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Some Chemistry of Difluorodiazine

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Difluorodiazine undergoes reaction with some sulfur oxides and sulfur and phosphorus fluorides and oxyfluorides. These reactions are characterized by fluorination or fluorination with oxygen elimination. The quantitative syntheses of difluoramidosulfuryl fluoride, FSO_2NF_2, and pentafluorosulfur difluoramine, SF_5NF_2, and a high yield preparation of sulfuryl bromide fluoride, FSO_2Br, are given. The isomerization of *trans*-N_2F_2 was accomplished at a temperature lower than formerly described.

Introduction

The isomers of difluorodiazine, N_2F_2, were first prepared by Haller in 1942[1] and later by others using various routes.[2-6] Besides an investigation of the relative reactivity of the isomers of N_2F_2 toward glass, mercury, and copper[2] and the observation that difluorodiazine behaves as a free radical source for the initiation of polymerization[2] and the cross linking of polymers,[7] virtually nothing is known of the chemistry of N_2F_2. To characterize more fully the chemical behavior of this reagent with substrates other than organic monomers, the compounds sulfur dioxide, sulfur trioxide, thionyl fluoride, sulfur tetrafluoride, disulfur decafluoride, phosphoryl fluoride, phosphorus trifluoride, fluorine fluorosulfonate, peroxydisulfuryl difluoride, and cesium fluorosulfonate were selected in this investigation. Use of these substrates allowed further characterization of the chemical behavior of N_2F_2.

Experimental

Reagents.—The sulfur dioxide in cylinder form and sulfur trioxide as "Sulfan B" were obtained from the General Chemical Division of the Allied Chemical Corp. The sulfur tetrafluoride was obtained from E. I. du Pont de Nemours and Co. in a cylinder. The thionyl fluoride was obtained from the sulfur tetrafluoride by allowing the latter to stand 0.5 hr. in moist air in a Pyrex vacuum apparatus and was purified by passing it through a trap maintained at −145° which retained the pure reagent. Cylinders of phosphorus trifluoride and phosphoryl fluoride were received from the Ozark-Mahoning Co. These commercially secured materials were of high purity and used without further purification. Peroxydisulfuryl difluoride[8] and fluorine fluorosulfonate[9] were prepared by literature methods. The disulfur decafluoride was prepared by fluorination of flowers of sulfur at −78°. The cesium fluorosulfonate was prepared by heating dry CsF, from Penn Rare Metals, Inc., at 100° for 1 day with excess SO_3. The excess SO_3 was removed by pumping *in vacuo* at 100°. The difluorodiazine mixture (95% *cis*, 4% *trans* isomer and 1% N_2O) and the tetrafluorohydrazine (99% N_2F_4 and 1% NO) were obtained from Air Products and Chemicals, Inc. The composition of the last two reagents was determined by mass spectral analysis.

Equipment and General Procedure.—A standard Pyrex glass vacuum apparatus was used for transferring gaseous materials and for obtaining pressure–volume information. The difluorodiazine cylinder was barricaded behind concrete and handled remotely. Prefluorinated stainless steel or Monel cylinders equipped with the corresponding Teflon-packed stainless steel or Monel Hoke valves were generally used as reactors for studies above room temperature although these were attacked slowly by *cis*-N_2F_2 at 95° to yield N_2 and metal fluorides. At elevated temperatures neither Pyrex nor Teflon vessels could be satisfactorily used due to formation of N_2O and SiF_4 in the former and fluorocarbons in the latter. No differences in the reactions were observed when either Monel or stainless steel was used. In the study involving SO_3, however, Pyrex reactors were also used. All gaseous reactants were condensed into the reactors at −196° and were allowed to warm to ambient temperature. The reactors were then placed in oil baths set at the required temperatures.

