

for *cis*-2-butene¹⁷ and for two of the methyl rotations in 2-methyl-2-butene.¹⁸

The contributions of anharmonicity to the thermodynamic functions were treated by the empirical method of McCullough, *et al.*¹⁹ The two empirical constants $Z = 1.17$ cal. deg.⁻¹ mole⁻¹ and $\nu = 1250$ cm.⁻¹ were selected to give a satisfactory fit to the calorimetric values of the heat capacity over the whole experimental temperature range. Use of Pennington and Kobe's tables²⁰ simplified the numerical calculations. The calculated contributions were insignificant at the lowest temperatures and amounted to 0.2% of the free energy function, 1.3% of the heat content function, 0.5% of the entropy and 2.1% of the heat capacity at 1500°K.

Thermodynamic Functions.—The vibrational assignment and molecular-structure parameters given in the two previous sections were used to compute the functions $(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, $H^\circ - H_0^\circ$, S° and C_p° for 2,3-dimethyl-2-butene for selected temperatures up to 1500°K. These functions are tabulated in Table X. Some values in Table X are given to more decimal places than is justified by their absolute accuracy in order to retain internal

consistency within the table. The satisfactory fit obtained with the calorimetric data may be judged by the comparisons of observed and calculated values of S° and C_p° in Tables VII and VI.

TABLE X

THE MOLAL THERMODYNAMIC FUNCTIONS OF 2,3-DIMETHYL-2-BUTENE

T , °K.	$(F^\circ - H_0^\circ)/T$, cal. deg. ⁻¹	$(H^\circ - H_0^\circ)/T$, cal. deg. ⁻¹	$H^\circ - H_0^\circ$, kcal.	S° , cal. deg. ⁻¹	C_p° , cal. deg. ⁻¹
273.16	- 65.59	19.04	5.200	84.63	27.71
298.16	- 67.30	19.85	5.918	87.15	29.54
300	- 67.42	19.91	5.972	87.33	29.68
400	- 73.62	23.33	9.331	96.95	37.48
500	- 79.20	26.93	13.46	106.13	45.04
600	- 84.43	30.54	18.32	114.96	51.78
700	- 89.38	34.01	23.81	123.39	57.67
800	- 94.14	37.30	29.84	131.44	62.78
900	- 98.71	40.39	36.35	139.09	67.25
1000	-103.11	43.28	43.28	146.39	71.14
1100	-107.37	45.96	50.56	153.33	74.55
1200	-111.48	48.47	58.16	159.95	77.51
1300	-115.46	50.80	66.04	166.26	80.08
1400	-119.30	52.97	74.16	172.27	82.33
1500	-123.03	54.99	82.49	178.02	84.31

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[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORIES OF THE OHIO STATE UNIVERSITY]

Observations on the Addition Compound of Silicon Tetrafluoride and Ammonia

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The addition compound $\text{SiF}_4 \cdot 2\text{NH}_3$ has been prepared in a highly purified form. Its X-ray diffraction pattern has measured, as well as its dissociation pressure over the range of 351.9 to 422.4°K. Observations concerning the susceptibility of this substance to ammonolysis and hydrolysis have been made.

The preparation of a diammoniate of silicon tetrafluoride was first reported nearly a century and a half ago¹ and has been discussed in a few publications^{2,3} since that time. However, the properties of the substance have not been well-defined. It became necessary, in connection with our research program, to prepare this material and to study some of its properties. We are hereby reporting some of the resulting observations. These fall under the following classifications: (a) susceptibility to hydrolysis, (b) resistance to ammonolysis, (c) vapor pressure measurements, and (d) X-ray diffraction pattern.

Preparation and Analysis.—The complex was prepared (method I) by passing silicon tetrafluoride (prepared by treating a mixture of sodium fluosilicate and silica with concentrated sulfuric acid, and dried by passing through concentrated sulfuric acid, glass wool, phosphorus(V) oxide,

and a trap cooled with Dry Ice) into a chamber containing an excess of gaseous ammonia. The complex settled out in the chamber as a fluffy, white powder.

