Kinetic Studies of the Reactions of Anions with Difluoramine

W. T. Yap, A. D. Craig, and G. A. Ward

Contribution from the Research Center, Hercules Incorporated,
Wilmington, Delaware 19899. *Received February 3, 1967*

Abstract: The kinetics of the reactions of difluoramine with a variety of anions in aqueous solution have been studied. The experimental method employed was to measure the concentration of HNF_2 in solution as a function of time by polarographic analysis. The concentration of anion was varied from 10^{-3} to 1.0 *M*, usually under pseudo-first-order conditions. In general, the reactions are first order in difluoramine and first order in the anion. The second-order rate constants for the reactions decrease in the order $OH^- > HSO_3^- > CN^- > I^- > SCN^- > N_3^- > Br^- > Cl^- > H_2PO_4^- > OAc^-$. Precise values of each rate constant were obtained for most of the ions, and analyses of the reaction products for each ion were made. With the exception of hydroxyl ion, this order of rankings of the ions corresponds to that of their expected nucleophilicities. This order is consistent with a mechanism which involves direct attack of the anion on HNF_2. The gross deviation of the behavior of hydroxyl ion from that of the other anions indicates that hydroxyl ion reacts with difluoramine by a mechanism different from that of the other anions.

Inorganic nitrogen–fluorine compounds are known to react with various anions and cations in aqueous solution. The reactions involve primarily hydrolysis or oxidation–reduction processes. Until recently, no kinetic or mechanistic studies of these reactions had been reported. The major experimental problems have been the low solubility of most of the compounds, the corrosive and sometimes explosive nature of some of the compounds and the lack of a convenient and accurate means by which to monitor the reactants. Recently, Hurst and Khayat reported on a study of the reactions of NF_3, N_2F_4, and N_2F_2 with various anions in aqueous solution.[1] Infrared spectroscopy was generally used for the analysis of the gaseous products of the reactions. We have found that the concentration of HNF_2 in aqueous and nonaqueous solution can be measured accurately by means of the polarographic reduction of HNF_2.[2] In a recent communication we reported a study of the kinetics of the alkaline hydrolysis of difluoramine.[3] In the present paper we report a study, using similar techniques, of the kinetics of the reactions of difluoramine with several other anions in aqueous solution.

Results

Reaction Products. The reactions of difluoramine with anions can be categorized into three general classes: (a) reaction with strong Brønsted bases to give difluorodiazine; (b) reaction with oxidizable anions to give products of oxidation–reduction processes; (c) slow replacement reactions to give ultimately nitrous oxide. These three classes of reaction can be exemplified by reactions a–c. These examples describe only the major products of the reactions.

$$2HNF_2 + 2OH^- \longrightarrow N_2F_2 + 2H_2O + 2F^- \quad (a)$$

$$HNF_2 + 4I^- + 2H_2O \longrightarrow NH_3 + 2I_2 + 2F^- + 2OH^- \quad (b)$$

$$2HNF_2 + 4OAc^- + H_2O \longrightarrow N_2O + 4F^- + \text{other products of decomposition} \quad (c)$$

In class a, other products such as N_2, NO_2^-, and N_2F_4 are often observed and appear to be the result of side reactions which occur after the initial attack on HNF_2 by the anion. The only strong base which we studied in aqueous solution was hydroxyl ion. This reaction has been discussed previously.[3] Methoxide ion attacks HNF_2 very rapidly in methanol to yield nitrogen as essentially the only nitrogen-containing product. Other alkoxide ions also rapidly attack HNF_2 in nonaqueous solvents, such as dimethyl sulfoxide and acetonitrile. Nitrogen is the major product in each reaction. These reactions in nonaqueous solvents should be the subject of another study and will not be discussed here.