The mass spectrograph (Consolidated Engineering Corp. 21-620 with heated source at 200°), calibrated using pure gaseous samples, and an infrared spectrophotometer (Perkin-Elmer Infracord) were used for product identification and determination of mole per cent composition. This information, together with *PVT* data, was used to determine the quantity of each species present in the mixture. Conditions were chosen such that all the products were gaseous. Reaction of SF_4, PF_5, and SO_3 in the inlet system prevented use of the mass spectrometer for analysis of these gases. Analyses of these substances, however, could be obtained from the abundances of the other products found and from *PVT* data. The values placed in parentheses shown below represent the number of millimoles, and they are generally accurate to within 2–3% relative, but those for SF_4, PF_5, and SO_3 may be less accurately known. When aliquots were taken for analysis at various stages of a reaction, the results shown are compensated for the known fractions removed. The values are also compensated for the N_2O initially present in the N_2F_2. Small quantities of reagents were used due to the hazardous nature of N_2F_2.

Reactions with SO_2.—In a preliminary experiment a 10-ml. copper tube was loaded with equimolar quantities of N_2F_2 and SO_2 such that the total pressure at room temperature was about 80 atm. The temperature was raised slowly in an electrically controlled heater and at 102° the mixture exploded. In a subsequent attempt, sulfur dioxide (0.25) and N_2F_2 (0.25) were charged into a 75-ml. stainless steel cylinder. After standing 1.5 hr. at 100°, some reaction did take place. Analysis: N_2F_2 (0.12), N_2O (0.05), SOF_2 (0.04), N_2 (0.10), SO_2 (0.14), SO_2F_2 (0.05), $S_2O_5F_2$ (0.01), and SOF_4 (trace). The mixture was allowed to stand an additional 17 hr. at 100°. Analysis: *trans*-N_2F_2 (0.01), N_2 (0.14), N_2O (0.09), SO_2 (0.07), SOF_2 (0.08), and SO_2F_2 (0.08).

Addition of N_2F_4.—Difluorodiazine and N_2F_4 (0.52 each) together with SO_2 (0.62) were charged into a 150-ml. Monel

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cylinder. The mixture was heated at 100° for 21 hr. Analysis: FSO_2NF_2 (0.63), NF_3 (0.11), N_2F_4 (0.15), N_2F_2 (0.12), N_2 (0.40), and traces of N_2O and NO.

Addition of Br_2.—Difluorodiazine (0.53), SO_2 (1.07), and Br_2 (0.52) were loaded into a 150-ml. stainless steel reactor and heated at 100° for 24 hr. Analysis: FSO_2Br (0.89), SO_2F_2 (0.08), SO_2 (0.10), N_2 (0.53), O_2 (0.03), and Br_2 (0.05).

Additional Characterization of FSO_2Br.—Sulfuryl bromide fluoride shows infrared bands at 6.89 (s), 8.12 (s), and 12.3 (br, vs) μ assigned to the asymmetric and symmetric S=O stretching frequencies and the S—F stretching frequency, respectively.[10] It has one ^{19}F n.m.r. resonance at -120.9 ϕ relative to CCl_3F as the internal standard. The m/e, species, and relative mass spectral intensities for the most prominent absorptions are 67, FSO^+, 39.6; 83, FSO_2^+, 100; 162, $FSO_2{}^{79}Br$, 31.3; 164, $FSO_2{}^{81}Br$, 30.8.

Reactions with SO_3 in Metal. (a) **Excess N_2F_2.**—Difluorodiazine (2.98) and SO_3 (0.43) were loaded into a 75-ml. stainless steel reactor and allowed to stand at room temperature for 1 hr. Analysis: N_2O (0.26), $S_2O_5F_2$ (0.17), SO_2F_2 (0.10), and N_2F_2 (2.72). An aliquot was removed and distilled into a 10-ml. Pyrex bulb which was allowed to stand for 17 hr. at room temperature. Only a slight decrease in the amount of $S_2O_5F_2$ and increase in that of SO_2F_2 was observed. However, the sample which was allowed to age at room temperature in the metal cylinder showed significant change. Analysis: N_2O (0.40), $S_2O_5F_2$ (0.05), SO_2F_2 (0.33), and N_2F_2 (2.54).

(b) **Excess SO_3.**—Difluorodiazine (0.36) and SO_3 (0.48) were placed into the same cylinder as above and were heated at 100° for 17 hr. Analysis: N_2O (0.27), $S_2O_5F_2$ (0.22), SO_2F_2 (0.01), SO_3 (small amount), and N_2 (0.10).

