

Contribution from the High Energy Solids Group,
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore—560012, India

Synthesis and Characterization of a New Fluoride Derivative of Hydrazine, $N_2H_5HF_2$

K. C. PATIL, R. SOUNDARARAJAN, and V. R. PAI VERNEKAR*

Received October 25, 1978

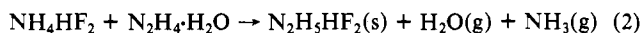
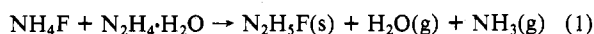
Hydrazinium bifluoride, $N_2H_5HF_2$, has been synthesized by chemical and thermal methods. Characterization of $N_2H_5HF_2$ has been made by chemical analysis and X-ray and infrared spectra. Thermal characteristics of $N_2H_5HF_2$ have been studied by DTA and compared with those of N_2H_5F and $N_2H_6F_2$.

Introduction

Hydrazine dihydrofluoride, $N_2H_6F_2$, is known and its crystal structure,¹ infrared spectrum,² and thermal analysis³ have been studied. However, hydrazine monohydrofluoride, N_2H_5F , was not known until 1967, when Glavik and Slivnik⁴ prepared it by the reaction of $N_2H_6F_2$ with anhydrous hydrazine. Infrared spectrum,⁴ crystal structure,⁵ and thermal properties³ of N_2H_5F have been reported. With hydrazine salts being analogous to ammonium salts, one would expect a third fluoride derivative of hydrazine similar to ammonium bifluoride, NH_4HF_2 , namely, hydrazinium bifluoride, $N_2H_5HF_2$. A detailed survey of the literature^{6,7} revealed that no attempt has been made to prepare $N_2H_5HF_2$. Acid fluorides like NH_4HF_2 and KHF_2 are usually prepared by the addition of hydrofluoric acid, HF, to the monofluoride. But the addition of HF to N_2H_5F appears to yield $N_2H_6F_2$ and not $N_2H_5HF_2$. Probably because of this difficulty there appears to be no report to date about $N_2H_5HF_2$. Recently, we reported⁸ the preparation of a number of hydrazine derivatives by the reaction of hydrazine hydrate with solid ammonium salts. Using this novel method we have now synthesized both N_2H_5F and $N_2H_5HF_2$. Further, $N_2H_5HF_2$ has been unequivocally characterized by X-ray and infrared spectra and differential thermal analysis (DTA). Hydrazine dihydrofluoride, $N_2H_6F_2$, was also synthesized by the addition of aqueous HF to alcoholic solution of N_2H_5F . X-ray and infrared spectra and DTA of N_2H_5F and $N_2H_6F_2$ were reinvestigated for the purpose of comparison with that of $N_2H_5HF_2$.

Experimental Section

Stoichiometric quantities of ammonium fluoride and bifluoride were mixed with calculated quantities of hydrazine hydrate (99–100%) and were allowed to react in polythene cups. Ammonia was evolved instantaneously. The products were crystallized from solution and dried over P_2O_5 in a vacuum desiccator. The reactions may be represented as shown in eq 1 and 2. Both N_2H_5F and $N_2H_5HF_2$ are



hygroscopic and need handling in dry atmosphere. Hydrazine dihydrofluoride, $N_2H_6F_2$, was obtained by the addition of aqueous HF to alcoholic hydrazine hydrate.⁶ It was also prepared by the addition of aqueous HF to the alcohol solution of N_2H_5F prepared by the above method. Hydrazine dihydrofluoride precipitates as a nonhygroscopic crystalline solid. Hydrazine dihydrofluoride prepared from the aqueous method¹ was hygroscopic. The composition of the compounds was fixed by hydrazine analysis. Hydrazine contents were determined by titration with 0.05 M potassium iodate solution under Andrew's conditions.⁸ Infrared spectra were recorded as Nujol mulls as well as KBr pellets by using a Carl-Zeiss UR-10 spectrophotometer. Differential thermal analysis (DTA) was carried out by using a DTA-02 Universal instrument manufactured by Franz Wagner Industrille Elektronik of the German Democratic Republic. Platinum cups were used as sample holders. All DTA experiments were carried out in air by using 100-mg samples. The heating rate employed was 7 °C/min. X-ray powder diffraction patterns were obtained by using a ISO-Debyelex 1001 instrument fitted with Cu $K\alpha$ radiation with nickel filter.