In class b, ammonia is the major nitrogen-containing product from the reaction of HSO_3^-, I^-, CN^-, SCN^-, or Br^- with HNF_2 in aqueous solution. With azide ion, essentially all of the difluoramine nitrogen is converted to nitrogen. With chloride ion, the primary product is nitrogen, but ammonia in varying amounts is also produced. All reactions of class b ultimately yield nitrogen-containing products by the reduction of HNF_2. The anions undergo oxidation and yield a variety of products. Azide ion and sulfite ion are converted to nitrogen and sulfate ion, respectively, and these products do not react further in their particular systems. The other oxidizable anions, all halogen or pseudo-halogen anions, apparently yield initially the free halogen or pseudo-halogen. The free halogens or halogenoids may be hydrolyzed to other products; *e.g.*, about half of the thiocyanate ion which underwent reaction with HNF_2 was converted to HCN. The reaction path apparently involves $(SCN)_2$ which is readily hydrolyzed to SCN^-, HCN, and SO_4^{2-}.[4] In general, a reaction of the halogen or pseudo-halogen with water to yield H^+, X^-, and HOX is expected. The HOX can oxidize unreacted HNF_2 to give N_2F_4. Chloride ion produces $ClNF_2$, apparently through oxidation of HNF_2 by Cl_2 or OCl^-. The $ClNF_2$ can be recovered from solution. $BrNF_2$ also appears to be produced by an analogous reaction. The oxidation products, $ClNF_2$ and $BrNF_2$, are in equilibrium with N_2F_4 and free halogen and thus decompose slowly in solution. The oxidation products of HNF_2 also react

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[1] G. L. Hurst and S. I. Khayat in "Advanced Propellant Chemistry," Advances in Chemistry Series, No. 54, American Chemical Society, Washington, D. C., 1966, p 245 ff.

[2] G. A. Ward, C. M. Wright, and A. D. Craig, *J. Am. Chem. Soc.*, **88**, 713 (1966).

[3] A. D. Craig and G. A. Ward, *ibid.*, **88**, 4526 (1966).

[4] T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p 463 ff.

with the halogen and halogenoid anions to yield ultimately ammonia or nitrogen as the final product of the over-all reaction. Hydrolysis of the intermediate species yields products such as NO.

In class c, the reactions of acetate, dihydrogen phosphate, and monohydrogen phosphate ions do not involve oxidation–reduction processes. These reactions apparently involve an initial elimination of fluoride ion. This fluoride elimination is followed by decomposition reactions to give N_2F_2 and N_2O when the phosphates are the attacking anion and N_2O when acetate ion is the attacking anion.

After the initial anion attack, the reactions which follow in each of the three classes described are quite involved and do not lend themselves to simple clarification. Consequently, we have concerned ourselves only with the rate of consumption of difluoramine as a function of the attacking anion concentration. A study of the rate of formation of product materials should be the subject of a further investigation. In the kinetic studies, the anion concentrations were usually in large excess of the difluoramine concentration so that contributions from any anions of the type OX^- which might be formed could be neglected. In kinetic experiments where the anion concentration was not in large excess of the HNF_2, we did not find any evidence of contributions to the rate of disappearance of HNF_2 from attack by anion product species; *i.e.*, no significant deviations from first-order dependence on the anion were observed even at low anion concentrations. Should there be an undetected difference in the observed rate as compared to the specific rate for any of the anions, the difference would be only by a stoichiometric factor.

Rate Constants. Good pseudo-first-order plots of the log of the HNF_2 concentration *vs.* time were obtained at anion concentration levels tenfold or more greater than the HNF_2 concentration. Tables of the polarographic diffusion current as a function of reaction time were prepared from the polarographic data for each kinetic run after suitable corrections had been made for OH^- contributions. From these data, the first-order, least-squares rate constant of the reaction was calculated with a FORTRAN computer program. This program is used to calculate a rate constant (k) and an effective concentration C_0 at time $t = 0$ in the least-squares sense; that is, k and C_0 are such that

$$\mathrm{F}(k, C_0) = \sum_{i=1}^{n} (\ln C_i - \ln C_0 + kt_i)^2 \qquad (1)$$

is a minimum. C_i and t_i are the experimental concentration and time data points in this expression. The second-order rate constant, K_2, is calculated from the relationship

$$K_1 = K_2 A_0 \qquad (2)$$

where A_0 is the concentration of the anion. Variations of anion concentration over a range of at least tenfold had no significant effect on values of K_2.