Reactions in Pyrex Glass. (a) **Excess SO_3.**—In an experiment performed in a 115-ml. Pyrex bulb, N_2F_2 (0.29) and a several-fold excess of SO_3 were allowed to stand for 1 hr. at room temperature and then were further treated at 75° for 2 hr. Analysis showed $S_2O_5F_2$ (0.20), a small amount of $S_3O_8F_2$, N_2O (0.25), SiF_4, and unreacted SO_3. The $S_3O_8F_2$ was identified only by its infrared spectrum.

(b) **Excess N_2F_2.**—The N_2F_2 (1.14) and SO_3 (0.38) were placed into the same reactor and then heated to 75°. The following are the quantities of $S_2O_5F_2$ and SO_2F_2 found after periodic monitoring: 2.5 hr. $S_2O_5F_2$ (0.04), SO_2F_2 (trace); 3 hr. $S_2O_5F_2$ (0.05), SO_2F_2 (>0.01); 15 hr. $S_2O_5F_2$ (0.14), SO_2F_2 (0.02); and 20 hr. $S_2O_5F_2$ (0.19), SO_2F_2 (0.03). The other materials present were unreacted SO_3 (except after 20 hr.) and N_2F_2 together with N_2, N_2O, and SiF_4.

Reactions with SF_4.—Sulfur tetrafluoride (0.12), high purity according to infrared analysis, and N_2F_2 (0.21) were charged into a 75-ml. stainless steel cylinder and heated at 80° for 1 hr. Mass spectral analysis indicated only a trace of SF_5-containing material had been formed. The mixture was further treated at 100° for 16 hr. Analysis: S_2F_{10} (0.05), SF_6 (0.02), N_2 (0.16), N_2O (0.02), and *trans*-N_2F_2 (0.01).

Addition of N_2F_4.—Tetrafluorohydrazine (0.62), SF_4 (0.57), and N_2F_2 (0.56) were charged into a 150-ml. Monel cylinder. The cylinder and contents were allowed to stand at 100° for 17 hr. Analysis: SF_5NF_2 (0.56), N_2 (0.51), NF_3 (0.44), *trans*-N_2F_2 (0.03), N_2F_4 (0.15).

Reactions with SOF_2.—The same cylinder was charged with N_2F_2 (0.31) and SOF_2 (0.33) and placed in a bath set at 100° for 44 hr. Analysis: SOF_4 (0.17), SOF_2 (0.09), SO_2F_2 (0.02), *trans*-N_2F_2 (0.01), N_2O (0.03), and N_2 (0.26).

Reactions with POF_3.—POF_3 (0.90) and N_2F_2 (1.18) were placed into a 150-ml. Monel cylinder. The vessel was then heated at 85° for 24 hr. Infrared analysis showed nearly complete conversion of the POF_3 to PF_5. Analysis: PF_5 (0.9), N_2 (0.89), O_2 (0.44), N_2O (0.04), and N_2F_2 (0.20). The reactor was not previously used or fluorinated.

Reactions with PF_3.—N_2F_2 (0.78) and PF_3 (0.78) were charged into a 75-ml. stainless steel reactor. After standing for 17 hr. at room temperature, infrared examination showed that most of the PF_3 was converted to PF_5, and a small quantity of POF_3 was observed. Analysis: PF_3 (0.22), PF_5 (0.5), POF_3 (trace), N_2 (0.53), N_2F_2 (0.20), and N_2O (0.04).

Attempted Reactions with $S_2O_6F_2$, SO_3F_2, and $CsOSO_2F$.—Approximately 2-mmole quantities of SO_3F_2 and $S_2O_6F_2$ were allowed to contact separately with an equal quantity of *cis*-N_2F_2 in 150-ml. Monel cylinders first at 100° for several hours and then the reactions were repeated at 150° for several hours. When $CsOSO_2F$ (5 g.) was used as the substrate the same conditions and procedure as above were employed. Only decomposition of the *cis*-N_2F_2 was observed in every case.

