CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THIOKOL CHEMICAL CORPORATION, REACTION MOTORS DIVISION, DENVILLE, NEW JERSEY

The Chemistry of Alane. II.[1] Polyiminoalanes[2]

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Polymers containing aluminum–nitrogen backbones have been prepared by the reaction of a trialkylamine alane and either ethylamine, acetonitrile, or ethylenimine, and by the reaction of lithium aluminum hydride and ethylamine hydrochloride. These polymers were soluble in organic solvents, possessed identical repeat units, and ranged in molecular weight from 750 to 2500. A similar polymer obtained from methylamine lacked this solubility.

The reaction of methylamine and alane in dioxane was first described by Wiberg and May in 1955.[3] A polymer, insoluble in organic solvents, was reported but not characterized other than to demonstrate that it still contained one equivalent of hydridic hydrogen per aluminum atom. These workers proposed a structure containing a network of alternating aluminum and nitrogen atoms. Laubengayer, *et al.*,[4] have reported the preparation of Al–N polymers from methylamine hydrochloride and triethylaluminum, methylamine and diethylaluminum chloride, and from triphenylaluminum and methylamine or dimethylamine.

There have also been several other reports of nitrogen–aluminum polymeric materials, but these were not defined. Fetter, *et al.*,[5] have reported polymer formation from hydrazine and trimethylamine alane, and Paterson and Onyszchuk[6] reported a polymer derived from aluminum chloride and hydrazine. However, the work with hydrazine–aluminum compounds is hampered by the fact that they have a tendency to be shock sensitive.

Another method of forming substituted iminoalanes was reported by Woods and McCloskey[7] by the reaction of triethylaluminum and borazines, but the polymeric materials were not examined further.

Experimental

All melting points are uncorrected. Elemental analyses were performed in our laboratories. Molecular weights were determined by freezing point depression in benzene under anhydrous conditions and inert atmospheres. All reagents and products were handled in a drybox under an argon atmosphere during transfer and filtration.

All of the reactions were run in a 1:1 mole ratio using benzene as the solvent. When amines were used as the reagents, the system was connected to a wet-test meter through two KOH drying towers in order to measure the hydrogen evolved during the reaction. A means for sampling the gas for identification was incorporated into the system. The soluble products were isolated by freeze-drying the benzene solutions. Hydrolyses were performed on a vacuum rack equipped with a Toepler pump and a calibrated collection system. The identity of the evolved gas was confirmed by mass spectrometry. The hydrolysate was analyzed for amine and aluminum.

Poly(N-ethyliminoalane). (A) From Ethylamine.—Anhydrous ethylamine (0.20 mole) in 50 ml. of anhydrous benzene was added dropwise with stirring at room temperature to 0.20 mole of triethylamine alane in 304 ml. of benzene. The mixture was stirred 16 hr. at 40° and 48 hr. at 50° during which time 0.396 mole of hydrogen was evolved (99%). The insoluble polymer, 2.551 g., was isolated by filtration and dried *in vacuo* at room temperature; sintered 195–205°, m.p. 218–220° with vigorous decomposition. The infrared spectrum and elemental analyses matched those of the main (soluble) fraction (*vide infra*). Hydrolysis of 0.2114 g. of material with 20 ml. each of wet benzene and 6 *N* hydrochloric acid showed the presence of 16.2 mg.-atoms of active hydrogen per gram and 2.42 mequiv. of ethylamine. On the basis of the amine isolated the theoretical active hydrogen content is 16.5 mg.-atoms/g.

The clear, colorless filtrate of the reaction was freeze-dried to give 11.53 g. of white polymer, sintering at 165–175° and melting at 190–194° with decomposition. The benzene distillate contained 0.183 mequiv. of triethylamine (92% of theory).

Anal. Calcd. for $(C_2H_6NAl)_x$: C, 33.80; H, 8.51; N, 19.72; Al, 37.97. Calcd. for I, $R = C_2H_5$, $n = 35$: C, 33.77; H, 8.59; N, 19.70; Al, 37.94. Found: C, 32.97; H, 8.76; N, 19.59; Al, 39.15.

Hydrolysis of 0.1926 g. of polymer yielded 15.6 mg.-atoms of active hydrogen per gram (theory 15.1 mg.-atoms/g. based on molecular weight). The molecular weight determination gave a value of 2490 *vs.* a calculated value of 2489.