Table I. Analytical and Thermal Data

com- pound	% N_2H_4		DTA peak temp, ^a °C	
	obsd	calcd	this work	from ref 3
N_2H_5F	61.11	61.53	95 (m), 180 (–), 230 (–)	110 (m), 126 (+), 214 (–)
$N_2H_6F_2$	44.40	44.44	184 (m), 242 (–)	168 (m), 176 (+), 215 (–)
$N_2H_5HF_2$	44.40	44.44	142 (–), 184 (m), 250 (–)	
$N_2H_5HF_2^b$	44.40	44.44	182 (–), 250 (–)	

^a Key: m, melting; (–), endotherm; (+), exotherm. ^b Prepared by heating N_2H_5F at 160 °C for 12 h.

Table II. X-ray Data (in Å)^a

N_2H_5F	$N_2H_5HF_2$	$N_2H_6F_2$
1.9433 m	1.3612 w	1.2419 w
2.0921 m	1.6289 vw	1.2886 w
2.3097 s	1.6987 w	1.3526 vs
2.4950 s	2.2276 vs	1.6289 vs
2.8851 vs	2.5999 s	1.7055 s
	2.8851 s	2.2275 vs
	3.3639 m	2.3986 s
	3.7861 s	2.6371 vs
		3.3639 w
		3.7861 vs
		4.7965 w

^a Key: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

Table III. Infrared Absorption Data (cm^{-1})^a

assignment	$N_2H_5HF_2$	N_2H_5F	$N_2H_6F_2$
$\nu_1 + \nu_3$ of HF_2^-	2100 m		
$\nu_1 + \nu_3$ of HF_2^-	1840 w		
NH_2 bending	1680 sh		
NH_3^+ def	1620 sh	1550 vb	1550 vb
HF_2^- asym str (ν_3)	1550 vb		
NH_2 rock	1260 s, sp	1260 vb	1264 s
HF_2^- def (ν_2)	1250 sp		1190 s
NH_3^+ bend	1120 s	1120 s	
	1100 s	1100 s	
ν_{N-N} str	960 s	960 s	980 s

^a IR spectra were recorded as KBr pellets. Key: vb, very broad; s, strong; vs, very strong; sp, sharp, sh, shoulder; m, medium; w, weak.

Results and Discussion

The analytical and thermal data of N_2H_5F , $N_2H_6F_2$, and $N_2H_5HF_2$ have been summarized and given in Table I. The compositions were fixed by hydrazine analysis and were characterized by X-ray (Table II) and infrared spectra. Some important infrared absorption frequencies in the region 2200–800 cm^{-1} have been tabulated in Table III. The IR and DTA results have been discussed in detail.

I. Infrared Spectra. Infrared absorption frequencies of $N_2H_5HF_2$ are listed along with those of N_2H_5F and $N_2H_6F_2$. Characteristic absorptions of $N_2H_5^+$, $N_2H_6^{2+}$, and HF_2^- have been observed and assigned on the basis of earlier work.^{2,4,9–11} Both N_2H_5F and $N_2H_5HF_2$ show an absorption at 960 cm^{-1} ,