For anion concentrations which are of the same magnitude as that of the HNF_2, the experimental data points (C_i, t_i) are fitted into the relation (eq 3), derived for the second-order reactions, where R is the known

$$C_i = \frac{C_0\left\{1 - \left[\dfrac{C_0}{A_0 + (R/K_2)}\right]\right\}\{\exp[-K_2(A_0 - C_0 + (R/K_2))t_i]\}}{1 - \left[\dfrac{C_0}{A_0 + (R/K_2)}\right]\{\exp[-K_2(A_0 - C_0 + (R/K_2))t_i]\}} \qquad (3)$$

rate constant for the reaction of the hydroxide and the buffer ions with HNF_2.[3] The least-square rate constant, K_2, and effective initial concentrations, C_0 and A_0, were obtained by use of a nonlinear regression computer program. Precision is better for the faster reactions because of experimental difficulties in the slower reactions; *e.g.*, less accurate sampling techniques had to be employed for the slower reactions. The second-order rate constants, for the reaction of HNF_2 with the various anions, decrease in the order shown in Table I.

Table I. Rate Constants for the Attack of Anions on HNF_2 at 25°

Anion	K_2, M^{-1} sec^{-1}
OH^-	$6.92 \times 10^2 \pm 0.30 \times 10^2$
HSO_3^-	$6.86 \times 10^{-1} \pm 0.48 \times 10^{-1}$
CN^-	$6.5 \times 10^{-1} \pm 1.5 \times 10^{-1}$
I^-	$2.33 \times 10^{-1} \pm 0.17 \times 10^{-1}$
SCN^-	$2.59 \times 10^{-2} \pm 0.45 \times 10^{-2}$
N_3^-	$1.07 \times 10^{-2} \pm 0.08 \times 10^{-2}$
Br^-	$7.0 \times 10^{-3} \pm 2.0 \times 10^{-3}$
Cl^-	$8.2 \times 10^{-4} \pm 3.0 \times 10^{-4}$
$H_2PO_4^-$	2.2×10^{-4}
HPO_4^{2-}	1.3×10^{-4}
OAc^-	$2.5 \times 10^{-5} \pm 0.3 \times 10^{-5}$

The K_2 values for the phosphates are tentative; they were obtained by assuming that the reaction is first order in both $H_2PO_4^-$ and HPO_4^{2-}. The reactions of bisulfite were done in pH 7.45 buffer solutions (due to experimental limitations mentioned below) where the sulfite and the bisulfite anions exist in approximately equimolar quantities. The K_2 value for the bisulfite in Table II was obtained by dividing the corresponding value of K_1 by the sum of the concentrations of the two anions.

Table II. Reaction of DNF_2 with Anions in D_2O

Anion	K_2, M^{-1} sec^{-1}	
	DNF_2 in D_2O	HNF_2 in H_2O
OD^-	6.25×10^2	6.92×10^2
I^-	2.00×10^{-1}	2.33×10^{-1}
N_3^-	5.01×10^{-3}	1.07×10^{-2}

The effects of deuteration on rates of reaction were studied in a completely deuterated system and in the reaction of DNF_2 with OH^- in H_2O. No significant changes in rate were observed (Tables II and III) for either system. The result with azide ion may be considered as a borderline situation, but a strong isotope effect is not indicated. The fact that the rate of reaction of DNF_2 in H_2O is essentially the same as that for

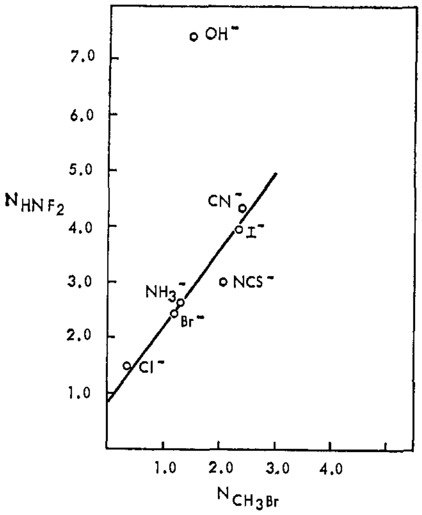

Figure 1. Correlation of nucleophilicity constants for reactions with HNF_2 and CH_3Br.

HNF_2 indicates that the hydrogen on the difluoramine exchanges with the water at a rate which is much faster than the rate of consumption of HNF_2 by hydroxyl ion. Thus, the observed value of K_1 (Table III) is most likely that for HNF_2. If the exchange were not faster, some isotope effect would be expected regardless of the mechanism. The values of OD^- concentration were calculated using data for the buffers.

