Notes

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Synthetic Methods and Reactions. 38.[1a] The Convenient Preparation of Sulfuryl Chloride Fluoride and Sulfur Tetrafluoride from Sulfuryl Chloride and Sulfur Dichloride with Pyridinium Poly(hydrogen fluoride)

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The use of fluorosulfur compounds in chemistry is of increasing significance. The preparation of these compounds is however frequently tedious, requiring rigorous conditions or equipment not found in the average laboratory. We would like now to report the simple preparation of two of the most used fluorosulfur compounds, sulfuryl chloride fluoride and sulfur tetrafluoride, from sulfuryl chloride and sulfur dichloride, respectively, via convenient fluorination with pyridinium poly(hydrogen fluoride).

Experimental Section

Pyridinium Poly(hydrogen fluoride). Into 42 g (0.53 mol) of reagent grade pyridine (dried over molecular sieves) at −78 °C in a polyethylene bottle was condensed 100 g (5 mol) of anhydrous hydrogen fluoride (Harshaw). The mixture was allowed to warm gradually to room temperature, the resulting solution being 30% by weight pyridine. The concentration of pyridine may be readily increased by decreasing the amount of HF added. When pyridinium poly(hydrogen fluoride) is already available it can be used as a convenient solvent medium to carry out the reaction of additional pyridine and anhydrous HF at low temperature.

Sulfuryl Chloride Fluoride. To 40 mL of pyridinium poly(hydrogen fluoride) (53% by weight pyridine) magnetically stirred at 30 °C in a polyethylene reaction vessel was added dropwise 38 g (0.28 mol) of SO_2Cl_2 (purified by reflux and subsequent distillation under reduced pressure). The product as formed was distilled out of the reaction vessel, was passed over a bed of anhydrous potassium fluoride to remove entrained HF, and was condensed into a cold trap at −78 °C. The SO_2ClF formed was purified by first refluxing for 2 h to remove low-boiling impurities and then by distillation from 1 g (0.004 mol) of antimony pentafluoride, to complex any sulfur dioxide present, to yield 27 g (80% yield) of SO_2ClF, bp 7 °C (^{19}F NMR and physical properties were identical with those of authentic sample).

Sulfur Tetrafluoride. To 200 mL of pyridinium poly(hydrogen fluoride) (30% pyridine by weight) was added 50 g (0.5 mol) of sulfur dichloride (technical) in a polyethylene reaction vessel. The reaction mixture was heated to 45 °C and the SF_4 formed was distilled into a cold trap at −78 °C. The product was purified by trap-to-trap distillation to yield 12.4 g (68% yield) of SF_4. (^{19}F NMR and physical properties are identical with those of the authentic compound.)

Results and Discussion

Because of its low nucleophilicity[2] and wide liquid range (−120 to +7 °C) sulfuryl chloride fluoride, SO_2ClF, has been extensively used as a solvent for the generation of stable carbocations[3] and is also useful as a synthetic reagent. Existing syntheses of SO_2ClF require the reaction of fluoride salts with sulfuryl chloride,[4] the treatment of potassium fluorosulfite with chlorine,[5] the reaction of hydrogen fluoride, chlorine, and sulfur dioxide with potassium bifluoride impregnated charcoal,[6] or the reaction of nitrogen trifluoride with sulfuryl chloride.[7] Schack and Wilson have also reported the preparation of SO_2ClF by the reaction of ClF and SO_2 at low temperature.[8] None of these methods is convenient. We have found that sulfuryl chloride reacts smoothly with pyridinium poly(hydrogen fluoride) ($C_5H_5N^+H(HF)_xF^-$)[9] to form SO_2ClF in good yield under mild conditions.

$$\mathrm{SO_2Cl_2} \xrightarrow[\mathrm{(HF)}_x]{\text{pyridine}} \mathrm{SO_2ClF}$$

Sulfur tetrafluoride has been shown to be an extremely useful reagent in the preparation of fluorine compounds.[10] Although a variety of procedures for the preparation of SF_4 are known[10c,11] the most convenient laboratory procedure to date is that of Tullock, Fawcett, Smith, and Coffman,[12] where SCl_2 is heated in a solvent of high dielectric constant, such as acetonitrile, with a metal fluoride, such as sodium fluoride. SF_4 was now found to be conveniently prepared from SCl_2 and pyridinium poly(hydrogen fluoride).

$$3\mathrm{SCl_2} \xrightarrow[\mathrm{(HF)}_x]{\text{pyridine}} \mathrm{SF_4} + \mathrm{S_2Cl_2}\ (\mathrm{S_2ClF})$$

Pyridinium poly(hydrogen fluoride), being extremely polar as well as containing a large reservoir of fluoride ion, is a good medium for the reaction, which proceeds smoothly at 45 °C and atmospheric pressure.

