data are consistent with the observation of Basila, et al.,[29] that pyridinium ions are formed reversibly when $H_2O$ is added to Lewis-bound pyridine on cracking catalysts. Thus, if a $C_3H_7^+$ carbonium ion is an intermediate in any of the chemistry of interest here, it is probably the nonclassical ion of Baird and Aboderin,[15] formed by interaction of Lewis-bound cyclopropane with hydroxyl hydrogen.

As pointed out earlier,[12] silica–alumina catalysts may contain a Brønsted function by virtue of a reversible reaction between a trigonal aluminum ion and an adjacent SiOH group, i.e.

$$\text{(12)}$$
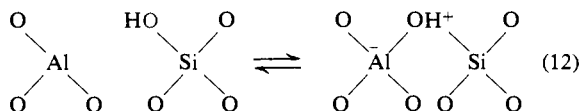
A change in coordination number of aluminum from 3 to 4 will occur whenever the tetrahedra so formed can be screened by a stable ion, e.g., $Na^+$, $NH_4^+$, or a carbonium ion; the four-coordinated aluminum is unstable only when the screening cation is a proton. This chemistry is inferred from consideration of the changes which must occur during decationation of the X and Y zeolites. In the sodium forms, the aluminum is entirely tetrahedrally coordinated; it so remains as $Na^+$ ions are replaced by $NH_4^+$. On heating, ammonia is evolved and the remaining proton attacks the lattice, breaking an AlOSi bond to form the entity indicated by the left-hand member of eq. 12. Presumably, if a molecule is chemisorbed on the trigonal aluminum ion, it may become protonated by the adjacent hydroxyl group. On a silica–alumina catalyst, the structure is not so well organized as with a zeolite. Hence, several hydroxyl (or deuteroxyl) groups may be adjacent to the same site and the behavior shown on Figure 1 could conceivably result. A slow rearrangement of the surface could similarly mislead us. Water presumably could function as cocatalyst as well as OH groups. Unfortunately, the model affords no explanation of the much more favorable ratio of

isomerization to exchange over silica–alumina than over alumina or why no isotope effect was observed.

Pairs of sites represented by the left-hand member of eq. 12 can be dehydroxylated, creating strongly electrophilic sites, i.e.

$$\text{(13)}$$
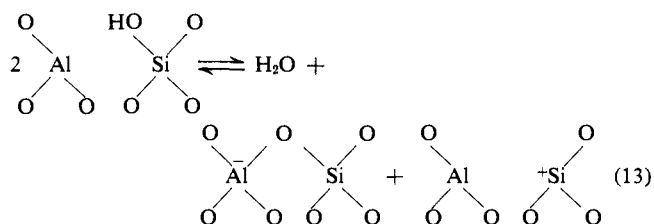
The strongly electrophilic defect sites, where an oxygen is missing, predominate in decationated zeolites after pretreatment equivalent to that used in the present work.[32] Presumably, analogous sites could function in silica–alumina.

In the present work, direct evidence for acidic protons was sought but not obtained; it cannot be categorically stated, however, that a protonic acid of concentration less than $10^{12}/cm.^2$ is not present. Until the basic question concerning the nature of the acid function of silica–alumina and alumina is settled, little real progress can be made towards a detailed understanding of the mechanisms of reactions occurring on these surfaces. This is demonstrated by the alternative mechanisms for the several types of intermediates considered herein. It is hoped that further work will lead to distinction among these possibilities.

(32) J. B. Uytterhoeven, L. G. Christner, and W. K. Hall, J. Phys. Chem., in press.

# The Preparation of Fluorodiazonium Hexafluoroarsenate ($N_2F^+AsF^-$) from cis-Difluorodiazine[1]

David Moy and Archie R. Young, II

Contribution from the Reaction Motors Division, Thiokol Chemical Corporation, Denville, New Jersey. Received December 23, 1964

cis-Difluorodiazine and arsenic pentafluoride react at or below ambient temperature to yield a 1:1 solid adduct. The adduct is stable under an atmosphere of dry nitrogen to 150°. It reacts violently with water but is soluble and stable in anhydrous hydrogen fluoride. Although no stable derivative of the fluorodiazonium cation ($N_2F^+$) has been reported previously, the $F^{19}$ nuclear magnetic resonance spectrum and X-ray diffraction pattern of the adduct strongly suggest an ionic constitution ($N_2F^+AsF_6^-$) in hydrogen fluoride and in the solid state.

