fluoride. *Anal.* Calcd.: Br, 15.51; S, 24.89; F, 14.75. Found: Br, 15.4; S, 24.7; F, 14.3.

Potassium tetrakis(fluorosulfonato)bromate(III) is a white solid which begins to decompose at 100° giving a dark red liquid having the appearance of $BrSO_3F$.[5]

Chlorotris(fluorosulfonato)tin.—This compound was prepared by contacting tin(IV) chloride with a large excess of peroxydisulfuryl difluoride in a sealed tube equipped with a break-seal attachment. A mild reaction took place just below room temperature and was complete within a few minutes. The reaction proceeded as indicated.

$$2SnCl_4 + 3S_2O_6F_2 \longrightarrow 2SnCl(SO_3F)_3 + 3Cl_2$$

It was found that heating the reactants at 100° for several days achieved no further replacement of the chlorine. $SnCl_4$ (0.518 mmole) yielded a weight of the above compound corresponding to 0.517 mmole.

The volatile material remaining after the reaction was distilled away. This material was fractionated into three products: chlorine, determined by molecular weight and color; $S_2O_6F_2$, determined by molecular weight and infrared spectrum; and a trace of an unidentified product. After hydrolysis of the solid material in sodium hydroxide solution, chloride and sulfate were determined gravimetrically as AgCl and $BaSO_4$, respectively. *Anal.* Calcd.: Cl, 7.87; S, 21.3. Found: Cl, 7.84; S, 21.0.

Chlorotris(fluorosulfonato)tin is a white solid decomposing at about 167°.

Dioxobis(fluorosulfonato)chromium(VI).—Chromyl chloride was found to react with excess $S_2O_6F_2$ at room temperature.

$$CrO_2Cl_2 + S_2O_6F_2 \longrightarrow CrO_2(SO_3F)_2 + Cl_2$$

CrO_2Cl_2 (0.362 mmole) yielded a solid having the weight of 0.345 mmole of $CrO_2(SO_3F)_2$. *Anal.* Calcd.: Cr, 14.74; S, 18.17; Cl, 0.00. Found: Cr, 14.23; S, 17.8; Cl, 0.99. Chromium was determined by iodometric analysis involving the chromate ion formed by alkaline hydrolysis of the solid. Chloride and sulfate were determined as AgCl and $BaSO_4$, respectively.

Dioxobis(fluorosulfonato)chromium(VI) is a dark brown, slightly volatile solid which decomposes very slowly at room temperature into a greenish compound. Hydrolysis of an aged sample yielded a yellow solution and a small amount of green flocculent precipitate resembling chromium(III) hydroxide.

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REDSTONE ARSENAL RESEARCH DIVISION,
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Nitrosodifluoramine (F_2NNO)

BY CHARLES B. COLBURN AND FREDERIC A. JOHNSON

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It has been reported by Johnson and Colburn[1] that when tetrafluorohydrazine is handled by conventional vacuum line techniques it possesses a light to dark blue-purple color in the liquid phase. This color originally was attributed to trace impurities and was found to be a function of the concentration of NF_2 radicals in the gas phase prior to condensation. In the present work evidence for the existence of nitrosodifluoramine and evidence that the purple color of condensed tetrafluorohydrazine is due to trace amounts of this compound are presented. It is estimated that as little as 0.1% NF_2NO in liquid N_2F_4 will give a pronounced purple color to the solution.

Preparation

When a mixture of tetrafluorohydrazine[2] (N_2F_4) and nitric oxide is passed through a coil at elevated temperatures (300°) and then allowed to impinge upon a Pyrex finger at liquid nitrogen temperature, a dark purple deposit is formed. The intensity of the color of this material is (within limits) proportional to the temperature (concentration of NF_2 radicals) of the incoming stream of gas and to the concentration of NO in the incoming stream.

In order to get maximum conversion of N_2F_4 into NF_2NO it is necessary to use excess NO. In a typical preparation a stream of gas consisting of 10 parts NO and 1 part N_2F_4 is passed through a coil at 300° and allowed to condense on a Pyrex finger at liquid nitrogen temperature. Purification is accomplished by substituting liquid oxygen for the nitrogen in the finger, and pumping off the excess NO (vapor pressure 3 mm. at $-183°$). Quite pure NF_2NO can be prepared in this way as shown below.

Characterization of NF_2NO

If a relatively pure sample of NF_2NO prepared as described above is allowed to warm up to room temperature, the gases produced have in a typical case the composition (as determined by mass spectrometric analysis): 32.4% N_2F_4, 65.0% NO, 1.8% N_2O, 0.6% SiF_4. This is the composition which would be expected if NF_2NO decomposed according to the equation

$$2NF_2NO \rightleftarrows N_2F_4 + 2NO \qquad (1)$$

We have as yet been unable to prepare NF_2NO completely free of N_2O and SiF_4. This is not surprising, however, as in Pyrex systems many NF compounds react with glass at elevated temperatures to form N_2O and SiF_4.