Aging of *cis*-N_2F_2.—One mmole of N_2F_2 (containing 4% *trans*) was allowed to stand in each a Monel and a stainless steel cylinder at 100° for 24 hr. Complete decomposition to N_2 and metal fluorides was observed. Analysis: N_2 (0.97), *trans*-N_2F_2 (0.01) in Monel; N_2 (0.96), *trans*-N_2F_2 (0.01) in stainless steel.

Aging of *trans*-N_2F_2.—A mixture containing *trans*-N_2F_2 (0.49) and *cis*-N_2F_2 (0.05) was charged into a 75-ml. stainless steel reactor and heated to 95° for 14 hr. Analysis: *cis*-N_2F_2 (0.41), *trans*-N_2F_2 (0.01), N_2 (0.11), and N_2O (trace).

Results and Discussion

It has been shown in this work that *cis*-N_2F_2 can behave (1) as a fluorination agent or (2) both as a deoxygenation and fluorination agent depending upon the nature of the substrate. An example of each reaction type has been provided previously by the behavior of the isomeric mixture toward metal at elevated temperatures and by the behavior of *cis*-N_2F_2 toward glass.[2] Reaction type 1 may also account for its free radical polymerization initiation and cross linking of polymers such as the Viton fluoroelastomers.[7] Both types of polymer reactions presumably involve the fluorination of a double bond to form the intermediate $>\mathrm{C}-\mathrm{C}<\mathrm{F}$ radical which may then form polymerized or cross-linked products.

Sulfur dioxide undergoes both types of reaction with *cis*-N_2F_2 on standing at 100° in a stainless steel cylinder to give as principal products SO_2F_2, SOF_2, N_2O, and N_2 and the transit minor products, $S_2O_5F_2$ and SOF_4. The intermediary appearance of $S_2O_5F_2$ is unexplained. It disappears as a result of a subsequent reaction with N_2F_2 discussed later in the text. The SOF_4 formation results from the fluorination of SOF_2 by N_2F_2 (described below). Its absence from the products after continued reaction and the lack of a complete material balance for the sulfur-containing species in this and in another experiment below may be explained by reaction with the metal fluorides present on the wall of the stainless steel reactor.[11] Although it was previously cited that N_2F_2 undergoes free radical reactions, it was of interest to determine whether an electrophile, such as BF_3, would catalyze the reaction between SO_2 and N_2F_2 as it does the fluorination of ketonic double bonds by SF_4.[12] However, in this case, BF_3 addition does not increase the rate of reaction or alter the nature or relative abundances of the products under the same conditions as in its absence. The existence of the FSO_2 radical and evidence that the reaction is not completely concerted is demonstrated by the quan-

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titative formation of FSO_2NF_2 at 100° by the addition of the radical trap, N_2F_4. This method of preparation of FSO_2NF_2, in addition to being quantitative, requires a lower temperature and a far shorter reaction time than those necessary in its preparation from SO_2 and N_2F_4. The reactions of both N_2F_4 and N_2F_2 with SO_2 appear to be initiated by fluorination.[10] The addition of Br_2 to the SO_2–N_2F_2 reaction mixture results in the formation of FSO_2Br at 100°. The yield was 83% based on the SO_2. In the SO_2–N_2F_2 system it appears that N_2F_4 and Br_2 are nearly equally good radical traps.

With SO_3 used as a substrate the type 2 reaction products $S_3O_8F_2$, $S_2O_5F_2$, SO_2F_2, and N_2O are formed. The nature and relative abundances of these products as well as the reaction rates are dependent upon the reactant ratios and type of reactor used. When excess SO_3 is used, the major sulfur-containing product is $S_2O_5F_2$ when either Pyrex or stainless steel is employed in the reactor. Trisulfuryl fluoride ($S_3O_8F_2$) is also formed in Pyrex when the excess is large. Complete consumption of the SO_3 is achieved in the presence of excess N_2F_2 in Pyrex after 20 hr. at 75°, but is very nearly accomplished after 1 hr. at room temperature using stainless steel. The reaction using excess N_2F_2 in metal at room temperature results in the initial formation of $S_2O_5F_2$ and N_2O as the major products. Once being formed, the $S_2O_5F_2$ may undergo further reaction with N_2F_2 in metal at room temperature (but only to a very limited extent in Pyrex even at elevated temperatures) to yield SO_2F_2 and N_2O. Reasonable material balances between N_2O and SO_2F_2 and/or $S_2O_5F_2$ were obtained.

