

both hexaethylidisilazane and N,N-dimethyltriethylsilylamine.

Tetrakis(triethylsilylamino)diborane(4) is a colorless, viscous liquid, stable at room temperature, but sensitive to moisture. It is soluble in nonpolar solvents such as toluene, ether, and cyclohexane. Tetrakis(triethylsilylamino)diborane(4) decomposes at 280° and reacts with dry hydrogen chloride. Ammonium chloride, triethylchlorosilane, and a small amount of a solid that reduces a solution of silver nitrate were formed in the hydrogen chloride reaction. The exact composition of this latter solid is not known, and further investigations will be carried out in an effort to identify both this substance and the products of the pyrolysis of tetrakis(triethylsilylamino)diborane(4).

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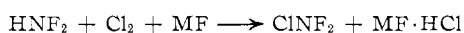
A Preparation of Chlorodifluoramine. Reaction of Chlorine and Difluoramine in the Presence of an Alkali Metal Fluoride

BY WILLIAM C. FIRTH, JR.

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Chlorodifluoramine has been prepared by the reactions of difluoramine with boron trichloride,^{2a} phosphine,^{2b} or hydrogen chloride.^{2b} It can also be obtained by treating a mixture of sodium azide and sodium chloride with fluorine.³ This paper reports the convenient synthesis of chlorodifluoramine by the reaction of chlorine and difluoramine in the presence of certain alkali metal fluorides.

The reaction appears to occur essentially as shown by the equation. Thus, chlorodifluoramine was formed in good yield when a gaseous mixture of equimolar amounts of chlorine and difluoramine was brought into contact with anhydrous potassium fluoride. The re-

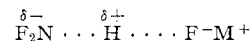


action was carried out in the dark to avoid possible photochemical reactions. The gaseous product amounted to 54% of the gaseous reagents charged and was mostly chlorodifluoramine according to infrared analysis. Purification of the gas by fractional codis-

tillation⁴ gave pure chlorodifluoramine in 66% yield. A control reaction showed that the potassium fluoride was necessary for significant reaction to occur.

Similar results were obtained when an excess of chlorine was allowed to react with difluoramine in the presence of rubidium fluoride. No other metal fluorides were investigated as possible catalysts.

The catalytic activity of the fluoride salt is probably due to the basic nature of fluoride ions.⁵ Interaction of the proton of difluoramine with a fluoride ion would increase the electron density on the nitrogen atom and hence promote electrophilic attack by chlorine.



Although the true intermediates involved are unknown, the postulation of an electrophilic attack by chlorine is supported by the known reaction of difluoramine with the Lewis acid, boron trichloride.^{2a}

Experimental

Caution.—Chlorodifluoramine and difluoramine are highly explosive compounds.⁶ Particular care must be used in condensing difluoramine.⁷

Vacuum line and drybox techniques were used, and the progress of the reactions was followed by infrared spectroscopy.⁸ The infrared spectrum of chlorodifluoramine has strong absorptions at 10.75 (triplet), 11.7 (doublet), and 14.4 (triplet)^{2a,8} μ and is easily distinguished from the spectrum of difluoramine, which has a strong triplet at 11.3 μ .⁹ The reactions were carried out in Pyrex glass bulbs. Joints and stopcocks were lubricated with Kel-F No. 90 grease, and a layer of Kel-F oil was used to protect the mercury manometer.^{2a}

The chlorine (Matheson Co.) was dried by repeated condensation onto phosphorus pentoxide. Finely ground anhydrous potassium fluoride (Baker and Adamson Co.) and anhydrous rubidium fluoride (American Potash and Chemical Co.) were used. They were handled in a drybox to avoid contact with atmospheric moisture. Difluoramine was prepared by the reaction of tetrafluorohydrazine with thiophenol.¹⁰

Reaction of Chlorine and Difluoramine in the Presence of Potassium Fluoride.—An equimolar mixture of chlorine and difluoramine was prepared by condensing⁷ the gases into a Pyrex glass bulb from which light was excluded by several layers of aluminum foil. The gases were allowed to equilibrate at ambient temperature. Part (1.3 mmoles) of the gaseous mixture was admitted to an evacuated 164-ml. Pyrex glass reactor (covered with aluminum foil) which contained 5.0 g. of potassium fluoride. After 18 hr. at ambient temperature, the product amounted to 0.7 mmole and was mostly chlorodifluoramine based on an infrared spectrum.^{2a,8} Analysis of the gas by fractional codistillation⁴ showed that only small amounts of impurities were present.