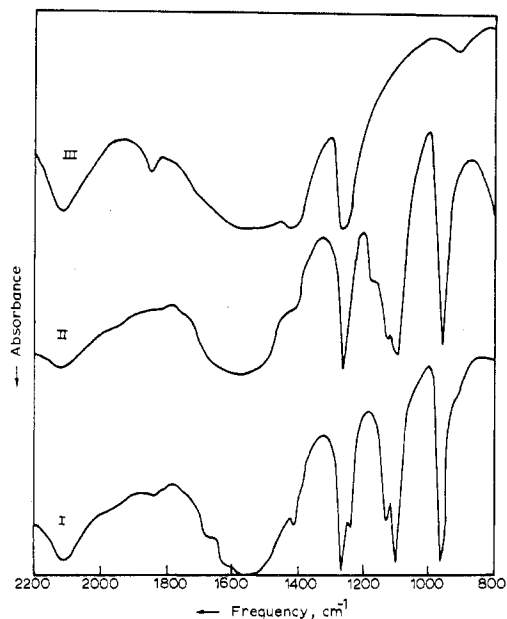


Figure 1. Infrared absorption frequencies of (I) $N_2H_5HF_2$, (II) N_2H_5F (heated to 160 °C, 12 h), and (III) NH_4HF_2 .

which has been assigned to ν_{N-N} of $N_2H_5^+$.⁹ The stretching frequency of the N–N bond can be used to differentiate between N_2H_4 , $N_2H_5^+$, and $N_2H_6^{2+}$, since the ν_{N-N} frequency varies with N–N bond distance, e.g., (N_2H_4) $d_{N-N} = 1.46 \text{ \AA}$ (880 cm^{-1}), ($N_2H_5^+$) $d_{N-N} = 1.432 \text{ \AA}$ (965 cm^{-1}), and ($N_2H_6^{2+}$) $d_{N-N} = 1.40 \text{ \AA}$ (1024 cm^{-1}).⁹ However, the observed ν_{N-N} frequency (980 cm^{-1}) for $N_2H_6F_2$ in our study is rather too low compared to the expected value (1024 cm^{-1}) for $N_2H_6^{2+}$. The lowering of this frequency could be expected and justified because the N–N bond distance in $N_2H_6F_2$ is reported¹ to be 1.42 \AA and the calculated ν_{N-N} frequency from the above data agrees with the observed frequency. Thus, the lowering of ν_{N-N} frequency in $N_2H_6F_2$ can be attributed to the presence of strong H bonding which is responsible for the increase in the N–N bond distance.

The bifluoride ion, HF_2^- , has characteristic absorptions 1600 cm^{-1} (ν_3) and 1200 cm^{-1} (ν_2).¹⁰ Additional bands due to combinations of the fundamentals of HF_2^- ion are observed at 2100 and 1840 cm^{-1} .¹¹ The ν_3 and ν_2 of HF_2^- ion lie in the region where deformation and bending of $-NH_2^-$ and NH_3^+ groups of $N_2H_5HF_2$ are observed. This makes the unequivocal assignment of HF_2^- rather difficult. We have therefore compared the IR spectrum of $N_2H_5HF_2$ with that of NH_4HF_2 (Figure 1). All four absorptions (2100 , 1840 , 1550 , and 1260 cm^{-1}) characteristic of HF_2^- are seen in $N_2H_5HF_2$ as in NH_4HF_2 . Ketelaar et al.¹⁰ have shown that ν_3 and ν_2 frequencies of HF_2^- are sensitive to the matrix, and the IR spectrum of NH_4HF_2 in KBr shows these bands at 1527 and 1258 cm^{-1} , respectively. It may be noticed that the 1260-cm^{-1} band of $N_2H_5HF_2$ is split due to the overlap of ν_2 of HF_2^- with the deformation of $N_2H_5^+$. In short, the following facts in the IR spectra make it possible to differentiate between $N_2H_5HF_2$ and $N_2H_6F_2$: (1) the presence of absorptions at 2100 and 1840 cm^{-1} in $N_2H_5HF_2$ as in NH_4HF_2 which are absent in $N_2H_6F_2$; (2) the presence of a doublet around 1260 cm^{-1} in $N_2H_5HF_2$ compared to the singlet in $N_2H_6F_2$; (3) the ν_{N-N} frequency of $N_2H_5HF_2$ observed at 960 cm^{-1} compared to the ν_{N-N} of $N_2H_6F_2$ observed at 980 cm^{-1} .