In addition to the analysis of NF_2NO given above, the following observations have been made on NF_2NO. The F^{19} n.m.r. spectrum of a mixture of NF_2NO and N_2F_4 has been observed. Two absorption peaks are observed; the peak on

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[1] F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **83**, 3043 (1961).

[2] C. B. Colburn and A. Kennedy, *ibid.*, **80**, 5004 (1958).

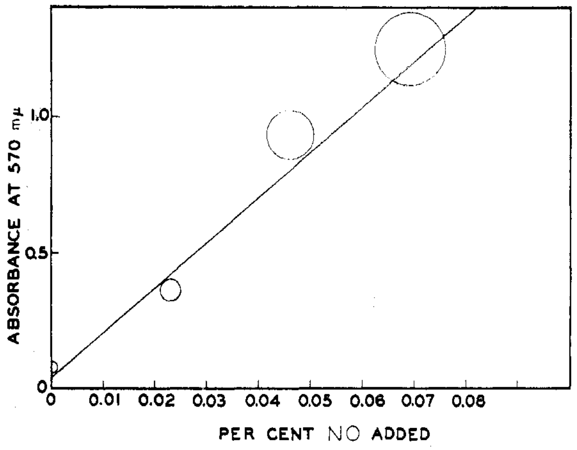

Fig. 1.—Absorbance of NF_2NO at 570 mμ (1 cm. liquid).

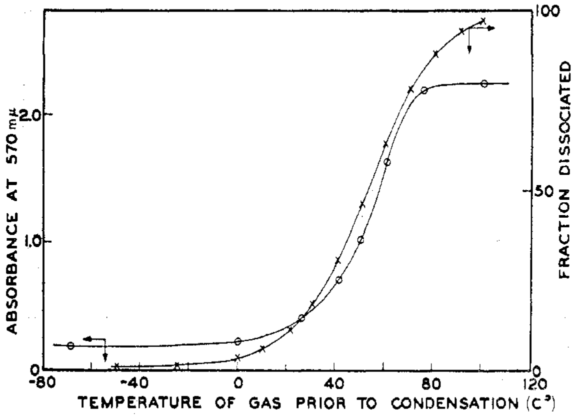

Fig. 2.—Absorbance of condensed gas and fraction N_2F_4 dissociated at 10^{-2} mm.

the low field side [−5736 cycles from trifluoroacetic acid] arises from the F^{19} absorption of NF_2NO, while the peak at higher field [−5485 cycles from trifluoroacetic acid] arises from the F^{19} absorption of N_2F_4. (The shifts observed for these compounds are not exactly the values which would be obtained from pure NF_2NO or pure N_2F_4 due to the presence of the paramagnetic impurity NO.) The fact that the relative magnitudes of these two peaks change with time even at −70° (the NF_2NO peak decreases while the N_2F_4 peak increases) indicates that NF_2NO is quite unstable even at these temperatures.

When solid NF_2NO is allowed to melt a dark purple liquid is formed. If drops of this liquid are allowed to fall onto a surface at −112° clouds of purple vapor arise immediately after each drop impinges on the glass. This purple gas rapidly decolorizes as the temperature of the gas increases.

The blue color of NF_2NO has not been observed at room temperature and atmospheric pressure. However, at −78° and atmospheric pressure a 2:1 mixture of NO and N_2F_4 has a light blue color (1-in. path) and at approximately 10 atmospheres pressure and room temperature this gas mixture has a pronounced blue color (a few millimeters path). Equation 1 indicates that the formation of NF_2NO would be favored by a high pressure of reactants.

Dependence of the Absorption at 570 mμ on the Concentration of NO and NF_2

The absorption spectrum of the blue liquid (NF_2NO) has been obtained at −160° in a Beckman DU spectrophotometer with a modified cell compartment.

The intensity of the 570-mμ absorption was determined as a function of the concentration of nitric oxide (at constant temperature and pressure of the N_2F_4–NO mixture being condensed). Under the conditions of this experiment various quantities of NO were reacted with a comparatively large constant concentration of NF_2 radicals. Since NO was never more than 0.1% of the N_2F_4 and since there was 5% NF_2 (2–3% dissociation at 25° and 0.1 mm.), $NF_2 >> NO$ in these experiments. The results are shown in Fig. 1 and indicate that the amount of the absorbing species is proportional to the amount of NO in the mixture being condensed.

An absorptivity of 110 ± 10 l./mole-cm. was calculated for NF_2NO at 570 mμ assuming that all of the NO was converted to NF_2NO.

Dependence of the 570-mμ absorption upon NF_2 concentration in the gas being condensed is more difficult to measure since the concentration of NF_2 cannot be varied independently if N_2F_4 is the main material present. In a gas mixture where the amount of N_2F_4 is small, however, changing the temperature changes the NF_2 concentration essentially independently of the total pressure. Therefore a gas mixture of 2.0% NO and 1.0% N_2F_4 in NF_3 was made up, the NF_3 playing the part of diluent in the gas phase and solvent in the condensed phase. At a given pressure of the mixture (about 1 mm. in our experiments), the relative concentration NF_2/NO can be varied between 0 and 1 simply by changing the temperature of the gas to change the degree of dissociation of the N_2F_4.