Repetition of the experiment, but keeping the reaction mixture at room temperature, gave a polymer, m.p. 188–192° dec., with a molecular weight of 1140, which still contained one mole of triethylamine per mole of polymer.

Anal. Calcd. for $C_{34}H_{102}N_{25}Al_{15}$: C, 37.05; H, 9.07; N, 19.21; Al, 34.67; mol. wt., 1126. Found: C, 37.14; H, 8.75; N, 19.40; Al, 35.70; mol. wt., 1140.

A portion of the solid was heated 16 hr. at 102° under high vacuum. The heated material did not melt or visibly decompose below 360° and was insoluble in benzene or tetrahydrofuran. The infrared spectrum was similar to that of the unheated polymer, except that the triethylamine absorptions had disappeared and the relative intensity of the Al–H bond had decreased. Hydrolysis showed a decrease in the active hydrogen content (5.79 mg.-atoms/g.), but the other elemental analyses were unchanged.

(B) From Acetonitrile.—The solid was pale green in color and decomposed at 200° without melting. Fractionation of the hydrolysate on a vacuum system and isolation of the fractions gave the theoretical quantity of ethylamine and a trace of ammonia and acetaldehyde.

Anal. Calcd. for II, $n = 33$: C, 33.80; H, 8.51; N, 19.72;

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[1] Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963. Paper I: *Inorg. Chem.*, **2**, 650 (1963).

[2] (a) The term "poly(iminoalane)" has been suggested by R. M. Adams, Chairman of the Committee on Inorganic Nomenclature of the American Chemical Society, for the $(Al-N)_n$ structure. (b) This investigation was supported by the Air Force Flight Test Center, Edwards Air Force Base, Calif., under Contract AF-33(616)-5935 (1959).

[3] E. Wiberg and A. May, *Z. Naturforsch.*, **10b**, 232 (1955).

[4] A. W. Laubengayer, J. D. Smith, and G. G. Ehrlich, *J. Am. Chem. Soc.*, **83**, 542 (1961); A. W. Laubengayer, K. Wade, and G. Lengnick, *Inorg. Chem.*, **1**, 632 (1962).

[5] N. R. Fetter, B. Bartocha, F. E. Brinckman, Jr., and D. W. Moore, *Can. J. Chem.*, **41**, 1359 (1963).

[6] W. G. Paterson and M. Onyszchuk, *ibid.*, **41**, 1872 (1963).

[7] W. G. Woods and A. L. McCloskey, *Inorg. Chem.*, **2**, 861 (1963).

Al, 37.97; active H, 14.6 mg.-atoms/g.; total amine, 7.64 mmoles; mol. wt., 2416. Found: C, 33.58; H, 8.19; N, 18.96; Al, 39.54; active H, 14.2 mg.-atoms/g.; total amine, 7.63 mmoles; mol. wt., 2400.

(C) **From Ethylenimine.**—The polymer had a softening range of 81–270°, at which point it decomposed without melting.

Anal. Calcd. for III, $n = 10$: C, 35.11; H, 8.57; N, 20.48; Al, 35.84; active H, 21.8 mg.-atoms/g.; mol. wt., 752. Found: C, 36.69; H, 8.54; N, 19.33; Al, 35.44; active H, 18.3 mg.-atoms/g.; mol. wt., 750; H/Al, 0.84. Fractionation of the hydrolysate as in the hydrolysis of poly(N-ethyliminoalane) from acetonitrile showed the presence of ethylamine, ammonia, and a trace of acetylene.

(D) **From the Reaction of Ethylamine Hydrochloride and Lithium Aluminum Hydride.**—To a suspension of 0.11 mole of powdered lithium aluminum hydride in 100 ml. of benzene was added 0.1 mole of ethylamine hydrochloride. The mixture was stirred 72 hr. at 45°, evolving 0.295 mole of hydrogen (98.3% of the theoretical). The mixture was filtered and the filtrate was freeze-dried to give 6.551 g. of white, crystalline polymer, m.p. 172–175° dec.

Anal. Calcd. for IV, $n = 19 + C_2H_5NH_3Cl$: Al, 34.73; N, 19.94; Cl, 2.40; active H, 12.8 mg.-atoms/g.; mol. wt., 1480. Found: Al, 33.51; N, 19.28; Cl, 2.19; active H, 11.7 mg.-atoms/g.; mol. wt., 1500.