To test whether the fluorosulfonate radical ($FSO_3\cdot$) is an important species in the SO_3–N_2F_2 system as the $FSO_2\cdot$ is in the SO_2 case, N_2F_4 was added. The addition resulted in the formation of only a negligible amount of FSO_2ONF_2[13,14] which, if present, was not found to react further. Hence, the fluorosulfonate radical is unimportant in this system. Since the rate of reaction is not the same in metal as it is in Pyrex, a reaction utilizing the reactor wall, perhaps in the presence of an adsorbed polymeric form of SO_3, is involved. Nevertheless, the formation of pyrosulfuryl and trisulfuryl fluorides by reaction of SO_3 with fluorinating agents has precedent.[15]

Furthermore, *cis*-N_2F_2 does not react with either fluorosulfonate radical or the fluorosulfonate anion, since only decomposition of the diazine was noted under conditions employed when peroxydisulfuryl difluoride, fluorine fluorosulfonate (sources of the radical), and cesium fluorosulfonate were employed as substrates. The latter was used to determine whether an ionic substrate would facilitate the formation of fluorine fluorosulfonate or type 2 reaction products and also because of its ease of being fluorinated[16] compared to the higher temperatures required for the other fluorosulfonate salts.[17]

The type 2 reaction between *cis*-N_2F_2 and POF_3 yields PF_5, N_2, and O_2 in a ratio of very nearly 2:2:1. No N_2O was found in this case.

The reactions involving SOF_2, SF_4, and PF_3 each with N_2F_2 represent reaction type 1 and may be expressed as follows.

$$SOF_2 + N_2F_2 \xrightarrow[44\text{ hr.}]{100^\circ} SOF_4 + N_2$$

$$SF_4 + \text{excess } N_2F_2 \xrightarrow[16\text{ hr.}]{100^\circ} SF_6 + S_2F_{10} + N_2 \text{ (not balanced)}$$

$$PF_3 + N_2F_2 \xrightarrow[17\text{ hr.}]{\text{room temp.}} PF_5 + N_2$$

Disulfur decafluoride is the major product formed by the reaction of *cis*-N_2F_2 with SF_4 and, once formed, cannot be further fluorinated to SF_6 on prolonged heating at 100° in the presence of a large excess of N_2F_2. The quantitative formation of SF_5NF_2 when N_2F_4 is added to the reaction mixture suggests the existence of the $SF_5\cdot$, and further fluorination by N_2F_2 must take place prior to dimerization of the SF_5 radical.

In contrast to the isomerization study of Colburn and co-workers[2] in a flow system at >225°, it was found that the isomerization of *trans*-N_2F_2 to the *cis* isomer takes place below 100° nearly quantitatively in a static system. This isomerization is consistent with the heats of formation,[18] $\Delta H_f^\circ = 16.4$ kcal. for *cis*-N_2F_2 and $\Delta \bar{H}_f^\circ = 19.4$ kcal. for *trans*-N_2F_2, which indicate that the *cis* isomer is the thermodynamically more stable. Yet the work of Colburn[2] and the fact that the reaction mixtures frequently contained several per cent *trans*-N_2F_2 (*ca.* 4% *trans*-N_2F_2 was present in the original N_2F_2 samples used) indicate that the *cis* isomer is the chemically more reactive. *cis*-N_2F_2 is also the more labile with regard to yielding fluorinated products and N_2 compared to the other binary N–F cognates. It is seen from this and other work that N_2F_2 will attack stainless steel, Monel, and SO_2 below 100°, whereas N_2F_4 will undergo reaction with copper and SO_2 above 110°.[10] The great inertness of NF_3 is well known.[19]

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