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Registry No. SO_2ClF, 13637-84-8; SF_4, 7783-60-0; SO_2Cl_2, 7791-25-5; SCl_2, 10545-99-0; pyridinium poly(hydrogen fluoride), 62778-11-4.

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Thermal Decomposition of Nitrosyl Cyanide

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Since the recent first synthesis of nitrosyl cyanide,[1,2] several physical chemical studies have been carried out on the compound,[2-4] but relatively little is known about its chemical

Table I. Product Yields in Decomposition of Nitrosyl Cyanide

ONCN pressure, Torr	Amt of ONCN, mmol	Amt of products, mmol						Fraction of element accounted for in products		
		N_2	N_2O	CO_2	$(CN)_2$	NO	CO	O	N	C
1	0.027	0.008	0.006	0.007	0.010	0.006		0.96	1.00	1.00
7	0.021	0.006	0.005	0.006	0.008	0.003		0.95	0.98	1.05
24	0.0611	0.0207	0.0205	0.0202	0.0201	Trace		1.00	1.00	0.99
27	0.080	0.029	0.027	0.027	0.027	Trace	Trace	1.01	1.04	1.01
33	0.098	0.033	0.032	0.032	0.034	Trace	Trace	0.98	1.01	1.02
64	0.173	0.058	0.057	0.058	0.058		Trace	1.00	1.00	1.01
156	0.464	0.167	0.166	0.165	0.170		Trace	1.07	1.08	1.09
201	0.598	0.225	0.223	0.218	0.231		~0.002	1.11	1.14	1.14

behavior. Nitrosyl cyanide undergoes both photochemical and thermal decomposition. In this study we mainly investigated the stoichiometry of the thermal decomposition. By isotopic tracer studies we also obtained some information about the mechanism of the reaction.

Experimental Section

Volatile materials were handled in a glass vacuum line with greaseless stopcocks and a manometer containing mercury under a 5-mm layer of Dow-Corning 704 silicone pump oil. Nitrosyl cyanide was prepared by the reaction of nitrosyl chloride (Matheson) with silver cyanide (J. T. Baker) in a 200-mL glass vessel equipped with a Teflon-covered magnetic stirring bar, a cap with an O-ring seal, and a greaseless stopcock. In a typical run, 6.0 mmol of nitrosyl chloride was condensed onto 1.6 mmol of powdered silver cyanide at −196 °C; the closed vessel was then placed in a −45 °C bath, and stirring was commenced. At 10-min intervals during a total reaction time of 2 h, the stopcock was briefly opened to allow the vapors in the vessel to condense in a train of traps at −95, −130, and −196 °C. Nitrosyl chloride collected in the −95 and −130 °C traps, and nitrosyl cyanide collected in the −196 °C trap. The crude nitrosyl cyanide was purified by fractional sublimation in a thermal gradient column of the type described by Dobson and Schaeffer.[5] The product (0.9 mmol; 56% yield) was shown to be pure by mass spectrometry and by the analysis effectively provided by the quantitative determination of the decomposition products.

Nitrosyl cyanide with the terminal nitrogen atom labeled with ^{15}N was prepared by essentially the same procedure, using ^{15}N-labeled AgCN. The latter was prepared in a darkroom by adding aqueous $KC^{15}N$ (Bio-Rad Laboratories, Richmond, Calif.) to excess aqueous $AgNO_3$, filtering, washing, drying in vacuo, pulverizing, and, finally, vacuum-drying at 50 °C for several hours. A portion of the $KC^{15}N$ used in the synthesis was converted to hydrogen cyanide; mass spectral analysis showed that the nitrogen was 79.5% ^{15}N.

The thermal decompositions were carried out in all-glass vessels with break-seals, having volumes ranging from 75 to 400 mL. After distillation of a known amount of ONCN into a vessel, the vessel was sealed, wrapped in aluminum foil to exclude light, and placed in an oven at 75 °C. After 10 days the vessel was cooled to −196 °C and opened to the vacuum line, and the noncondensable gas was Toepler-pumped into a gas buret and measured. Mass spectral analysis generally showed the gas to be essentially pure N_2; only small amounts of NO or traces of CO were found. The condensable products were separated by fractional condensation in traps at −130 and −196 °C. The −130 °C trap collected cyanogen, which was measured and identified mass spectrometrically. The −196 °C trap collected N_2O and CO_2. This mixture of gases and the N_2O remaining after treatment of the mixture with Ascarite (to remove CO_2) was measured; the amount of CO_2 was obtained by difference. Occasionally the CO_2/N_2O ratio was determined from the ratio of the m/e 12 and m/e 30 peak heights in the mass spectrum of the mixture.