Table III. Reaction of DNF_2 with Hydroxyl Ion in H_2O

pH	K_1, sec^{-1} (obsd) DNF_2 in H_2O	K_1, sec^{-1} (calcd) HNF_2 in H_2O
7.83	0.433×10^{-3}	0.466×10^{-3}
8.96	5.11×10^{-3}	6.15×10^{-3}
9.24	12.3×10^{-3}	12.0×10^{-3}

Discussion

Rate constants for the SN2 attack of nucleophiles on various substrates are generally correlated with the nucleophilic character of the reagent using a nucleophilic constant first proposed by Swain and Scott.[5] This constant, N, is defined by

$$N = \log k/k_0 \qquad (4)$$

k is the rate of the reaction of a given reagent with the substrate, and k_0 is the rate of reaction of a reference reagent with the substrate under the same conditions. The reactivity, or "nucleophilic character," measured in this manner is only roughly dependent on the basicity of the reagent to protons. It has been shown to be more closely related to the electron density on the reagent. Edwards, for example, has shown a close correlation between the nucleophilic constant and the standard oxidation potential for a number of anions.[6]

In treating the data, the rate of the reaction between acetate ion and HNF_2 was chosen as k_0, and N was calculated from eq 4 using the data in Table I. A plot of the N values obtained in this manner *vs.* the N values for the reaction of the various anions with methyl bromide (N_{CH_3Br}) is shown in Figure 1. The N_{CH_3Br} values were recalculated from the data collected by Eliel using acetate ion as a standard reagent rather than water, which was used in the original work.[7]

Figure 1 shows that a good correlation is obtained between N_{HNF_2} and N_{CH_3Br} for all anions except OH^-. The rate of reaction of OH^- with HNF_2 is, however, faster than would be predicted from the nucleophilicity correlation by a factor of more than 10^4. Edwards has proposed the use of a "dual basicity scale" in which a nucleophilicity coefficient is defined, as in eq 5, to

$$N = \alpha E_n + \beta H \qquad (5)$$

include contributions of both nucleophilicity and proton basicity.[6] In eq 5, α and β are empirically determined coefficients, E_n is the nucleophilicity parameter calculated from the oxidation–reduction potential of the reagent, and H is a basicity parameter calculated from the aqueous pK_a of the reagent. Attempts were made to fit the data in Table I to eq 5 using E_n and H values given by Edwards and various empirical values of α and β to obtain the best fit. It was found that as β increased, the N value for OH^- could be brought into better agreement with the data for the other ions, but that the scatter of the other points increased considerably. This indicates that the contribution due to the basicity of OH^- is most important and probably predominant for this anion, but the estimated H values for some of the other ions, principally for those forming strong acids, are probably less reliable than are the E_n values.

With the exception of hydroxyl ion, the first-order dependence of the reactions involving the various anions on both the HNF_2 concentration and the anion concentration, coupled with good correlation of the rate data with nucleophilicity, indicates that the reactions studied are taking place *via* an SN2 mechanism.

Variations in ionic strength had no significant effect on values of K_2; thus the initial reactions apparently involve the anion and an uncharged species. This species is most likely a solvated HNF_2 molecule. Difluoramine acts as only a weak base toward Lewis acids such as BF_3, indicating that the electron density on the nitrogen is not very high.[8] Calculations of electron densities on the fluorines in various nitrogen fluorides have shown that the fluorines carry a partial negative charge relative to that of the nitrogen.[9,10] Attack is thus probably directly on the nitrogen. Attack *via* the hydrogen is less likely since the observed rates do not correlate with the Brønsted basicity of the anions. Also, since deuteration of the difluoramine had no significant effect upon K_2 (in D_2O), breaking of the N–H bond apparently does not occur in the rate-determining step. Reaction of azide ion with HNF_2 to yield nitrogen as essentially the only nitrogen-containing product

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(5) C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, 75, 141 (1953).

(6) J. O. Edwards, *ibid.*, 76, 1540 (1964).

(7) E. L. Eliel in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 156.

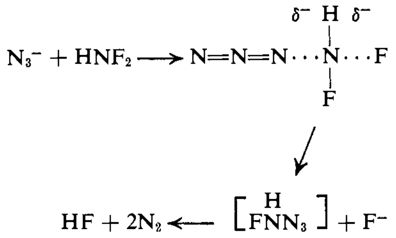
(8) A. D. Craig, *Inorg. Chem.*, 3, 1628 (1964).

