, were used to collect the product. The reaction product was 35 ml of pale yellow liquid. The solid material which was suspended in the product was removed by filtration, and two distillations of the product through an 8-in. Vigreux column gave 21.3 g of a colorless liquid which distilled at 123–124° *vs.* a reported boiling point of 125°[19] for phosphorus(V) sulfochloride. This represents an 18% yield of phosphorus(V) sulfochloride based on the amount of anhydrous iron(III) chloride taken as a starting material or a 14% yield based on phosphorus(V) sulfide. *Anal.* Calcd for $PSCl_3$: S, 18.29; P, 18.93. Found: S, 17.88; P, 18.64.

During the course of the reaction large amounts of sulfur and iron(III) chloride sublimed out of the reaction vessel, and a great deal of hydrogen sulfide was evolved. The reaction of phosphorus(V) sulfide with anhydrous iron(III) chloride may be formulated as

$$P_4S_{10} + 4FeCl_3 \longrightarrow 4PSCl_3 + 4FeS + 2S$$

Attempts to prepare phosphorus(V) sulfochloride from phosphorus(V) sulfide and anhydrous aluminum chloride were unsuccessful. Large amounts of sulfur sublimed out of the reaction mixture, and only very small amounts of liquid were collected in the receivers.

(H) The Preparation of Benzoyl Chloride from Sodium Benzoate.—A reaction mixture of sodium benzoate, anhydrous aluminum chloride, and "chloride mixture" was slowly heated to 200° at atmospheric pressure and colorless vapors were observed condensing in the top of the reaction vessel. The reaction system was then evacuated, and the temperature of the reaction mixture was increased to 475° over a period of 3 hr. The reaction was essentially complete at 400°. As the temperature of the reaction mixture was increased above 400°, a small amount of solid material with an aromatic odor sublimed out of the reaction mixture and solidified in the water-cooled condenser.

In successive preparations of benzoyl chloride, the crude product was either a deep green or purple liquid. Two successive vacuum distillations of the crude product through a 12-in. Vigreux column gave pure material. The infrared spectrum of the benzoyl chloride prepared by this method was identical with the infrared spectrum of a reagent grade sample of benzoyl chloride.

The reaction does not appear to be especially sensitive to the presence of excess aluminum chloride, since the yields did not vary appreciably when larger than stoichiometric amounts of aluminum chloride were used. The reaction of sodium benzoate with aluminum chloride may be represented as

$$3C_6H_5CO_2Na + 2AlCl_3 \longrightarrow 3C_6H_5COCl + 3NaCl + Al_2O_3$$

The deep coloration of the crude product together with the formation of small amounts of solid materials with aromatic odors indicates that some of the sodium

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[18] Table I, footnote g.

[19] H. S. Booth and M. C. Cassidy, *J. Am. Chem. Soc.*, **62**, 2369 (1940).

benzoate reacts with itself, with benzoyl chloride, or its thermal decomposition products *via* a Friedel–Crafts mechanism. There was a considerable amount of carbonaceous material in the reaction vessel.

Attempts to prepare thiobenzoyl chloride from monothiobenzoic acid salts by this method were not successful. It was found, however, that acetyl chloride could be prepared by this technique from sodium acetate in 25% yield based on sodium acetate.

(I) **The Preparation of Sulfuryl Fluoride from Potassium Pyrosulfate and Sodium Fluoride.**—The reaction mixture of 63 g of sodium fluoride (1.5 moles) and 254 g of recently fused and finely ground potassium pyrosulfate (1 mole) was placed in a Vycor reaction vessel, mixed thoroughly, and heated to 450° over a period of 3 hr. A series of three receiving vessels cooled in (1) ice–salt, (2) Dry Ice–acetone, and (3) liquid nitrogen was used to collect the product.

The liquid which condensed in the Dry Ice–acetone cooled bath was allowed to distil into the liquid nitrogen bath and was then purified by two successive passes through a series of three 500-ml gas-washing bottles fitted with fritted glass dispersion tubes filled with saturated potassium iodide solution.[20] The product was dried by passing it through "Drierite."