The mass spectra were obtained with a Finnigan Instruments quadrupole mass spectrometer. When the data were to be treated quantitatively, peak heights were corrected for background. In the analysis of the products of the decomposition of ^{15}N-labeled ONCN, the distribution of ^{15}N and ^{14}N in N_2, N_2O, and $(CN)_2$ was determined directly from the appropriate m/e peaks. The heights of the peaks at m/e 30 and 46 ($^{15}N_2$ and $^{15}N_2O$, respectively) were always within experimental error of zero and were assumed to be exactly zero in the calculations.

Table II. Distribution of ^{15}N in Each of the N-Containing Products, Calculated on the Basis of 100% Labeling of the Terminal Nitrogen of ONCN

Isotopic species	Fraction of compound as the isotopic species			
	Run 1	Run 2	Run 3	Run 4
N*CCN*	0.85	0.95	0.93	0.93
N*CCN	0.12	0.05	0.08	0.08
NCCN	0.03	0.00	−0.01[a]	−0.01[a]
N*N	0.32	0.45	0.30	0.47
NN	0.68	0.55	0.70	0.53
N*NO	0.85	0.82	0.77	0.86
NNO	0.15	0.18	0.23	0.14

[a] Negative fractions are a consequence of our use of the binomial coefficients in the statistical calculations and our assumption of 79.5% isotopic purity of the ^{15}N.

Results and Discussion

Preliminary experiments showed that nitrosyl cyanide decomposes at room temperature but that about 6 weeks is required for complete reaction. All the experiments reported in this note were carried out in the absence of light at 75 °C with reaction times of 10 days. These conditions apparently sufficed to give complete reaction, because longer reaction times at 75 °C did not give significantly different results. The amounts of the gaseous products formed in a series of experiments are listed in Table I. Except in the two highest pressure runs, the total amounts of oxygen, nitrogen, and carbon, calculated from the measured product gases, were in good agreement with the initial amounts of nitrosyl cyanide. The principal products were N_2, N_2O, CO_2, and $(CN)_2$, generally formed in equimolar amounts according to the equation

$$3ONCN \rightarrow N_2 + N_2O + CO_2 + (CN)_2$$

In the two lowest pressure runs, a significant amount of NO and an equivalent extra amount of $(CN)_2$ formed. Apparently at low pressures the following side reaction occurs to an important extent

$$ONCN \rightarrow NO + {}^1/_2(CN)_2$$

In the studies of the decomposition of ONCN having the terminal nitrogen atom labeled with ^{15}N, the distribution of ^{15}N among the nitrogen-containing products was determined mass spectrometrically. Because the isotopic purity of our labeled ONCN was only 79.5%, we corrected, using simple probability theory,[6] the observed ^{15}N values to the values corresponding to 100% labeling of the terminal nitrogen of the ONCN. These corrected data are presented in Table II. The data show that most of the labeled nitrogen ends up as the two nitrogen atoms of cyanogen and the terminal nitrogen atom of nitrous oxide. However small amounts of singly labeled $(CN)_2$ and N_2 form, and the amount of labeled N_2 is always greater than the amount of unlabeled N_2O. The data as a

Table III. Fraction of ONCN Decomposed by the First Mechanism, Calculated in Two Different Ways

	Run 1	Run 2	Run 3	Run 4
$f(NN)/f(N^*NO)$	0.80	0.67	0.91	0.62
$[f(N^*NO) - f(N^*CCN)]/f(N^*NO)$	0.86	0.94	0.90	0.91

whole can be quantitatively accounted for in terms of two concurrent mechanisms. We propose the principal mechanism

$$2ONCN \rightarrow 2NO + (CN)_2 \qquad (1)$$

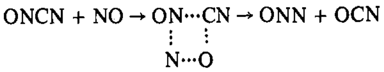
$$NO + ONCN \rightarrow N_2O + OCN \qquad (2)$$

$$NO + OCN \rightarrow CO_2 + N_2 \qquad (3)$$

Reaction 1 is quite reasonable as the initiation step in view of the very low C–N bond dissociation energy of nitrosyl cyanide. Reaction 2 can be envisaged as taking place in either of two ways. In the first way, the NO molecule essentially plucks off the terminal nitrogen atom from the ONCN molecule to form the fulminate radical, ONC

$$ONCN + NO \rightarrow ONC\cdots N\cdots NO \rightarrow ONC + NNO$$

This radical has been observed as a short-lived product of the photolysis of ozone–cyanogen mixtures.[7] We assume that it rapidly rearranges to the more stable cyanate radical, OCN.[8] When labeled ONCN is used, this first way leads to labeled N_2O and unlabeled OCN. In the second way, the NO and ONCN molecules react by a four-center process



$$ONCN + NO \rightarrow \begin{array}{c} ON\cdots CN \\ \vdots \quad \vdots \\ N\cdots O \end{array} \rightarrow ONN + OCN$$