II. Differential Thermal Analyses. The DTA of hydrazinium bifluoride, $N_2H_5HF_2$, exhibits three endotherms (Figure 2). The first two endotherms are reversible and are assigned to phase change and melting, respectively. The final endotherm is due to the volatilization of $N_2H_5HF_2$. The phase

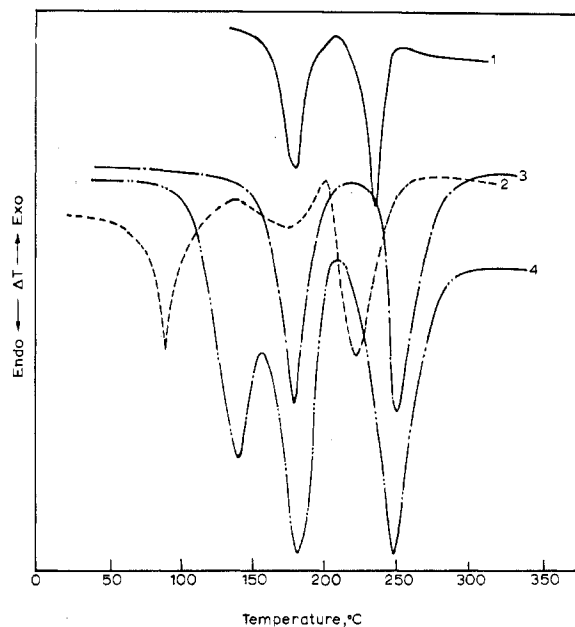
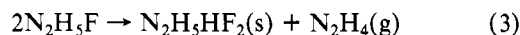


Figure 2. DTA curves of (1) $N_2H_6F_2$ (—), (2) N_2H_5F (---), (3) $N_2H_5HF_2$ obtained by thermal methods (- · - ·), and (4) $N_2H_5HF_2$ obtained by chemical methods (· · · ·).

transition peak at 140 °C disappears on repeated thermal cycling, probably stabilizing the high temperature form of $N_2H_5HF_2$.

Hydrazine dihydrofluoride, $N_2H_6F_2$, exhibits only two endotherms in DTA. The first endotherm at 180 °C is sharp and reversible and is assigned to melting. The second endotherm has been assigned to volatilization of $N_2H_6F_2$. No exotherm was observed as reported.³

The DTA curve of hydrazine monohydrofluoride, N_2H_5F , shows three endotherms. The first endotherm is sharp and reversible and was attributed to melting. The second endotherm is initially broad but becomes narrow during the second heating (see Figure 2) and is found to be reversible. This peak has been assigned to the dissociation of N_2H_5F to $N_2H_5HF_2$.



Formation $N_2H_5HF_2$ was confirmed by observed weight loss in the isothermal thermogravimetry of N_2H_5F at 160 °C . The weight loss corresponded to the loss of a hydrazine molecule (30.0% weight loss observed, 30.76% calculated). The loss of hydrazine was qualitatively tested by its basic action on pH paper. Further, the residue from the isothermal TG was analyzed for hydrazine content and was found to contain 44.4% N_2H_4 as in $N_2H_5HF_2$. The DTA of the residue did not show any endothermic peak below 180 °C indicating absence of melting of N_2H_5F and phase transition peak of $N_2H_5HF_2$. This appears to suggest that the high temperature form of $N_2H_5HF_2$ is formed by heating N_2H_5F at 160 °C . The possibility of formation of $N_2H_6F_2$ instead of $N_2H_5HF_2$ is ruled out by the infrared spectrum of the residue which is identical with that of $N_2H_5HF_2$ (Figure 1) and shows characteristic IR absorption of $N_2H_5^+$ at 960 cm^{-1} and not of $N_2H_6^{2+}$ which is observed around 980 cm^{-1} . This property of N_2H_5F dissociating to $N_2H_5HF_2$ is similar to that of NH_4F . Ammonium fluoride¹² is known to dissociate to ammonium bifluoride and ammonia on heating. The final endotherm in the DTA of N_2H_5F has been attributed to the volatilization of $N_2H_5HF_2$ formed.