Approximately 5 g of purified sulfuryl fluoride was obtained. This represented a 7% yield based on the amount of sodium fluoride taken as a starting material. Analyses were performed for fluoride and sulfate. *Anal.* Calcd for SO_2F_2: F, 37.23; S, 31.42. Found: F, 36.96; S, 30.89.

The reaction of sodium fluoride with molten potassium pyrosulfate to produce sulfuryl fluoride may be formulated as

$$2K_2S_2O_7 + 2NaF \longrightarrow SO_2F_2 + 2K_2SO_4 + Na_2SO_4$$

The product was highly contaminated with silicon tetrafluoride and the yield was low, but this reaction does provide a simple method for preparing small amounts of sulfuryl fluoride from readily available materials.

Discussion

The successful preparation of vanadium oxytrichloride, phosphorus oxytrichloride, nitrosyl chloride, nitryl chloride, chromyl chloride, selenium(IV) oxychloride, benzoyl chloride, and acetyl chloride by the reaction of aluminum chloride with oxides or oxyanions in the chloride eutectic indicates the general nature of this reaction. In order for a reaction of this type to be utilized as a preparative method, the reaction products should be volatile or have properties that would permit convenient separation from the complex reaction mixtures. The range of systems studied here indicates that a large number of stable oxides and oxyanions can very probably be easily converted to the corresponding oxyhalides. The high thermodynamic stability of the aluminum–oxygen bond undoubtedly provides a large driving force in these systems.

Of the reactions studied here, several constitute procedures which challenge present methods for preparation of the oxyhalides either from the standpoint of yield or convenience or both. It should be pointed out that extensive experimentation aimed at optimization of the yields was not undertaken.

Smith and Jackson[18,21] have outlined in detail the preparation of selenium(IV) oxychloride. In this procedure selenium(IV) oxide is converted to dichloroselenious acid by treatment with anhydrous hydrogen chloride and the dichloroselenious acid is then dehydrated with concentrated sulfuric acid. The preparation of selenium(IV) oxychloride from selenium(IV) oxide and anhydrous aluminum chloride in the "chloride mixture" gives only slightly higher yields, but the use of large quantities of anhydrous hydrogen chloride is eliminated together with the hazardous dehydration with concentrated sulfuric acid. The yield of selenium(IV) oxychloride is not reduced greatly if the reaction is run by a procedure similar to the one reported here but instead in a round-bottom flask heated with an ordinary heating mantle. Consequently, this is a considerably simpler reaction to run than the usual preparations of selenium(IV) oxychloride.

The preparation of nitrosyl chloride from potassium nitrate and anhydrous aluminum chloride in the "chloride mixture" gives yields which compare favorably with the yields obtained by other preparative methods. The reaction requires no elaborate apparatus, and the procedure is simple. However, this preparation requires a long, uninterrupted period of time for the temperature of the reaction mixture must be increased very slowly to avoid excessive contamination by oxides of nitrogen.

The preparation of nitryl chloride by the procedure reported here is more convenient than the reported procedure involving the reaction of anhydrous nitric acid with chlorosulfonic acid.[22,23] Although very good yields are obtained by this latter procedure, the preparation of anhydrous nitric acid and the handling of the reactants are difficult.

The preparation of chromyl chloride by the reaction of chromium(VI) oxide with aluminum chloride in a "chloride mixture" gives lower yields than the procedure in *Inorganic Syntheses*,[24] but the reaction is not difficult to run, and this method gives a simple procedure by which the inexperienced chemist can obtain reasonable quantities of chromyl chloride of a high degree of purity with little effort.

Recently, Johannesen[25] developed a preparation of vanadium oxytrichloride which involved heating vanadium(V) oxide with anhydrous aluminum chloride. The vanadium oxytrichloride produced by this reaction contained no vanadium(IV) chloride, and its purifi-

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[20] E. L. Muetterties, *Inorg. Syn.*, **6**, 158 (1960).

[21] G. B. L. Smith and J. Jackson, *J. Am. Chem. Soc.*, **62**, 543 (1940).

[22] W. Steinkoff and M. Kuhnel, *Ber.*, **75**, 1323 (1942).

[23] H. Brintzinger and K. Pfannstiel, *Z. Anorg. Allgem. Chem.*, **255**, 325 (1948).