Poly(N-methyliminoalane).—In a closed, evacuated system 0.10 mole of methylamine was allowed to react with 0.10 mole of triethylamine alane in 133 ml. of benzene at 50° for 5 days. Periodically during this time, unreacted methylamine was recondensed into the reaction mixture. A total of 0.201 mole of hydrogen was evolved (theoretical, 0.200 mole) and 5.340 g. of a white, benzene-insoluble polymer was isolated and dried *in vacuo* at room temperature. From the filtrate was obtained 0.050 g. of material. Both fractions failed to melt below 360° and only turned slightly gray during the heating. Hydrolyses were run as usual. Because of the small quantity of material, no elemental analyses were obtained for the soluble fraction.

Anal. Calcd. for $(CH_4NAl)_x$: C, 21.06; H, 7.07; N, 24.57; Al, 47.30. Calcd. for V, $n = 14$: C, 20.30; H, 7.18; N, 23.68; Al, 48.84; active H, 20.5 mg.-atoms/g.; methylamine, 16.9 mequiv./g. Found: C, 20.65; H, 7.15; N, 23.51; Al, 48.88; active H, 20.4 mg.-atoms/g.; methylamine, 15.6 mequiv./g.

The hydrolysis of the soluble fraction showed the presence of 29.1 mg.-atoms/g. of active hydrogen. The calculated values for V, $n = 2$, 3, and 4 are 34.7, 29.9, and 27.1 mg.-atoms/g., respectively.

Discussion

The present paper describes the results of a study of the reaction of trialkylamine alanes, $R_3N \cdot AlH_3$, with acetonitrile, ethyl- and methylamine, and ethylenimine. A similar reaction involving lithium aluminum hydride, $LiAlH_4$, and ethylamine hydrochloride also was examined.

When the reagents were mixed in a 1:1 mole ratio in benzene, the final product, in all cases, was a benzene-soluble polymer which contained one hydrolyzable hydrogen per aluminum atom and had an average molecular weight in benzene solution of less than 2500. The infrared spectra of the products were alike with an absorption at 1840 cm.$^{-1}$ assigned to the Al–H stretching vibration.[1] This band shifted to 1830 cm.$^{-1}$ in the infrared spectrum of the product obtained from the reaction of methylamine. No tertiary amine could be detected in the polymer by infrared if the molecular weight was above 1100; below that value the tertiary amine frequencies could be observed at 1035, 1068, and 2800 cm.$^{-1}$. It is also significant that the third hydrogen on the aluminum was never displaced by an excess of amine or nitrile.

Although the exact mechanism of the polymerization reaction has not been established, a reasonable route would involve, in all cases, displacement of trialkylamine from the alane by the attack of the amine or nitrile nitrogen atom on the aluminum. Such a displacement has been shown to occur in the preparation of dimethylaminoalane, $(CH_3)_2NAlH_2$, by the reaction of dimethylamine and trimethylamine alane.[8] The resulting new alane addition product could then undergo loss of hydrogen, or the appropriate hydrogen shift, to give a polyiminoalane, $[RNAlH]_n$. The value of n ranged from 3 to 35 and could be duplicated readily by control of the time and temperature of the reaction. Higher temperatures or longer reaction times gave higher values of n and a product less soluble in benzene.

The experimental results can be summarized by eq. 1–4. In no case was an attempt made to isolate intermediates, although the existence of such intermediates has been shown by other workers. Thus, the intermediate $[RNH_2 \cdot AlH_3]$ has been shown to be stable below −40° by Wiberg,[3] and Ruff and Hawthorne[9] suggest the existence of $R_2NH \cdot AlH_3$ from −40 to −10°. In reaction 2, after the initial coordination of alane to the nitrile, the aluminum bonds to the nitrile nitrogen,[10] probably forming an iminoalane intermediate, $RCH{=}N{-}AlH_2$.[11] The iminoalane intermediate then can polymerize by the intermolecular addition of Al–H to the imino linkage. The isolation of a trace of ammonia on hydrolysis of the polymer may be due to an imino end group, $-AlH-N{=}CHCH_3$, which would be expected to give ammonia and acetaldehyde on hydrolysis (5).