## Introduction

Difluorodiazine was first prepared by Haller[2] in 1942. Its electron diffraction pattern is consistent

(1) Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(2) J. Haller, Doctoral Dissertation, Cornell University, Ithaca, N. Y., Sept. 1942.

with a mixture of *cis* and *trans* isomers.[3] Colburn, et al.,[4] first separated the isomers and showed that the infrared spectrum of the higher melting isomer was consistent with a *trans* configuration. The results of a recent nuclear magnetic resonance study[5] appear to confirm the assignment of a *cis* configuration to the lower melting isomer.

We are investigating the chemistry of difluorodiazine with particular emphasis on determining whether it can undergo addition reactions at the N=N double bond. Upon examining the possibility that arsenic pentafluoride might act as a catalyst for such addition reactions, it was observed that *cis*-difluorodiazine reacts with arsenic pentafluoride to yield a stable white solid. An investigation of the composition and constitution of this solid was undertaken. The results show that the solid is a 1:1 adduct, the most likely structure of which is $N_2F^+AsF_6^-$.

### Experimental

*Materials.* Arsenic pentafluoride was obtained from Peninsular ChemResearch and contained silicon tetrafluoride and boron trifluoride impurities in small amounts (<5%). *cis*-Difluorodiazine was obtained from Air Products, Inc., and contained *trans*-difluorodiazine (*ca.* 8%) as the principal impurity. Nitronium hexafluoroarsenate was obtained from Ozark-Mahoning, Inc. The materials were used without further purification.

*Preparation of cis-$N_2F_2 \cdot AsF_5$.* Quantities of *cis*-difluorodiazine and arsenic pentafluoride were measured separately in a 1-l. Monel bulb and then condensed into a Kel-F reaction tube at $-196°$. The tube was allowed to warm to room temperature, and after 1–2 hr. the residual pressure in the tube was measured and gas samples were taken for infrared analysis. The white solid product was pumped for several hours to remove traces of volatile impurities ($SiF_4$, $BF_3$, and *trans*-$N_2F_2$). The product was removed from the reaction tube in a dry nitrogen atmosphere box and stored under nitrogen in Kel-F vials.

Under the same conditions, *trans*-difluorodiazine did not react with arsenic pentafluoride.

*Analysis of cis-$N_2F_2 \cdot AsF_5$. 1. Elemental Analysis.* Independent N, F, and As analyses were performed on the solid adduct.

*Anal.* Calcd. for $N_2F_2 \cdot AsF_5$: N, 11.88; F, 56.36; As, 31.76. Found: N, 11.83; F, 56.79; As, 31.59.

*2. Mass Spectrum.* A Monel tube containing a small sample of the adduct was attached to a Bendix Time-Of-Flight mass spectrometer (Model 12-101) and evacuated. No cracking pattern was observed at ambient temperature. When the tube was heated to 150°, only fragments attributable to the presence of arsenic pentafluoride and a mixture of the isomers of difluorodiazine were observed.

*3. Hydrolytic Decomposition.* Two samples, 0.172 and 0.269 g., of the solid adduct produced 0.67 mmole of nitrous oxide (theory for $N_2F_2 \cdot AsF_5$, 0.73 mmole) and 1.12 mmoles of nitrous oxide (theory for $N_2F_2 \cdot AsF_5$, 1.14 mmoles), respectively, on reaction with water in a closed Kel-F tube. $N_2O$ was distilled from the

(3) S. Bauer, *J. Am. Chem. Soc.*, **69**, 3104 (1947).
(4) C. Colburn, *et al.*, *ibid.*, **81**, 6397 (1959).
(5) J. Noggle, *et al.*, *J. Chem. Phys.*, **38**, 169 (1963).

reaction tube at $-80°$ and identified by its infrared spectrum.