Milojevik and Slivnik³ have observed an exotherm in the DTA of both N_2H_5F and $N_2H_6F_2$. Similar exotherms have been observed in the DTA's of hydrazine halides (Cl^- , Br^- ,

I⁻).^{3,13} These exotherms were assigned to the decomposition of hydrazine halides to the corresponding ammonium halides. However, formation of ammonium fluoride during the decomposition of N₂H₅F and N₂H₆F₂ was not observed in our studies¹⁴ as has been mentioned by Milojevic and Slivnik.³ The presence of strong H bonding, in both N₂H₆F₂ and N₂H₅F, probably does not allow the formation of ammonium fluoride during the decomposition of these fluorides.

Conclusions

Hydrazinium bifluoride, N₂H₅HF₂, has been prepared for the first time by both chemical and thermal methods. The characterization has been done by chemical analysis and X-ray and infrared spectra. Thermal properties of N₂H₅HF₂ have been studied.

Registry No. N₂H₆F₂, 13537-45-6; N₂H₅F, 18820-64-9; NH₄HF₂, 1341-49-7; NH₄F, 12125-01-8; N₂H₄, 302-01-2.

References and Notes

(1) Kronberg, M. L.; Harker, H. D. *J. Chem. Phys.* **1942**, *10*, 309-17.

- (2) Snyder, R. G.; Decius, J. C. *Spectrochim. Acta* **1959**, *13*, 280-90.
 (3) Milojevic, M.; Slivnik, J. *Therm. Anal., Proc. Int. Conf.*, **3rd** **1971**, *3*, 19-29.
 (4) Glavik, P.; Slivnik, J. *Monatsh. Chem.* **1967**, *98*, 1878-80.
 (5) Golic, L.; Lazarini, F. *Monatsh. Chem.* **1974**, *105*, 735-841.
 (6) Mellor, J. "A Comprehensive Treatise on Inorganic and Theoretical Chemistry"; Longmans, Green and Co.: London, 1927; Vol. VIII, p 323; *ibid.*, 1967; Supplement IIN (Part II), p 84.
 (7) Audrieth, L. F.; Ogg, B. A. "The Chemistry of Hydrazine", Wiley: New York, 1951; p 168.
 (8) Patil, K. C.; Soundararajan, R.; Pai Verneker, V. R. *Proc. Indian Acad. Sci., Sect. A* **1978**, *87*, 281-84.
 (9) Braibanti, A. I.; Dallavalle, F.; Pellinghelli, H. A.; Laporati, E. *Inorg. Chem.* **1968**, *7*, 1430-3.
 (10) Ketelaar, J. A. A.; Haas, C.; Vander Elsken, J. *J. Chem. Phys.*, **1956**, *24*, 624-5.
 (11) Cote, G. L.; Thompson, H. W. *Proc. R. Soc. London, Ser. A* **1951**, *210*, 206-16.
 (12) Remy, H. "Treatise on Inorganic Chemistry"; Elsevier: London, 1956; Vol. I, p 795.
 (13) Patil, K. C.; Soundararajan, R.; Pai Verneker, V. R. *Thermochim. Acta*, in press.
 (14) Patil, K. C.; Soundararajan, R.; Pai Verneker, V. R. Paper presented at the 1st National Symposium on Thermal Analysis held at I.I.T., Madras, Dec 21-23, 1978.