The reaction between ethylenimine and triethylamine alane (3) probably occurred in three steps by means of the initial coordination of alane with the imine, hydrogen elimination to form the aminoalane, and a hydride ion shift to open the imine ring. The aminoalane intermediate may not actually be formed in this reaction since it has been reported that aziridinoalane decomposes explosively.[12]

It is not clear in any of the reactions whether the trialkylamine is displaced in the initial step or remains bonded to the aluminum until the polymerization occurs.

In the case of the poly(N-methyliminoalane), the analytical results seem to indicate a formula such as V rather than I ($R = CH_3$). This polymer is unique in

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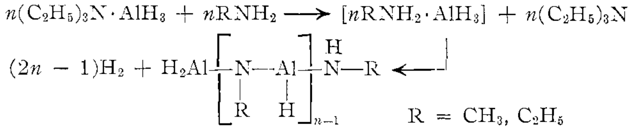
(8) J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 2835 (1961).

(9) J. K. Ruff and M. F. Hawthorne, *ibid.*, **82**, 2141 (1960).

(10) That the aluminum bonds to the nitrogen and not to the carbon during the reduction of a nitrile group by a hydridic aluminum compound has been shown, for instance, by L. M. Saffer, *J. Org. Chem.*, **22**, 998 (1957).

(11) Such alkylated iminoalanes have been isolated and identified by L. I. Zakharkin and I. M. Khorlina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 550 (1959), in their work on the thermal decomposition of the reaction products of diisobutylalane and nitriles. Also, an iminoaluminum structure has been proposed by H. W. Johnston, *J. Org. Chem.*, **25**, 454 (1960), for the intermediate in the reaction of triphenoxyaluminum with nitriles.

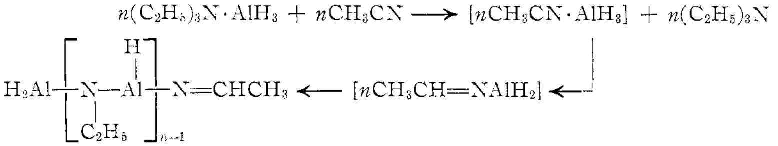
(12) W. Marconi, A. Mazzei, F. Bonati, and M. deMalde, *Gazz. chim. ital.*, **92**, 1062 (1962).



$$n(C_2H_5)_3N\cdot AlH_3 + nRNH_2 \longrightarrow [nRNH_2\cdot AlH_3] + n(C_2H_5)_3N$$

$$(2n-1)H_2 + H_2Al\left[-\underset{R}{N}-\underset{H}{Al}-\right]_{n-1}\overset{H}{N}-R \longleftarrow$$

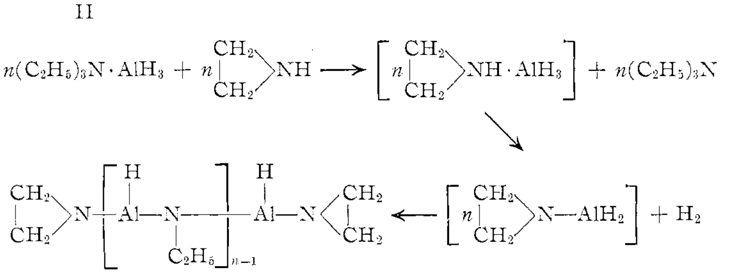
I   R = CH_3, C_2H_5 (1)



$$n(C_2H_5)_3N\cdot AlH_3 + nCH_3CN \longrightarrow [nCH_3CN\cdot AlH_3] + n(C_2H_5)_3N$$

$$H_2Al\left[-\underset{C_2H_5}{N}-\overset{H}{Al}-\right]_{n-1}N{=}CHCH_3 \longleftarrow [nCH_3CH{=}NAlH_2] \longleftarrow$$

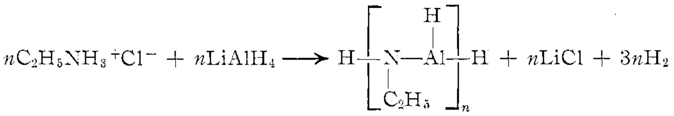
II   (2)



$$n(C_2H_5)_3N\cdot AlH_3 + n\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>NH \longrightarrow \left[n\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>NH\cdot AlH_3\right] + n(C_2H_5)_3N \searrow$$