A second method (method II) used for the preparation involved the freezing out, at liquid air temperatures, of a sample of silicon tetrafluoride, and then freezing out on top of this an excess of ammonia. The cooling bath was then removed and the mixture allowed to warm up and the excess ammonia to evaporate.

The products were analyzed for ammonia by distillation with sodium hydroxide into a 4% boric acid solution followed by titration with standard HCl solu. Fluorine and silicon determinations were made on the same sample of complex. The sample was added to water and any silicic acid which formed was filtered off and retained. Fluorine was then determined in the filtrate as lead fluorochloride.⁴ The filtrate obtained upon removal of the lead fluorochloride was evaporated to dryness, taken up in concentrated HCl, and the silicic acid filtered off. This was combined with the previously obtained material and ignited and weighed.

The typical product prepared by method I gave the following analytical results: Found: NH_3 , 23.0, 22.8; Si, 20.8, 20.9, 21.9, 20.8; F, 55.6, 56.4, 56.1, 55.7. Calcd. for $\text{SiF}_4 \cdot 2\text{NH}_3$: NH_3 , 24.7; Si, 20.3; F, 55.0. The ammonia analysis is, therefore, low. On standing with no special

(1) J. Davy, *Phil. Trans.*, **102**, 353 (1812).

(2) W. Mixer, *Am. Chem. J.*, **2**, 153 (1881).

(3) J. Gierut, F. Sowa and J. Nienland, *THIS JOURNAL*, **58**, 786 (1936).

(4) R. Belcher and J. Tatlow, *The Analyst*, **76**, 593 (1951).

precautions against atmosphere, the product gradually loses ammonia, and after a period of one year the ammonia content had decreased to about 18%.

Method of X-Ray Measurements.—Since the ammonia content of the sample prepared by the first method was somewhat lower than theoretical for $\text{SiF}_4 \cdot 2\text{NH}_3$, it was decided to examine this product by means of X-ray diffraction. For this purpose samples were ground so as to pass through a 325-mesh screen and were placed in Pyrex capillaries. A 114.6 mm. Debye-Scherrer camera using $\text{CoK}\alpha$ radiation in conjunction with an iron filter was used. A Phillips Metallix Model 5100 X-ray diffraction unit was employed and the films were measured on a Norelco illuminator and a measuring device capable of an accuracy of ± 0.05 mm. The relative intensities of the lines were estimated visually.

The diffraction pattern of $(\text{NH}_4)_2\text{SiF}_6 \cdot \text{NH}_4\text{F}$ was identified by the pattern listed by ASTM⁵ Card File. The pattern for ammonium fluosilicate was identified both by comparison with the ASTM data and by comparison with an X-ray pattern determined on our equipment on a known sample of ammonium fluosilicate.

Heterogeneity of Product Prepared by Method I.—It was found that the product prepared by method I partially sublimed at 60–65° *in vacuo* to yield a sublimate A, with an ammonia content of 24.2% and an unsublimed residue with an ammonia analysis of 17.8%. The residue when heated to 120–130° *in vacuo* yielded a further sublimate B of nearly the same ammonia content (17.9%). The small amount of residue was entirely nonvolatile even at the maximum temperature of a Méker burner.

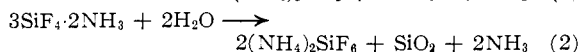
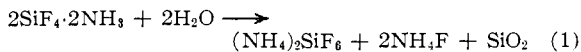
Sublimate B was identified by its X-ray pattern as ammonium fluosilicate. Sublimate A gave an X-ray pattern which contained no lines attributable to $(\text{NH}_4)_2\text{SiF}_6$, NH_4F , $(\text{NH}_4)_2\text{SiF}_6 \cdot \text{NH}_4\text{F}$ or any other conceivable possible product for which X-ray patterns have been determined. Further, the ammonia analysis of sublimate A agrees well with the formula $\text{SiF}_4 \cdot 2\text{NH}_3$. Sublimate A, was therefore, assumed to be pure $\text{SiF}_4 \cdot 2\text{NH}_3$. The lines found in the X-ray pattern of this substance are reported in Table I.