(9) J. C. W. Chien, Hercules Powder Company, Annual Report, April 15, 1965, Contract No. DA-31-124-ARO(D)-62, ARPA Order No. 402.

(10) E. C. Curtis and J. S. Muirhead, *J. Phys. Chem.*, 70, 3330 (1966).

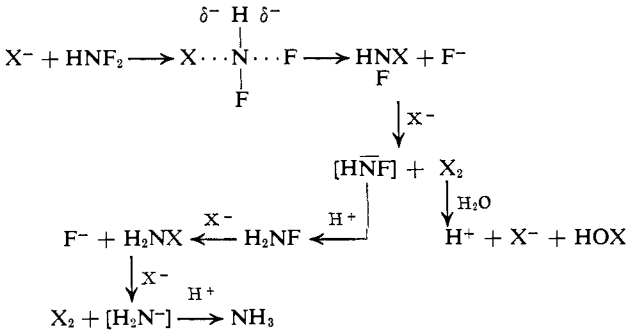
may be cited as chemical evidence supporting direct attack on the HNF_2 nitrogen. If attack by azide ion were on any site other than the HNF_2 nitrogen, different and more varied products would be expected. A reaction sequence such as shown in Scheme I is envisioned.

Scheme I



Possible reaction sequences after the initial attack involving the other anions can be only speculative at this point, but may involve routes such as shown in Scheme II. This reaction sequence for the chemical reduction of HNF_2 is analogous to that proposed for the electrochemical reduction of HNF_2.[2]

Scheme II



The value of K_2 for the hydroxide reaction is completely out of the expected order for nucleophilicity, and, relatively speaking, is exceptionally high. Thus, hydroxide ion probably reacts by a mechanism different from that of the other anions. The route of attack by hydroxyl ion could be an assisted S_N1 mechanism, *i.e.*, proton removal, or could involve a preionization of HNF_2 to give H^+ and NF_2^-. The latter route, the B1 mechanism, as well as the assisted S_N1 mechanism are in contrast to the bimolecular displacement which takes place when hydroxyl ion reacts with H_2NCl, CH_3NHCl, and $(CH_3)_2NCl$.[11] The kinetic experiments with DNF_2 in H_2O indicate that the exchange of D for H is rapid enough to expect that a labile equilibrium exists between the hydrogen on HNF_2 and the hydrogens on the water molecules. The existence of such a labile equilibrium, however, does not make one reaction mechanism more probable than the other.

Experimental Section

Materials. Difluoramine was prepared by the reaction of concentrated H_2SO_4 with trityldifluoramine.[12] Reagent grade acids, bases, and salts were used without further purification.

Kinetic Experiments. The reactions were studied at a level of concentration of HNF_2 of about 10^{-3} M and anion concentrations of from 10^{-3} to 1.0 M. The concentration of HNF_2 in solution was measured as a function of time by polarographic reduction of HNF_2.[2] The experimental procedure was essentially that which was described previously.[3] In some of the systems reported here, a residual current was observed which is caused by the reduction of product species, *e.g.*, N_2F_4 and N_2F_2. Fortunately, the reduction of the product species occurred at less negative potentials than that of HNF_2. In all of the kinetic experiments the contribution of the reduction of product species to the total diffusion current was constantly monitored. The residual current, when present, was subtracted from the total diffusion current. In earlier work with hydroxyl ion studies, the addition of methanol completely eliminated the residual current.[3] Addition of methanol to the systems reported here had no appreciable effect. Thus, methanol was not added to any of these systems.

In acidic or neutral solutions, bisulfite has two reduction waves: at about −0.8 and −1.5 v *vs.* saturated calomel electrode. To avoid the interference of these waves, the reactions of bisulfite were run in slightly basic, phosphate buffer solutions. The reactions of azide and cyanide ions were also measured in basic, phosphate buffer solutions (pH 7.5 to 8.0) to prevent loss of HN_3 and HCN, respectively. The reaction of acetate ion was studied in about equimolar sodium acetate–acetic acid buffer systems. The phosphate ions were studied in 0.05 to 0.5 M NaH_2PO_4–Na_2HPO_4 buffer systems. The remaining anions were all studied in acidic systems with no buffer present. The reaction rates of the hydroxide and buffer anions with HNF_2 in the solutions were taken into consideration in calculating the rate constants of the various anions.