(4) G. H. Cady and D. P. Siegarth, *Anal. Chem.*, **31**, 618 (1959).

(5) L. Rand, J. V. Swisher, and C. J. Cronin, *J. Org. Chem.*, **27**, 3505 (1962), and references cited therein; E. A. Lawton and D. Filipovich, U. S. Patent 3,109,711 (1963), describe the reaction of difluoramine with alkali metal fluorides.

(6) The various types of shielding to be used with such compounds are described by C. L. Knapp, *Ind. Eng. Chem.*, **55**, No. 2, 25 (1963).

(7) Difluoramine can probably be condensed more safely at -142° than at -196° (ref. 2b). Solid difluoramine is particularly explosive (ref. 8), and a referee has pointed out that a condensing bath higher than -116° should be used. It does appear possible to condense mixtures of difluoramine and certain reagents at -196° .

(8) Actual spectra of difluoramine and chlorodifluoramine have been published (C. B. Colburn in "Advances in Fluorine Chemistry," M. Stacey, J. C. Tatlow, and A. G. Sharpe, Ed., Butterworths, Washington, 1963, p. 113).

(9) A. Kennedy and C. B. Colburn, *J. Am. Chem. Soc.*, **81**, 2906 (1959); J. J. Comeford, D. E. Mann, L. J. Schoen, and D. R. Lide, Jr., *J. Chem. Phys.*, **38**, 461 (1963).

(10) J. P. Freeman, A. Kennedy, and C. B. Colburn, *J. Am. Chem. Soc.*, **82**, 5304 (1960).

(1) This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by the Bureau of Naval Weapons, RMMP, under Contract No. NOrd 18728.

(2) (a) R. C. Petry, *J. Am. Chem. Soc.*, **82**, 2400 (1960); (b) E. A. Lawton and J. Q. Weber, *ibid.*, **85**, 3595 (1963).

(3) T. A. Austin and R. W. Mason, *Inorg. Chem.*, **2**, 646 (1963).

After purification by fractional codistillation, the yield of chlorodifluoramine isolated was 66%.

That part of the mixture of chlorine and difluoramine which was not contacted with the potassium fluoride was largely unchanged after 18 hr. in the dark at ambient temperature. The infrared spectrum showed strong difluoramine absorptions and only weak absorptions due to chlorodifluoramine.

Reaction of Chlorine and Difluoramine in the Presence of Rubidium Fluoride.—Chlorine (3.9 mmoles) and difluoramine (1.0 mmole) were condensed⁷ at -196° into a 220-ml. Pyrex glass reactor which contained 5.0 g. of rubidium fluoride. The reactor was allowed to warm to room temperature and then allowed to stand at room temperature for approximately 2 hr. An infrared spectrum then showed that all of the difluoramine had reacted and that chlorodifluoramine was a major product.

The product was purified by a method similar to that used by Petry.^{2a} The yield of purified material was 63%, but small amounts of impurities were present.

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Preparation of $\text{Ba}(\text{Na}_{0.25}\text{Ta}_{0.75})\text{O}_3$ and $\text{Sr}(\text{Na}_{0.25}\text{Ta}_{0.75})\text{O}_3$ with the Perovskite Structure

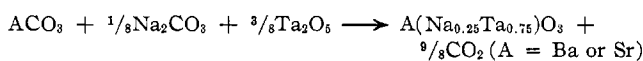
BY F. GALASSO AND J. PINTO

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The perovskite structure, when it is adopted by oxides with the general formula ABO_3 , can be described by a cubic unit cell with a large A cation at the center, a smaller B cation at the corner, and oxygen ions at the edges. In recent years, a large number of new compounds which contain two B elements with different valence states in the octahedrally coordinated cation position of the perovskite structure have been prepared, *i.e.*, $\text{Ba}(\text{M}^{\text{II}}_{0.33}\text{Ta}^{\text{V}}_{0.67})\text{O}_3$ ¹ and $\text{Ba}(\text{M}^{\text{III}}_{0.5}\text{Nb}^{\text{V}}_{0.5})\text{O}_3$ ² where M represents various divalent and trivalent ions. In each of the examples, the average valence for the B ions has to be 4+ because of the necessity for electrostatic balance. A search for new compounds of this type has resulted in the preparation of $\text{Ba}(\text{Na}_{0.25}\text{Ta}_{0.75})\text{O}_3$ and $\text{Sr}(\text{Na}_{0.25}\text{Ta}_{0.75})\text{O}_3$, which also have the perovskite structure.