In Fig. 2 both the absorbance of the condensed material (−196°) at 570 mμ and the calculated degree of dissociation[1] of N_2F_4 at 10^{-2} mm. (1% of 1 mm.) are plotted against the temperature of the gas phase prior to condensation. The great similarity of the two curves makes it evident that the intensity of the 570-mμ absorption and the concentration of NF_2 (*i.e.*, degree of dissociation) exhibit the same temperature dependence as expected if NF_2NO is the species absorbing at 570 mμ.

The heat of dissociation of NF_2NO and gas phase equilibrium measurements

$$N_2F_4 \rightleftarrows 2NF_2 + 2NO \rightleftarrows 2NF_2NO$$

are currently under investigation in these Laboratories.

Acknowledgment.—The authors wish to express their appreciation to Mrs. Carolyn Haney for her valuable assistance in obtaining the F^{19} n.m.r. spectrum of NF_2NO. This work was carried out under Army Contract DA-01-021 ORD-11878 and Air Force Contract DA-01-021 ORD-784.

CONTRIBUTION FROM CASE INSTITUTE OF TECHNOLOGY,
CLEVELAND 6, OHIO

A Phthalocyaninosiloxane[1]

BY RALPH D. JOYNER AND MALCOLM E. KENNEY

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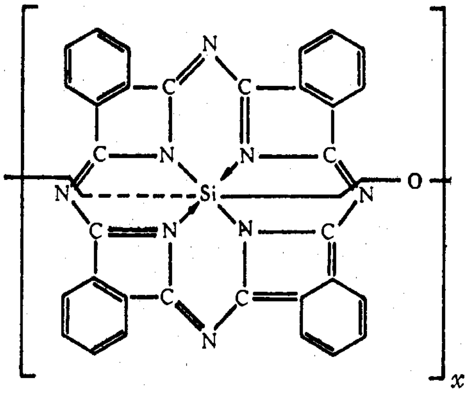
Recently it has been reported that oxy-linked polymers are formed by both phthalocyaninogermanium and phthalocyaninomanganese(IV) systems.[2,3] Work now has been carried out which shows that a related siloxane, $HO(PcSiO)_xH$, is formed by the dehydration of $PcSi(OH)_2$. The reaction by which it is formed, $x PcSi(OH)_2 \rightarrow HO(PcSiO)_xH + (x-1)H_2O$,[4] entails the cleavage of Si–O bonds in the presence of Si–N bonds.

The infrared spectra of $HO(PcSiO)_xH$ and of the material thought to be $HO(PcGeO)_xH$[5a] are very similar (720–1150 cm.$^{-1}$) except that a large broad band appears in the siloxane spectrum at 987 cm.$^{-1}$ and a similarly shaped band in the other spectrum at 872 cm.$^{-1}$. The 987-cm.$^{-1}$ band in the siloxane can be assigned to the Si–O stretching motion.

Because of the planar phthalocyanino ring encircling each silicon atom, the oxygen atoms must occupy *trans* positions. The minimum thickness typical of aromatic rings and the length characteristic of SiO bonds combine to suggest that the SiOSi bond angle approaches 180° and thus that the siloxane is nearly linear. This stereochemistry excludes small rings and the maximum of two OH groups per silicon atom rules out branched chains. Such a structural arrangement is consistent with the observed inertness of the siloxane.



Experimental

Thermal Dehydration of $PcSi(OH)_2$.—Measurements of the amounts of water vapor evolved during the thermal dehydration of $PcSi(OH)_2$ were used to obtain experimental evidence about the nature of the siloxane formed. The $PcSi(OH)_2$ was prepared from sublimed $PcSiCl_2$ by hy-

TABLE I

$PcSi(OH)_2$		H_2O				
Wt. (mg.)	mmoles (n_1)	P (mm.)	V (ml.)	T (°K.)	mmoles (n_2)	n_2/n_1
22.6	0.0393	14.6	49.3	300	0.0386	0.98
21.7	.0378	12.6	49.6	299	.0337	0.89
21.7	.0378	14.3	49.5	301	.0378	1.00
21.2	.0369	13.7	49.4	302	.3060	0.97
25.6	.0445	16.8	4.99	302	.0445	1.00

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[1] This paper is based on a thesis submitted by R. D. Joyner in partial fulfillment of the requirements for the Ph.D. degree. The work was supported by the Research Corporation and by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, and was presented at the 139th National American Chemical Society Meeting.

[2] R. D. Joyner and M. E. Kenney, *J. Am. Chem. Soc.*, **82**, 5790 (1960).

[3] J. A. Elvidge and A. B. P. Lever, *Proc. Chem. Soc.*, 195 (1959).

[4] Pc = $C_{32}H_{16}N_8$.

[5] (a) Spectra available in the thesis of R. D. Joyner, University Microfilms No. 61-3317, p. 49; (b) spectrum shown in the thesis of J. E. Owen, University Microfilms No. 61-3309, p. 91.