*4. Reaction with Sodium Fluoride in Hydrogen Fluoride.* Anhydrous HF was obtained by allowing water-contaminated HF to react with the solid adduct until $N_2O$ was no longer evolved. The anhydrous HF was then distilled onto a fresh sample of the adduct. The adduct dissolved readily above 0°, and could be recovered unchanged upon removal of the HF.

Excess NaF was added to a solution of 0.205 g. of the solid adduct in HF. The reactor was cooled to $-80°$, and 0.85 mmole of gas was distilled out of the reactor. On the basis of its infrared spectrum, the gas was estimated to be 95+% or 0.81 mmole of *cis*-$N_2F_2$ (theory for $N_2F_2 \cdot AsF_5$, 0.87 mmole), the balance being $N_2O$.

*Characterization of cis-$N_2F_2 \cdot AsF_5$. 1. Infrared Spectrum.* A conventional low temperature infrared cell constructed of Pyrex with an internal silver chloride plate supported on a hollow copper block was used to obtain a spectrum of *cis*-$N_2F_2 \cdot AsF_5$. Arsenic pentafluoride and *cis*-difluorodiazine were condensed onto the silver chloride plate at $-196°$. The cell was pumped as the plate warmed to room temperature. A thin film of solid remaining on the plate at room temperature was scanned on a Perkin-Elmer Model 21 spectrometer from 2 to 15 $\mu$.

*2. $F^{19}$ Nuclear Magnetic Resonance Spectrum.* The $F^{19}$ n.m.r. spectrum of a solution of the adduct in anhydrous HF (*ca.* 40% solution) was obtained on a Varian HR-60 spectrometer at room temperature. Trifluoroacetic acid (TFA) was used as an external reference. Approximate chemical shifts (uncorrected for bulk susceptibility effects) and N–F coupling constants were obtained from the location of TFA side bands with an accuracy of ±10 c.p.s. A Teflon tube (6 in. × 0.5 in.) fitted to a valve and ball joint by means of Swagelock connections was used as a sample tube. A sealed Kel-F capillary containing TFA was inserted directly into the sample tube.

*3. Powder Diffraction Pattern.* Powder diffraction patterns were obtained on samples of the adduct from separate preparative runs and on samples recovered from HF solutions. All the patterns were identical. The patterns were photographed with Cu K$\alpha$ radiation from a nickel filter. The X-ray samples were sealed under nitrogen in Pyrex capillaries.

*4. Density.* The density of a perfluorinated ether, FC-75,[6] with which the adduct was compatible, was determined to be 1.77 g./ml. at 25°. The density of the solid adduct at 25° was determined to be 2.6 g./ml. by displacement of FC-75.

### Discussion

*Stoichiometry of Solid Adduct.* The data presented in Table I show that arsenic pentafluoride and *cis*-difluorodiazine react in a 1:1 mole ratio as indicated by eq. 1. The only gases recovered when equimolar

$$cis\text{-}N_2F_2 + AsF_5 \longrightarrow N_2F_2 \cdot AsF_5 \qquad (1)$$

quantities of the reagents were mixed were $SiF_4$, $BF_3$, and *trans*-$N_2F_2$, all of which were present initially as impurities. The use of an excess of either reagent

(6) Trade name, Minnesota Mining and Manufacturing Co.

resulted in the quantitative recovery of that portion of reagent in excess of an equimolar amount. The results of separate fluorine, arsenic, and nitrogen analyses substantiate the 1:1 stoichiometry.

**Table I.** Preparation of $N_2F_2 \cdot AsF_5$

| —Initial reagents, mmoles— | | Volatile products recovered, mmole |
|---|---|---|
| $N_2F_2$ | $AsF_5$ | |
| 1.0 | 1.0 | <0.2 $\begin{cases} trans\text{-}N_2F_2, \\ SiF_4, BF_3 \end{cases}$ |
| 2.0 | 1.0 | ~1.0 $\begin{cases} cis\text{-}N_2F_2\text{-}trans\text{-}N_2F_2, \\ SiF_4, BF_3 \end{cases}$ |
| 1.0 | 2.0 | ~1.0 $\begin{cases} AsF_5, trans\text{-}N_2F_2, \\ SiF_4, BF_3 \end{cases}$ |