TABLE I

X-RAY POWDER DIFFRACTION PATTERN FOR $\text{SiF}_4 \cdot 2\text{NH}_3$					
<i>d</i> , Å.	<i>I</i> / <i>I</i> ₀	<i>d</i> , Å.	<i>I</i> / <i>I</i> ₀	<i>d</i> , Å.	<i>I</i> / <i>I</i> ₀
4.995	80	2.484	50	1.716	8
4.767	8	2.402	40	1.884	8
4.450	100	2.338	30	1.670	10
4.295	8	2.063	20	1.609	10
3.881	60	2.006	35	1.583	20
3.614	30	1.935	20	1.495	5
3.165	50	1.878	20	1.416	7
3.031	30	1.814	10	1.294	20
2.608	50	1.756	10		

Hydrolysis of $\text{SiF}_4 \cdot 2\text{NH}_3$.—The observations made in connection with the sublimation of the product of method I suggested that an investigation of the hydrolysis of $\text{SiF}_4 \cdot 2\text{NH}_3$ and of its volatility should be carried out. A sample of sublimate A ($\text{SiF}_4 \cdot 2\text{NH}_3$) was, therefore, added to a large excess of water and the precipitate of silica which formed was removed by filtration. The filtrate was then evaporated to dryness at from 20 to 40°. The resulting solid residue which had an ammonia content of 23.5% was examined by X-ray diffraction and found to consist predominantly of the double salt $(\text{NH}_4)_2\text{SiF}_6 \cdot \text{NH}_4\text{F}$ along with some $(\text{NH}_4)_2\text{SiF}_6$.

We may consider that the ammonolysis of the complex proceeds by such reactions as those indicated by the equations



When the silica is removed and the solution evaporated some of the ammonium fluosilicate crystallizes with the ammonium fluoride to form the double salt.

The fact that on standing in air the product of method I slowly loses ammonia to form a mixture of $\text{SiF}_4 \cdot 2\text{NH}_3$,

(5) Alphabetical and Numerical Indexes of X-Ray Diffraction Patterns. American Society for Testing Materials, 1953, p. 12.

$(\text{NH}_4)_2\text{SiF}_6$ and SiO_2 was interpreted as indicating that hydrolysis of $\text{SiF}_4 \cdot 2\text{NH}_3$ by atmospheric moisture proceeds in accordance with equation 2 and that equation 1 is unimportant in this process.

Experiments in which $\text{SiF}_4 \cdot 2\text{NH}_3$ was placed in an excess of liquid ammonia at 100° for a period of 7 days indicated the $\text{SiF}_4 \cdot 2\text{NH}_3$ does not undergo any ammonolysis under these conditions. In fact preliminary experiments at 300° also gives no indication of ammonolysis.

Dissociation Pressure of $\text{SiF}_4 \cdot 2\text{NH}_3$.—Measurements of the dissociation pressures of $\text{SiF}_4 \cdot 2\text{NH}_3$ in the temperature range of 80 to 150° were made using a thermostated sample chamber connected to a mercury filled manometer. The sample chamber was submerged in an oil-bath. The system was arranged so that the gas over the sample could be pumped out at will. At the beginning of a run, the system, while being maintained at constant pressure, was alternately pumped on and allowed to come to equilibrium until the pressure recorded returned to a constant value after each cycle, thus assuring that foreign gases had been removed from the system. The pressure was then recorded and the temperature raised to a new value, and so on. When the maximum temperature in such a series of readings was reached, the system was once again pumped out so that a new sample of vapor was present in the chamber, and a new series of readings taken as the temperature was lowered stepwise. Dissociation pressure data were taken on two different runs, using samples of $\text{SiF}_4 \cdot 2\text{NH}_3$ prepared in different sublimations. The data, recorded in Table II,