The kinetic experiments involving DNF_2 and D_2O were run in the same manner as those experiments involving nondeuterated species. DNF_2 was prepared by making a 0.1 M solution of HNF_2 in D_2O and allowing the solution to reach equilibrium overnight. The DNF_2 (>97%) was removed from solution by conventional vacuum-system techniques. Purity was ascertained by mass spectrometry and by the infrared spectrum of the DNF_2.[13]

Analysis of Reaction Products. All work was carried out with a conventional, glass, high-vacuum system. Fluorocarbon grease was used to lubricate the stopcocks. The solution reactions are summarized below. In general, the experiments were run in a closed reactor with volume of 75 or 150 ml. The volume of solution was usually 50 ml. The concentration of the anions in solution varied from 0.1 to 0.6 M. Difluoramine sufficient to make 0.1 M solutions was distilled into the various reaction mixtures at −126° after they had been suitably degassed. All of the reactions were carried out at room temperature. The time allowed for each reaction varied from 0.5 to 40 hr, depending on the half-life of the reaction. The gaseous products of the reactions were separated by low-temperature vacuum distillations and identified by their infrared spectra. The gaseous products were analyzed by mass spectrometry, and products in solution were analyzed by elemental or group analysis.

Nitrate ion was determined by the phenoldisulfonic acid method,[14] and nitrite ion was determined by the diazotization method.[15] These ions were present in the products from every reaction system studied but were never present in significantly large amounts. Chloride was determined by the Volhard method,[16] and fluoride ion was determined colorimetrically as a Ce(III) chelate of alizarin.[17] The expected amount of fluoride was usually found in each solution at the end of the reaction. Ammonia was determined by the magnesium oxide distillation method.[18] Sulfate was determined by the barium sulfate method, and thiocyanate and cyanide were determined by a combination of the Volhard and Liebig methods.[19]

Hydroxyl Ion. The reaction of difluoramine with hydroxyl ion at pH values above 10 yields approximately 60% N_2F_2 and 20% N_2. The remainder of the nitrogen-containing products are varying

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(11) W. J. le Noble, *Tetrahedron Letters*, No. 7, 727 (1966).

(12) W. H. Graham and C. O. Parker, *J. Org. Chem.*, **28**, 850 (1963).

(13) J. J. Comeford, D. E. Mann, L. J. Schoen, and D. R. Lide, *J. Chem. Phys.*, **38**, 461 (1963).

(14) "Standard Methods for the Examination of Water, Sewage, and Industrial Wastes," 10th ed, American Public Health Association, Inc., New York, N. Y., 1955, p 149.

(15) Reference 14, 153.

(16) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, The Macmillan Co., New York, N. Y., 1955, p 455.

(17) R. Belcher and T. S. West, *Talanta*, **8**, 853 (1961).

(18) "Methods of Analysis of the Association of Official Analytical Chemists," 10th ed, Association of Official Analytical Chemists, Washington, D. C., 1965, paragraph 2.050.

(19) "Scott's Standard Methods of Chemical Analysis," 6th ed, D. Van Nostrand Co., Princeton, N. J., 1962.

amounts of N_2F_4, N_2O, NO_3^-, and NO_2^-. At lower pH values, less N_2 and more N_2F_2 is formed.

Bisulfite Ion. The reaction of this ion with difluoramine yielded 2 mmoles of sulfate ion for every millimole of HNF_2 that was consumed. The major nitrogen-containing species which was produced was ammonia. No nitrogen gas was produced.

Iodide Ion. One millimole of difluoramine reacted quantitatively with 4 mmoles of this ion to give NH_4^+.[20] If less than 4 mmoles of iodide per mmole of HNF_2 is employed, then a corresponding amount of N_2F_4 is formed. The N_2F_4 is apparently the product of the oxidation of unreacted HNF_2 by the iodine liberated.

Cyanide Ion. The reaction of excess CN^- (0.2 *M*) with HNF_2 was run in a solution buffered at pH 8.35 to prevent loss of HCN. The yield of nitrogen-containing material was 50% NH_3, 10% N_2, and 35% N_2F_2. The other products were N_2O and NO. The N_2F_2 and much of the nitrogen result from the reaction of hydroxyl ion with HNF_2. There is probably some contribution to the products from reactions of HCN with HNF_2 or intermediate species, as cyanide ion is in equilibrium with HCN at this pH. At the end of the reaction, a large amount of HCN was pumped out of the solution. No cyanogen was detected.