Arsenic pentafluoride does not react with *trans*-difluorodiazine under the conditions which lead to a stable adduct with the *cis* isomer. The difference in reactivities of the *cis* and *trans* isomers toward arsenic pentafluoride parallels their different reactivities toward glass and mercury.[2]

In addition to the elemental analyses and preparative data, the stoichiometry of the solid adduct can be inferred from the results obtained by allowing it to react with water and with sodium fluoride. The reaction with water consistently produced quantities of nitrous oxide in excellent agreement with the theoretical quantities predicted by eq. 2. Difluorodiazine itself
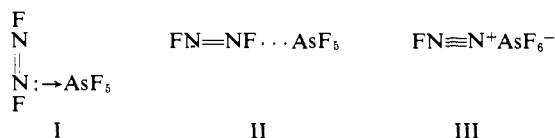
$$N_2F_2 \cdot AsF_5 + H_2O \longrightarrow N_2O + HF + HAsF_6 \qquad (2)$$
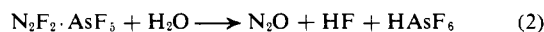
does not undergo acidic or basic decomposition in water in the absence of reducing agents.[7]

The reaction with sodium fluoride in hydrogen fluoride also serves to confirm the 1:1 stoichiometry. The total nitrogen recovered as *cis*-difluorodiazine and nitrous oxide was in excess of 98% of the theoretical quantities predicted by eq. 3. The presence of a small

$$N_2F_2 \cdot AsF_5 + NaF \longrightarrow cis\text{-}N_2F_2 + NaAsF_6 \qquad (3)$$
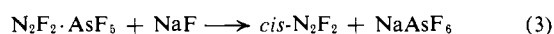
amount of water in the sodium fluoride could account for the nitrous oxide formation *via* the reaction shown in eq. 2.

*Constitution of the Adduct.* There are three readily apparent structures that one might write for a 1:1 *cis*-difluorodiazine–arsenic pentafluoride adduct; namely, two molecular adduct structures involving, respectively, nitrogen lone-pair donation (I), fluorine bridging (II), and a fluorodiazonium salt structure (III). Although no precedent has been established in difluorodiazine chemistry that might indicate a preferred

$$\begin{array}{ccc} \begin{matrix} F \\ N \\ \| \\ N : \rightarrow AsF_5 \\ F \end{matrix} & FN{=}NF \cdots AsF_5 & FN{\equiv}N^+AsF_6^- \\ I & II & III \end{array}$$

structure for the adduct, these three structures do not appear to be of equal plausibility. In our judgment only the fluorodiazonium salt structure (III) is consistent with all of the results obtained upon examining $F^{19}$ n.m.r. absorption of the adduct in hydrogen fluoride, as well as X-ray diffraction and infrared absorption of the solid.

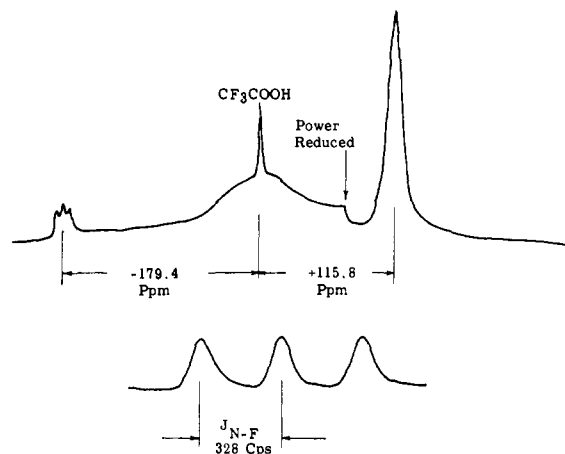(7) M. Schmeisser and P. Sartori, *Angew. Chem.*, **71**, 523 (1959).



Figure 1. $F^{19}$ n.m.r. spectrum of $N_2FAsF_6$ in anhydrous HF.