TABLE II
DISSOCIATION PRESSURE OF $\text{SiF}_4 \cdot 2\text{NH}_3$

<i>T</i> , °K.	<i>P</i> , mm.	Trial ^a	<i>T</i> , °K.	<i>P</i> , mm.	Trial ^a
351.9	1.9	2D	402.7	48.3	1U
354.2	2.0	1D	403.0	49.1	1U
363.2	4.3	1D	403.7	49.7	1U
363.6	4.3	2D	405.2	54.9	2D
364.2	5.0	1U	407.9	64.4	1D
370.4	6.6	2D	412.3	82.2	1U
371.7	7.5	1D	412.5	82.1	2D
383.2	15.7	1U	412.7	82.7	1U
390.2	22.7	2D	413.0	86.3	2U
391.7	25.1	1D	416.0	103.5	1D
395.5	33.5	1U	421.9	136.9	1U
397.9	38.0	1U	422.4	140.3	1D
399.0	39.2	2U			

^a 1 and 2 refer to the two different samples used. D refers to readings taken on the down part of the cycle; U refers to readings taken on the up part of the cycle.

are quite consistent. Values of $\ln P$ vs. $1000/T$ are plotted in Fig. 1. These points fall on a straight line, the slope of

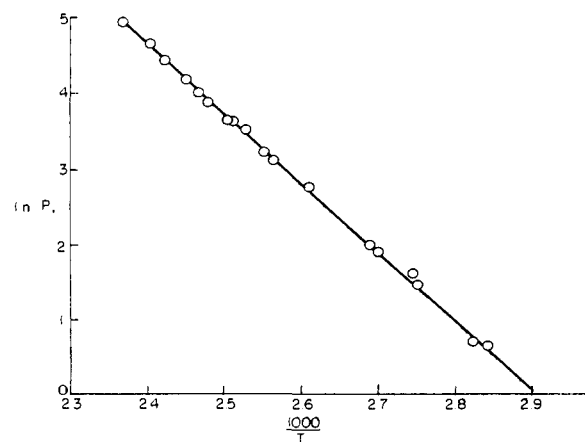
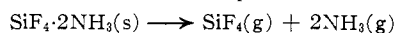


Fig. 1.—Logarithms of dissociation pressure of the complex plotted against reciprocal of the absolute temperature.

which was used to obtain the value

$$\frac{d(\ln P)}{d(1/T)} = -9.18 \times 10^3$$

From this the value of ΔH for the process



was calculated using the equation

$$\frac{d(\ln P)}{d(1/T)} = \frac{-\Delta H}{R}$$

The value obtained was 18.2 kcal./mole.

The data in Table II can be expressed by the equation

$$\ln P = 25.06 - \frac{8050}{T - 21.9}$$

where P is in mm. and T is in $^{\circ}\text{K}$. Extrapolation indicates that the dissociation pressure would become equal to 760 mm. at about 185° .

From the dissociation pressures at various temperatures

the equilibrium constants were calculated using the expression

$$K = (2/3 P)^2(1/3 P) = 4/27 P^3$$

Expressing P in atmospheres rather than mm., we derive the expression

$$\ln K_{\text{atm}} = 53.37 - \frac{24,150}{T - 21.9}$$

where T is the absolute temperature. Then using the relation $\Delta F^{\circ} = -RT \ln K$, and expressing ΔF° in kcal./mole we obtain the following expression for the ΔF° for the dissociation as a function of temperature

$$\Delta F_{\text{T}}^{\circ} = -0.1061T + \frac{47.99T}{T - 21.9}$$

whence

$$\Delta F_{298}^{\circ} = 20.2 \text{ kcal./mole } (25^{\circ})$$

and

$$\Delta F_{455}^{\circ} = 1.85 \text{ kcal./mole } (185^{\circ})$$

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS]

Hydrazides of Sulfuric Acid and their Derivatives. I. Hydrazinosulfuric Acid

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Hydrazinosulfuric acid (HSA) was prepared by the sulfonation of hydrazine with N-pyridiniumsulfonic acid. It is a monobasic acid ($pK_a = 3.85$). A quantitative study of the hydrolysis of the acid at 45° has revealed that HSA is less stable than sulfamic acid under comparable conditions. A 0.3036 M solution of hydrazinosulfuric acid hydrolyzes completely to hydrazine hydrogen sulfate in 5.5 hours at 45° . The infrared spectrum of solid HSA indicates the presence of an ammonium type zwitterion.