[24] Table I, footnote *f*.

[25] R. B. Johannessen, *Inorg. Syn.*, **7**, 119 (1960).

cation was much simpler than that for products of the classical preparations. Yields were 60% of the theoretical amount, which is about the same as those obtained by the more tedious classical procedures. However, when the reaction is run in the "chloride mixture" as reported here the yield is approximately 20% better than when the chloride is not present. In addition, the reaction occurs at temperatures low enough so that the reaction can be run in a 1-l. round-bottom flask in an ordinary heating mantle. This modification of Johannesen's procedure represents a significant improvement in the method for the preparation of vanadium oxytrichloride. The procedures reported here do not have any advantages over the conventional ways of preparing the other volatile halides reported in this article.

It is of interest to generalize about these reactions to aid in the extension of the reactions to other systems. The reactions of aluminum chloride with oxides to form acid chlorides may be formulated generally as

$$EO_m + nAlCl_3 \longrightarrow EO_xCl_y + {}^{n}/_{2}Al_2O_3 \qquad (1)$$

where E is the general symbol for an element. Undoubtedly, these formulations of the reactions are greatly oversimplified and the actual products may be various aluminum oxychlorides. The reactive aluminum-containing species is also unknown. It may be $AlCl_3$ or a cationic chloroaluminum complex. The chloride atoms which appear in the volatile acid chlorides likely come from the solvent rather than from aluminum chloride molecules or any chloroaluminum complex species. The greater concentration of chloride ion and the anticipated greater nucleophilicity of this species compared with the tetrachloroaluminate ion suggest this. Of course, rapid exchange of all chloride in this system is expected and eventual displacement of chloride from aluminum by oxide is indicated in eq 1. Two mechanisms which conveniently explain the experimentally observed facts can be proposed. One is an ionic mechanism in which the chloroaluminum species coordinates with an oxygen-containing species through the oxygen. The resulting complex is sufficiently polarized that the bond between the central element and the oxygen which is coordinated to the aluminum is broken, leaving a cationic species. This cation could then combine with one or more chlorides from the solvent to form the volatile oxychloride molecule. A second possibility would be an S_N2 mechanism, in which a neutral $AlCl_3$ molecule or a cationic chloroaluminum species could coordinate with an oxygen of an oxide or oxyanion. This could result in polarization of the central element–oxygen bond, so that a chloride ion could attack the relatively positive central element and an oxide ion could be displaced. When a cation is formed by displacement of oxygen by chlorine, additional chloride can be obtained from the solvent to form the volatile nonmetal halide.

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Notes

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF DELAWARE, NEWARK, DELAWARE

The Lattice Energy of Sodium Tetrachloroaluminate and the Heat of Formation of the Tetrachloroaluminate Ion[1]

BY R. H. WOOD AND L. A. D'ORAZIO

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In the past, most of the work on the interaction energies of donor–acceptor complexes has been limited to complexes with no net charge.[2] This restriction has been imposed by the difficulty of calculating lattice energy effects in solids and solvent effects in solutions. In the last few years, however, machine computation of electrostatic energies has been achieved, and lattice energy effects have become easily calculable.[3,4] The present paper reports the results of applying the crystal lattice energy calculation to the determination of the energy of the aluminum chloride–chloride ion complex.

Calculation of the Madelung Constant

The Madelung constant of $NaAlCl_4$ was calculated by the method of Wood[3a,5] for the crystal structure proposed by Baenziger.[6] He reports the symmetry[7] as $P2_12_12_1$ with $a = 10.36$, $b = 9.92$, and $c = 6.21$. The coordinates of the different kinds of atoms have been given by Baenziger.

The Madelung constant was calculated for the process

$$NaAlCl_4(c) \longrightarrow Na^+(g) + AlCl_4^-(g)$$

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(2) Reviews of several aspects of this subject are given in the chapters by R. J. Gillespie, M. Baaz and V. Gutman, D. R. Martin and J. R. Cannon, and N. N. Greenwood and K. Wade in "Friedel–Crafts and Related Reactions," G. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

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(5) The authors thank the Computing Center of the University of Delaware for the use of their facilities.

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