When labeled ONCN is used, the second way yields unlabeled N_2O and labeled OCN. Reaction 3 is probably a four-center process. The fact that NO does not abstract the nitrogen atom from OCN, giving CO and N_2O, is probably related to the fact that the latter products are less stable by 87 kcal/mol than the observed products CO_2 and N_2.[9]

According to the first mechanism, the use of terminally labeled ONCN should yield only doubly labeled cyanogen, and the amount of labeled N_2 should equal the amount of unlabeled N_2O. To account for the fact that the observed data deviate from these predictions, we propose that the following mechanism occurs concurrently with, but to a lesser extent than, the first mechanism

$$NO + ONCN \rightarrow N_2O + OCN \qquad (2)$$

$$OCN + ONCN \rightarrow NO_2 + (CN)_2 \qquad (4)$$

$$NO_2 + ONCN \rightarrow CO_2 + N_2 + NO \qquad (5)$$

This mechanism consists of three chain-propagating steps, involving the chain carriers NO, OCN, and NO_2. Reactions 1 and 3 can serve as the chain-initiating and -terminating steps, respectively, of this mechanism. It should be noted that the first step of the second mechanism (reaction 2) is the same as the second step of the first mechanism. The second step (reaction 4) is probably a four-center process; it yields singly labeled $(CN)_2$ when the OCN is unlabeled and the ONCN is labeled. The third step (reaction 5) may occur directly as a complicated multicenter process or may actually be a two-step process, involving nitryl cyanide as an intermediate.

The fraction of the nitrous oxide which is formed in reaction 2 by the abstraction by nitric oxide of the terminal nitrogen atom of nitrosyl cyanide is equal to the fraction of labeled N_2O formed in the experiments with labeled nitrosyl cyanide, $f(N^*NO)$. The average value of this quantity in runs 1–4 was 0.82 ± 0.03. The fraction of the nitrosyl cyanide which decomposed by the first mechanism, f_1, can be calculated from two independent sets of data

$$f_1 = f(NN)/f(N^*NO)$$

$$f_1 = [f(N^*NO) - f(N^*CCN)]/f(N^*NO)$$

The values of f_1 calculated in these ways for each of the four ^{15}N-labeled runs are given in Table III. The values calculated by the two different ways are in good agreement except in the case of runs 2 and 4. In spite of these discrepancies, all the data clearly indicate that the first mechanism (reactions 1–3) predominates in the thermal decomposition.

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Registry No. ONCN, 4343-68-4; nitrosyl chloride, 2696-92-6; silver cyanide, 506-64-9; $ONC^{15}N$, 63089-51-0.

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Crystal and Molecular Structure of Allyl(bromo)bis(triethylphosphine)platinum(II). An Example of σ Bonding of an η^1-Allyl Group

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Interest in transition metal σ-allyl complexes stems from their postulation as intermediates in the rearrangement reactions of fluxional π-allyl complexes.[1] Although much work has been devoted to the study of such fluxional π-allyl complexes of the platinum triad, until recently only a few stable σ-allyl derivatives of these metals had been isolated or even detected.[1-3] In the past year, a surprising number of reports have described various Pt(σ-allyl) complexes in solution or in the solid state.[4-10] Presently, we wish to report the crystallographic structure of *trans*-$Pt(\eta^1\text{-}C_3H_5)Br(PEt_3)_2$. An important feature of this x-ray structural study is the refinement of all the atoms in the molecule allowed by the excellent diffraction data obtained at −160 °C.

Experimental Section

The complex *trans*-η^1-allylbromobis(triethylphosphine)platinum(II) was synthesized from tetrakis(triethylphosphine)platinum(0) and allyl bromide as described elsewhere.[10] Crystals suitable for crystallographic examination were obtained by evaporation of a hexane solution of the complex at room temperature.

Structure Determination. A small fragment cleaved from a larger crystal was used for characterization and data collection. Precession photographs and a diffractometer search of reciprocal space revealed a monoclinic cell, space group $P2_1/c$. The crystal was mounted on an ultrastable goniometer head of local design using silicone grease and cooled to −160 °C on the goniostat using a nitrogen vapor cooling system.[11] The diffractometer used was locally designed and