Introduction

Although the chemistry of the aquo ammonosulfuric acids, such as sulfamic acid and sulfamide, has been the subject of considerable study,³ comparatively little is known about the analogous hydrazine compounds.⁴ Theoretically, it should be possible to synthesize a whole series of compounds which are related to hydrazine as the parent substance in much the same way that the better known aquo ammono derivatives of sulfuric acid have been characterized and related to each other. However, only two of these compounds, hydrazinosulfuric acid (I), $\text{H}_2\text{NNHSO}_3\text{H}$, and hydrazidisulfuric acid, $[\text{NH-SO}_3\text{H}]_2$,⁵ have been described adequately. Sulfanylhydrazide (N-aminosulfamide), $\text{SO}_2\text{NH}_2(\text{N}_2\text{H}_3)$, has been described as a very unstable intermediate, whereas sulfuryl dihydrazide, $\text{SO}_2(\text{N}_2\text{H}_3)_2$, appears to be relatively stable.⁶ N-Substituted derivatives of I are better known than the free acid.

The present investigation has concerned itself with the stability of aqueous solutions of hydrazinosulfuric acid and its structure in the solid state. It has been found that hydrazinosulfuric acid is much more susceptible to hydrolysis than sulfamic acid

and that, like the latter substance,⁷ it exists in the solid state as a zwitterion complex.

Experimental

Preparation of Hydrazinosulfuric Acid.—The Baumgarten procedure⁸ entailing sulfonation of hydrazine with freshly prepared pyridine-sulfur trioxide⁹ was modified only with respect to recovery of the crystalline acid from an aqueous solution of the barium salt, $\text{Ba}(\text{SO}_3\text{N}_2\text{H}_3)_2 \cdot \text{H}_2\text{O}$. To 10.0 g. (0.027 mole) of the barium salt monohydrate dissolved in 200 ml. of water, 2.83 g. (0.028 mole) of sulfuric acid (96.6%) was added dropwise with rapid stirring. Immediately after removal of the barium sulfate by filtration, addition of ethanol and ether to the filtrate precipitated 4.50 g. of white, crystalline hydrazinosulfuric acid corresponding to a yield of 75.8% based on the weight of the barium salt; m.p. $217\text{--}217.5^{\circ}$ (lit. 217°).¹⁰

Anal. Calcd. for $\text{N}_2\text{H}_5\text{SO}_3\text{H}$: N, 25.00. Found: N, 25.00.

Acid Strength.—Figure 1 depicts the curve obtained for the titration of hydrazinosulfuric acid with sodium hydroxide. The pH of a 0.00745 M solution of the acid was found to be 3.02. This leads to a value for $K_a = 1.40 \times 10^{-4}$ or $pK_a = 3.85$.

Stability in Aqueous Solution.—Earlier workers¹⁰ had reported (a) that hydrazinosulfuric acid is stable in aqueous solution forming sulfuric acid very slowly, (b) that mineral acids cause slow decomposition in the cold, and (c) that hydrazine and sulfuric acid are formed rapidly on heating. It became apparent during the course of the present investigation that hydrolysis is extensive both at elevated temperatures and in the presence of acids in the cold.

From the data of Sommer and Weise,¹¹ who determined the hydrogen ion concentrations of solutions of hydrazine

(1) Abstracted from the doctoral dissertation presented to the Graduate College of the University of Illinois, 1955.

(2) Western Cartridge Company (Division of Olin Mathieson Chemical Corporation) Fellow in Chemistry, University of Illinois, 1953–1954.

(3) For a comprehensive review of sulfamic acid, sulfamide and related aquo ammonosulfuric acids see: L. F. Audrieth, M. Sveda, H. H. Sisler and M. Josetta Butler, *Chem. Revs.*, **26**, 49 (1940).

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(5) E. Konrad and L. Pellens, *Ber.*, **59B**, 135 (1926).

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(8) P. Baumgarten, *Ber.*, **59**, 1978 (1926).

(9) H. H. Sisler and L. F. Audrieth, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., New York, N. Y., 1946, p. 173.

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