Contribution from the Department of Chemistry,
University of California, Riverside, California 92521

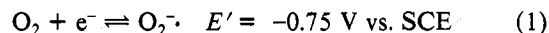
Oxidation-Reduction Chemistry of Hydrogen Peroxide in Aprotic and Aqueous Solutions

MARK M. MORRISON, JULIAN L. ROBERTS, JR., and DONALD T. SAWYER*

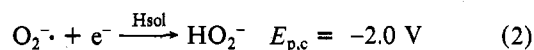
Received October 6, 1978

Electrochemical reduction of hydrogen peroxide in pyridine at a platinum electrode yields superoxide ion as the major product. The primary reduction step is $\text{H}_2\text{O}_2 + e^- \rightarrow \text{HO}_2^- + \frac{1}{2}\text{H}_2$ which is followed by a disproportionation reaction $\text{HO}_2^- + \text{H}_2\text{O}_2 \xrightarrow{k_2} \text{O}_2^- + \text{H}_2\text{O} + \text{sol}(-\text{OH})$ oxidation products. In pyridine the approximate value for k_2 is $4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, assuming a second-order rate law. In alkaline aqueous solutions HO_2^- is oxidized at a mercury electrode by an overall two-electron process to molecular oxygen. Because HO_2^- is inert at gold and carbon electrodes, the electrochemical oxidation mechanism must involve Hg(I) and Hg(II) intermediate complexes with HO_2^- and/or O_2^- . Electrochemical and ESR studies have been used to determine the products and the reaction stoichiometries for these processes.

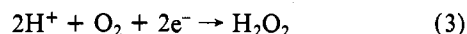
The oxidation-reduction chemistry of dioxygen is a fundamental property of its essential role in terrestrial life cycles. In such systems it is reduced by overall one-, two-, or four-electron processes to O_2^- , H_2O_2 , or H_2O (or their conjugate acids and bases), respectively.¹ Comparable oxidation states are observed in the electrochemical reduction of O_2 . For example, in aprotic solvents, such as dimethyl sulfoxide, oxygen is reduced by a one-electron process to superoxide ion (eq 1).



At more negative potentials O_2^- is reduced further to HO_2^- with the solvent involved (eq 2).² When O_2 is reduced in the



presence of excess protons in nonaqueous solvents, the apparent primary process yields H_2O_2 (eq 3).



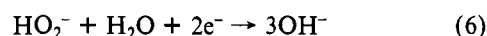
In aqueous solutions O_2 is reduced at mercury electrodes by two electrons to H_2O_2 (eq 3), or for alkaline conditions to HO_2^- (eq 4). Hence, hydrogen peroxide and its anion are



frequent intermediate reduction products of O_2 . However, in the presence of hydrophobic surfactants a one-electron reduction of oxygen predominates in alkaline solutions (eq 1).^{3,4}

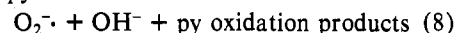
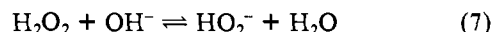
In aqueous solutions, hydrogen peroxide and its anion are reduced at mercury electrodes by a two-electron process to

hydroxide ion ($E_{1/2} = -1.00 \text{ V vs. SCE}$).⁵



Under alkaline conditions HO_2^- is oxidized to oxygen at mercury electrodes ((eq 4; $E_{1/2} = -0.18 \text{ V}$).⁵ While O_2 is reduced reversibly to O_2^- in the presence of hydrophobic surfactants (triphenylphosphine oxide or quinoline),^{3,4} whether HO_2^- can be reduced under these same conditions is not clear.

In contrast to the numerous studies of the electrochemistry of H_2O_2 in aqueous media, little is known of its redox chemistry in nonaqueous media. Although H_2O_2 can be reduced in benzene-methanol at -0.93 V vs. SCE ,⁶ the electron stoichiometry and products have not been determined. In a recent communication⁷ we reported that when tetraalkylammonium hydroxide is added to H_2O_2 in pyridine solution, O_2^- and pyridine oxidation products are produced:



The present paper summarizes the results of electrochemical investigations of H_2O_2 in nonaqueous and alkaline aqueous media, of O_2 reduction in nonaqueous media with excess protons, and of the reaction of H_2O_2 with OH^- to yield O_2^- .⁷

Experimental Section

Reagent grade H_2O_2 (30% in water) was used in all experiments, and all organic solvents were spectral grade. Tetra-*n*-propylammonium