The $F^{19}$ n.m.r. spectrum of a 40% solution of the adduct in anhydrous hydrogen fluoride (Figure 1) shows a fluorine on nitrogen triplet at a chemical shift of $-179.4$ p.p.m. from trifluoroacetic acid. The N–F coupling constant $(J_{N-F})$ is 328 c.p.s. The HF absorption appears at a chemical shift of $+115.8$ p.p.m., which is approximately 10 p.p.m. upfield of the chemical shift of pure hydrogen fluoride relative to trifluoroacetic acid. There is no peak in the spectrum assignable to fluorine on arsenic. The observed N–F coupling constant of 328 c.p.s. in the spectrum of the adduct is more than twice the values reported for $J_{N-F}$ of *cis*- and *trans*-difluorodiazine[5] (Table II).

**Table II.** $F^{19}$ Chemical Shifts and N–F Coupling Constants of N–F Compounds

| Compound | $\delta$, from $CF_3COOH$ | $J_{N-F}$, c.p.s. |
|---|---|---|
| $NF_3{}^a$ | $-220$ | 155 |
| $cis\text{-}N_2F_2{}^a$ | $-228$ | 145 |
| $trans\text{-}N_2F_2{}^a$ | $-167$ | 136 |
| $N_2FAsF_6$ | $-179.4$ | 328 |

*a* See ref. 5.

This indicates an increase in the "s-character" of the nitrogen bonding orbitals in the adduct.[8] Since such a change in bond hybridization would occur in going from $FN{=}NF$ (sp²) to $N{\equiv}N^+F$ (sp) but would not occur upon formation of a molecular complex either by electron-pair donation or fluorine bridging, the magnitude of the observed $J_{N-F}$ is consistent only with the fluorodiazonium salt structure (III). The appearance of only one fluorine on nitrogen resonance peak (Figure 1) is also consistent with the fluorodiazonium structure. Structures such as I and II, involving nonequivalent N–F fluorine atoms, would be expected to exhibit two N–F resonance peaks. The absence of a fluorine on arsenic peak and the upfield displacement of the solvent peak are indications of rapid fluorine exchange between the solvent and the As–F species present (presumed to be $AsF_6^-$). The same results were obtained with a solution of sodium hexafluoroarsenate in hydrogen fluoride at room temperature.

(8) E. Muetterties and W. Phillips, *Advan. Inorg. Chem. Radiochem.*, **4**, 224 (1962).

Attempts to observe the n.m.r. spectrum of the adduct below ambient temperatures were unsuccessful because of insufficient solubility.

The infrared spectrum of a thin film of the solid adduct (Figure 2) shows a single absorption in the region normally assigned to N–F stretching vibrations, occurring at 1050 cm.$^{-1}$. cis-Difluorodiazine[9] ex-
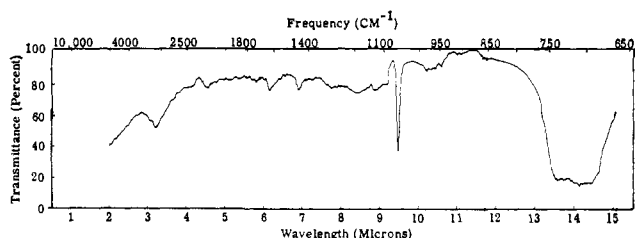


Figure 2. Infrared spectrum of $N_2FAsF_6$ film on AgCl.

hibits two absorptions in this region at 896 and 952 cm.$^{-1}$. The shift to higher frequency observed in the spectrum of the adduct is indicative of N–F bond shortening, which eliminates from consideration any structure for the solid that involves fluorine bridging. No choice can be made between the remaining structures (I and III) on this basis, since N–F bond shortening would be predicted for both. However, the absence of a second N–F stretching band in the region from 1100 to 850 cm.$^{-1}$ may be advanced as evidence, admittedly negative, in favor of the fluorodiazonium structure (III) for the solid. The broad absorption centered at 715 cm.$^{-1}$ is in the region normally assigned to the hexafluoroarsenate anion.[10]

The X-ray diffraction pattern of the adduct is almost identical with that of the hexafluoroarsenate salt of the linear nitronium ion (Table III). This is evidence that the solid adduct contains a cation similar in size and shape to the nitronium ion. The $N_2F^+$ ion is isoelectronic with $NO_2^+$, and the evidence from X-ray data that it is linear supports our interpretation of the $F^{19}$ n.m.r. spectrum of the adduct.