Thiocyanate Ion. The reaction of SCN^- with HNF_2 was run in an unbuffered system so that the pH of the system was well below 7. All of the HNF_2 was converted to ammonia in essentially quantitative yield. About half of the thiocyanate was converted to HCN. Small amounts of SO_2 were found in each experiment.

Azide Ion. Experiments with this ion were run in solutions buffered between pH values of 7.4 and 7.8. In every experiment more than 90% of the HNF_2 was converted to nitrogen. About 5 to 6% of the HNF_2 was converted to ammonia. The contribution to the reaction products from the reaction of hydroxyl ion with HNF_2 to yield N_2F_2 is subtracted from the over-all reaction. This contribution approached zero in the presence of large amounts of azide ion.

Bromide Ion. Reactions of Br^- with HNF_2 were studied in unbuffered solutions so that pH values were always below 7. Most of the solutions were 0.1 *M* in HNF_2 and 0.6 *M* in bromide ion (NaBr). Approximately one-third of the HNF_2 was converted to ammonium ion and two-thirds of the HNF_2 was oxidized to N_2F_4. Small amounts of nitric oxide were also found. This product is probably a result of the hydrolysis of the N_2F_4.

Chloride Ion. Experiments with Cl^- and HNF_2 were also conducted in unbuffered solutions. The solutions were 0.1 *M* in HNF_2 and from 0.2 to 0.5 *M* in chloride ion (NaCl). In a typical experiment, 39% of the HNF_2 was converted to nitrogen, 40% to N_2F_4, and the remainder to N_2F_2, NO, $ClNF_2$, and NH_3.

Acetate Ion. The reaction of this ion with HNF_2 was studied in solutions which were 0.1 *M* in HNF_2 and 0.35 *M* in sodium acetate and acetic acid. In a typical run, 5.05 mmoles of HNF_2 yielded 0.61 mmole of N_2O after 20 hr; 3.60 mmoles of HNF_2 remained unconsumed. After 40 hr, 1.40 mmoles of N_2O was produced and 2.00 mmoles of HNF_2 remained unconsumed. Only trace amounts of other materials, such as N_2F_2, N_2F_4, NO_3^-, and NO_2^-, were found. Small amounts of carbon dioxide were also formed and reached a level of 0.14 mmole after 40 hr.

Phosphate Ions. The reactions of $H_2PO_4^-$ and HPO_4^{2-} ions with HNF_2 were studied in solutions which were 0.1 *M* in HNF_2 and 0.2 *M* in both of the phosphate ions. The pH was about 7.1. After 20 hr at these initial concentration levels, 38% of the HNF_2 was converted to N_2O, 34% was converted to N_2F_2, and 20% of the HNF_2 was unconsumed. Trace amounts of ammonia and N_2F_4 were also found.

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(20) See also E. A. Lawton and J. Q. Weber, *J. Am. Chem. Soc.*, **81**, 4755 (1959).

Trifluoromethyl-Substituted Boranes. Trifluoromethyldi-*n*-butylborane and Trifluoromethylboron Difluoride

Theran D. Parsons, James M. Self, and Lewis H. Schaad

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon. Received January 3, 1967

Abstract: The preparation and properties of trifluoromethyldi-*n*-butylborane and trifluoromethylboron difluoride are reported. Loss of difluorocarbene from the trifluoromethyl group bonded to electron-deficient boron was observed in the presence of catalysts, but in *vacuo* at room temperature the substances were stable for months. Infrared spectra and vapor pressure data for *n*-butylboron difluoride and di-*n*-butylboron fluoride are reported.

In a previous report[1] the preparation of a trifluoromethylboron compound, CF_3BF_2, was described. It was prepared *via* an intermediate, presumed to be $CF_3(n\text{-}C_4H_9)_2B$, but not isolated in a pure state nor further characterized. The synthesis of both of these compounds and their partial characterization is now reported, together with information about other boranes isolated in the course of this study.

Experimental Section

Reagents. Reagents not available commercially were prepared according to literature methods, with minor variations. These include tri-*n*-butylborane,[2] di-*n*-butylboron chloride,[3] sodium-potassium alloy,[4] and trifluoromethyl iodide.[5]

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