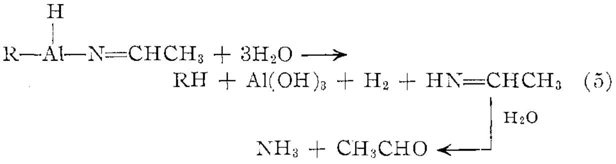
$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>N\left[-\overset{H}{Al}-\underset{C_2H_5}{N}-\right]_{n-1}\overset{H}{Al}-N\!\!<\begin{matrix}CH_2\\|\\CH_2\end{matrix} \longleftarrow \left[n\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>N-AlH_2\right] + H_2$$

III   (3)



$$nC_2H_5NH_3{}^+Cl^- + nLiAlH_4 \longrightarrow H\left[-\underset{C_2H_5}{N}-\overset{H}{Al}-\right]_{n}H + nLiCl + 3nH_2$$

IV   (4)

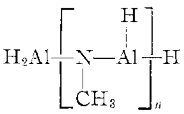


$$R-\overset{H}{Al}-N{=}CHCH_3 + 3H_2O \longrightarrow RH + Al(OH)_3 + H_2 + HN{=}CHCH_3$$

$$NH_3 + CH_3CHO \xleftarrow{H_2O}$$

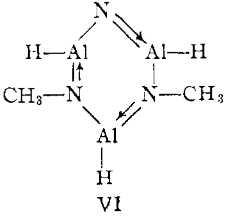
(5)

that for values of n below 15 in structure V, the difference in theoretical active hydrogen content for successive degrees of polymerization is sufficiently large to permit an approximate determination of the molecular weight. Quantitative hydrolyses showed that the insoluble fraction had a degree of polymerization of about 14, while the soluble fraction contained only three mer units. The structure of the latter is unknown, but a cyclic trimer can definitely be excluded on the basis of the hydrolysis results. A cyclic structure, such as VI, would contain only 17.5 mg.-atoms of active hydrogen per gram, while the soluble fraction contained 29.1 mg.-atoms/g. A ring structure, such as VII, formed by coordinate N→Al bonds, can be ruled out on the basis of the fact that, at room temperature, reaction between the hydridic hydrogen on the aluminum and the protonic hydrogen on the nitrogen is very rapid.[3,13]

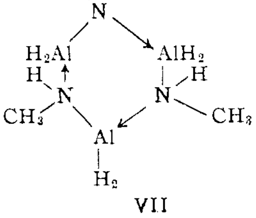


$$H_2Al\left[-\underset{CH_3}{N}-\overset{H}{Al}-\right]_{n}H$$

V



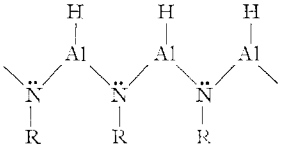
VI



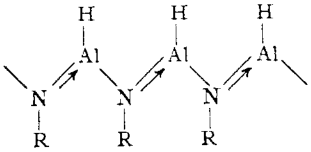
VII

The difference in the solubility of the methyl and ethyl polymers in benzene is marked. (The former is soluble only when $n \leq 3$, while the latter dissolves for values of $n \leq 35$.) This difference could be ascribed to cross linking through association and hydrogen bonding in the case of the poly(N-methyliminoalane), as well as to the lower carbon content, rendering the latter polymer more insoluble in neutral organic solvents. The steric effect of a methyl group is considerably less than that of an ethyl group, and less restriction would therefore be offered to coordinative cross linking in the methyl-substituted polymer.

At the present time there is no evidence available to define the structure of the polyiminoalanes. It is unlikely that the polymer is purely linear since this would require either a tricoordinated aluminum atom (VIII) or a double-bonded structure involving the more stable tetracoordinated aluminum (IX), and the



VIII



IX

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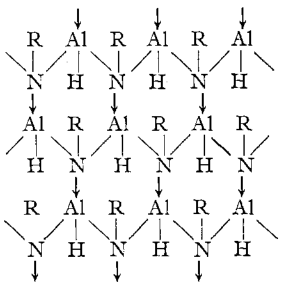
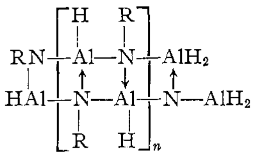
[13] E. Wiberg and A. May, *Z. Naturforsch.*, **10b**, 230 (1955).