*Properties of Fluorodiazonium Hexafluoroarsenate.* $N_2FAsF_6$ is a white solid having a density of 2.6 g./cc. at 25°. It is stable at ambient temperature under dry nitrogen in glass, Kel-F, Teflon, or metal containers. When heated under dry nitrogen it decomposes without melting at 150°. No vapor pressure is observed above $N_2FAsF_6$ at ambient temperature, but it sublimes with some decomposition above 75° *in vacuo.* $N_2FAsF_6$ is soluble and stable in anhydrous hydrogen fluoride at ambient temperature, but is rapidly decomposed by water, arsenic trifluoride,
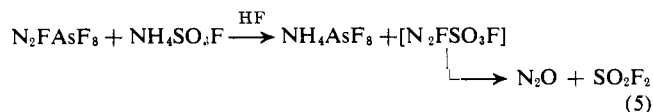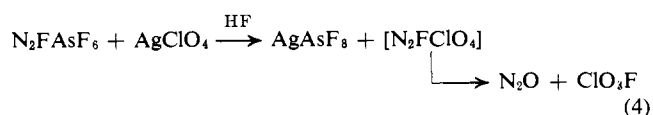
(9) R. Sanborn, *J. Chem. Phys.*, 33, 1855 (1960).
(10) R. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 2762 (1959).

**Table III.** Power Diffraction Patterns of $N_2FAsF_6$ and $NO_2AsF_6$

| $N_2FAsF_6$ | | $NO_2AsF_6$ | |
|---|---|---|---|
| $I/I_0$ | d, Å. | d, Å. | $I/I_0$ |
| 20 | 5.18 | 5.17 | 5 |
| 80 | 4.92 | 5.03 | 20 |
| | | 4.85 | 15 |
| 50 | 4.59 | 4.59 | 30 |
| | | 4.46 | 30 |
| | | 4.03 | 3 |
| 100 | 3.57 | 3.53 | 100 |
| 20 | 3.42 | 3.36 | 10 |
| 30 | 2.92 | 2.92 | 5 |
| 10 | 2.71 | 2.67 | 3 |
| 5 | 2.58 | 2.54 | 1 |
| 20 | 2.46 | 2.45 | 3 |
| 20 | 2.40 | 2.37 | 12 |
| 30 | 2.22 | 2.21 | 20 |
| 10 | 2.09 | 2.06 | 1 |
| 10 | 1.93 | 1.92 | 2 |
| 15 | 1.86 | 1.85 | 10 |
| 30 | 1.79 | 1.78 | 7 |
| 10 | 1.70 | 1.69 | 15 |
| 5 | 1.65 | 1.64 | 3 |
| 5 | 1.62 | 1.61 | 5 |
| 5 | 1.57 | 1.56 | 2 |
| 5 | 1.53 | | |
| 5 | 1.47 | | |
| 5 | 1:45 | 1.46 | 5 |
| 5 | 1.41 | 1.43 | 5 |
| 5 | 1.38 | | |
| 5 | 1.31 | | |
| 5 | 1.29 | | |
| 5 | 1.28 | | |

chlorine trifluoride, and bromine trifluoride. It undergoes metathesis with sodium fluoride (eq. 3), silver perchlorate (eq. 4), and ammonium fluorosulfonate (eq. 5) in anhydrous hydrogen fluoride. The mechanism by which only the cis isomer of difluorodiazine

$$N_2FAsF_6 + AgClO_4 \xrightarrow{HF} AgAsF_6 + [N_2FClO_4]$$
$$\xrightarrow{} N_2O + ClO_4F \quad (4)$$

$$N_2FAsF_6 + NH_4SO_3F \xrightarrow{HF} NH_4AsF_6 + [N_2FSO_3F]$$
$$\xrightarrow{} N_2O + SO_2F_2 \quad (5)$$

is obtained from the reaction of $N_2FAsF_6$ with sodium fluoride (eq. 3) is not immediately apparent.