Experimental

Reagent grade BaCO_3 or SrCO_3 , Na_2CO_3 , and Ta_2O_5 were mixed in the proper proportions according to the equation



The compound $\text{Ba}(\text{Na}_{0.25}\text{Ta}_{0.75})\text{O}_3$ was prepared by firing the mixture in air in a combax boat, composed mainly of zircon, at 900° for 15 hr., 1100° for 6 hr., and then 1250° for 1 hr. The samples were ground in an agate mortar after each firing. The compound $\text{Sr}(\text{Na}_{0.25}\text{Ta}_{0.75})\text{O}_3$ was prepared by a single firing of the appropriate reactants in air at 900° for 2.5 hr. Prolonged heating of these compounds at temperatures higher than those reported above resulted in decomposition of the perovskite com-

TABLE I
COMPARISON OF OBSERVED AND CALCULATED INTENSITIES AND d VALUES FOR $\text{Ba}(\text{Na}_{0.25}\text{Ta}_{0.75})\text{O}_3$

hkl	d Obsd.	d Calcd.	Obsd. intensities	Calcd. intensities
100	4.14	4.13	w ⁻	<1
110	2.92	2.92	s	100
111	2.386	2.385	w ⁻	<1
200	2.064	2.066	m ⁺	23
211	1.685	1.686	s ⁻	40
220	1.460	1.460	m ⁻	14
310	1.307	1.307	m	17
222	1.192	1.192	w	4
321	1.105	1.105	m	15
400	1.033	1.034	w ⁻	2
411, 330	0.974	0.975	w ⁺	9
420	0.924	0.924	w	6
332	0.881	0.882	w	7
422	0.844	0.844	w ⁺	9
510, 431	0.811	0.811	s ⁻	30

pounds with the subsequent formation of $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ or $\text{Sr}_5\text{Ta}_4\text{O}_{15}$.³

X-Ray powder diffraction photographs of the compounds were taken with a Philips 114.6-mm. diameter camera and high intensity copper $K\alpha$ radiation with a setting of 50 kv. and 40 ma. for 8 hr. The X-ray patterns were indexed on the basis of a simple cubic cell of $a_0 = 4.137 \text{ \AA}$. for $\text{Ba}(\text{Na}_{0.25}\text{Ta}_{0.75})\text{O}_3$ and $a_0 = 4.055 \text{ \AA}$. for $\text{Sr}(\text{Na}_{0.25}\text{Ta}_{0.75})\text{O}_3$. It should be noted, however, that if the structure of the strontium compound was distorted slightly it could not be detected because the back reflections of the X-ray pattern were poor. The relative intensities were calculated for $\text{Ba}(\text{Na}_{0.25}\text{Ta}_{0.75})\text{O}_3$ by assuming that the barium ion was in the A position and the sodium and tantalum ions were randomly distributed in the B position of the perovskite structure. Structure amplitudes were determined using atomic scattering factors for sodium and oxygen ions from a paper by Berghuis, *et al.*,⁴ and those for tantalum and barium ions from a paper by Thomas and Umeda.⁵ The agreement between the observed and calculated intensities given in Table I indicates that the positions of the atoms selected were probably correct.

Discussion

The compounds $\text{Ba}(\text{Na}_{0.25}\text{Ta}_{0.75})\text{O}_3$ and $\text{Sr}(\text{Na}_{0.25}\text{Ta}_{0.75})\text{O}_3$ contain a different ratio of B ions than has been reported previously in $\text{A}(\text{B}'_x\text{B}''_y)\text{O}_3$ type compounds, where B' and B'' represent two elements having different valence states and x and y are fractions whose sum is equal to 1. However, it should be pointed out that while the existence of these compounds was not surprising, the fact that they did not have an ordered perovskite structure, in spite of the large differences in the radii (0.26 \AA .) and charges of the sodium and tantalum ions, was not expected. A study of $\text{Ba}(\text{B}'_{0.5}\text{Nb}_{0.5})\text{O}_3$ -type compounds, for example, showed that the B ions ordered if their radii differed by more than 15%,² and a comparable investigation of $\text{Ba}(\text{B}'_{0.33}\text{Ta}_{0.67})\text{O}_3$ -type compounds pointed out that the B ions would order even when the size difference was smaller than 15% if the charge difference was large.⁶ It may well be, however, that much of the previous knowledge of ordering in $\text{A}(\text{B}'_x\text{B}''_y)\text{O}_3$ -type compounds cannot be applied to these new compounds where the ratio of the two B ions is 3.

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