X



XI

latter type of structure has so far not been found in nitrogen–aluminum compounds. It is much more likely that the aluminum is tetracoordinate by virtue of cross linking with other chains through the free pair of electrons on the nitrogen. Such cross-linked polymers could be built up into systems forming cyclic networks such as X or XI,[14] or in a random manner.

A cyclic network probably would be preferred because of its inherently greater stability. Six-membered coordinated Al–N rings have been suggested as the structure for the trimer of dimethylaminoalane, $(CH_3)_2NAlH_2$,[8] for $C_2H_5Al(Cl)NHCH_3$, and for the polymer derived from this compound.[4] A three-dimensional cubic Al–N compound has been prepared recently[15] and the type of cross-linked network present in this material is also possible for the polyiminoalanes.

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[14] We are indebted to one of the referees for the suggestion of this folded-chain structure (XI).

[15] J. I. Jones and W. S. McDonald, *Proc. Chem. Soc.*, 366 (1962).

CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL SCIENCES,
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Reactions of Peroxodisulfuryl Difluoride with Organic Halides

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The preparation of the new compounds, chlorotrifluorobis(fluorosulfato)ethane and octafluorobis-2,3-(fluorosulfato)butane, from peroxodisulfuryl difluoride, $S_2O_6F_2$, and chlorotrifluoroethylene and *cis-trans*-perfluoro-2-butene, respectively, is reported and some of their chemical and physical properties are given. Reactions of $S_2O_6F_2$ with several other organic halides have been examined.

Peroxodisulfuryl difluoride ($S_2O_6F_2$) has been shown to add readily across the carbon–carbon double bond in tetrafluoroethylene and perfluorocyclopentene and to react slowly with carbon tetrachloride.[1] Addition reactions have not been attempted with other than perfluoroolefins nor have the reactions with other halomethanes been examined. This present work is concerned with the reactions of $S_2O_6F_2$ with olefins containing other halogens in addition to fluorine, with olefins containing hydrogen, and with halomethanes containing other halogens in addition to fluorine.

Reaction of $S_2O_6F_2$ with carbon tetrachloride gives rise to carbonyl chloride, and if the $S_2O_6F_2$ is present in excess, carbon dioxide is obtained. With phosphorus trifluoride, phosphoryl fluoride is the product. It now has been shown that if the halomethane contains one other halogen, in addition to the trifluoromethyl group (*e.g.*, CF_3Cl, CF_3Br), oxygenation does not occur but rather the nonfluorine halogen is replaced by a fluorosulfate group. This reaction is similar to that of iodine monochloride and potassium chloride with $S_2O_6F_2$ where chlorine is replaced by fluorosulfate groups to give $I(SO_3F)_3$ and KSO_3F, respectively.[1]

Preliminary examination of the products of the reaction of $S_2O_6F_2$ and chlorodifluoromethane showed carbonyl fluoride, chlorine, fluorosulfuric acid, pyrosulfuryl fluoride ($S_2O_5F_2$), and unidentified volatile materials which could contain one or more fluorosulfate groups. Pyrosulfuryl fluoride is a product when $S_2O_6F_2$ acts as an oxygenating agent. Apparently, in this case, both the carbon–hydrogen and carbon–chlorine bonds were broken to allow formation of the carbon–oxygen double bond contained in COF_2.

Experimental

Reagents.—All gaseous reactants were obtained from the Matheson Company, Inc., and were used without further purification. Reagents used for analyses were of analytical reagent grade. Peroxodisulfuryl difluoride was obtained by the catalytic fluorination of sulfur trioxide.[2]

Vapor pressure measurements were obtained through the use of an apparatus similar to that described previously.[3] Vapor densities were determined by using Regnault's method with a glass flask of 253.4 ml. volume. A codistillation apparatus[4] was utilized to separate reaction products. Identification of previously known reaction products, after separation, was made using vapor density and infrared determinations. Infrared spectra were obtained by using a Perkin-Elmer Model 138 Infracord spectrophotometer. Cells were of Pyrex glass with a 5-cm. path length and sodium chloride windows or with a 10-cm. path

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[1] J. M. Shreeve and G. H. Cady, *J. Am. Chem. Soc.*, **83**, 4521 (1961).

[2] J. M. Shreeve and G. H. Cady, *Inorg. Syn.*, **7**, 124 (1963).

[3] K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).

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