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

$$SiF_4 \cdot 2NH_3(s) \longrightarrow SiF_4(g) + 2NH_3(g)$$

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 °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

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

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

$$\Delta F^0{}_T = -0.1061T + \frac{47.99T}{T - 21.9}$$

whence

$$\Delta F^0_{298} = 20.2 \text{ kcal./mole} \quad (25°)$$

and

$$\Delta F^0_{458} = 1.85 \text{ kcal./mole} \quad (185°)$$

Columbus, Ohio

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

By L. F. Audrieth and Sherwood F. West[1,2]

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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), H_2NNHSO_3H, and hydrazi-disulfuric acid, $[-NHSO_3H]_2$,[5] have been described adequately. Sulfamyl hydrazide (N-aminosulfamide), $SO_2NH_2(N_2H_3)$, has been described as a very unstable intermediate, whereas sulfuryl dihydrazide, $SO_2(N_2H_3)_2$, 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 procedure[8] entailing sulfonation of hydrazine with freshly prepared pyridine-sulfur trioxide[9] was modified only with respect to recovery of the crystalline acid from an aqueous solution of the barium salt, $Ba(SO_3N_2H_3)_2 \cdot H_2O$. 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. 217-217.5° (lit. 217°).[10]

Anal. Calcd. for $N_2H_3SO_3H$: 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 workers[10] 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

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[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).

[4] L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, New York, N. Y., 1951, pp. 220-222.

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

[6] F. Ephraim and E. Lasocki, *ibid.*, **44**, 395 (1911).

[7] F. A. Kanda and A. J. King, This Journal, **73**, 2315 (1951).

[8] P. Baumgarten, *Ber.*, **59**, 1976 (1926).

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

[10] W. Traube and A. Vockerodt, *Ber.*, **47**, 938 (1914).

[11] F. Sommer and K. Weise, *Z. anorg. allgem. Chem.*, **94**, 86 (1916).

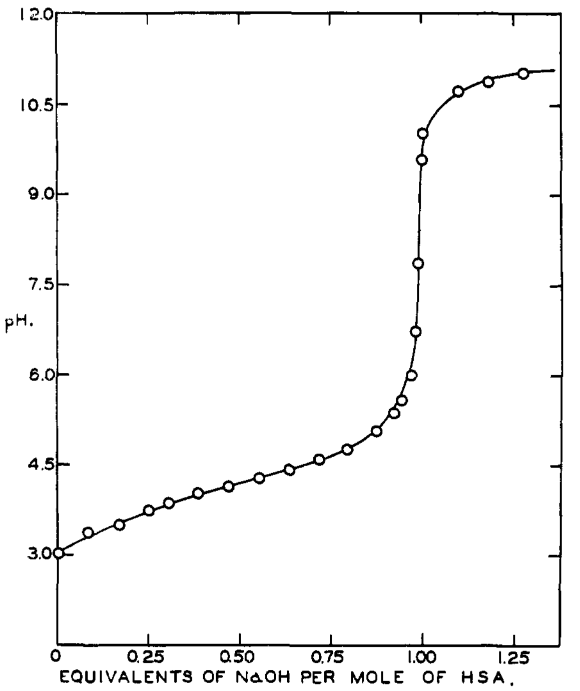

Fig. 1.—*p*H titration curve of hydrazinosulfuric acid with sodium hydroxide.

hydrogen sulfate, it follows that solutions of hydrazinosulfuric acid should undergo significant changes in *p*H on hydrolysis. In a preliminary study, 0.1 and 0.3 *M* solutions of hydrazinosulfuric acid were maintained at 45 ± 0.5°, and the *p*H determined periodically. After 5.5 hours, the *p*H of the 0.3026 *M* solution had fallen to 1.02, corresponding approximately to the *p*H of a hydrazine hydrogen sulfate solution of the same concentration. The *p*H of the 0.1002 *M* solution dropped to 1.33 after 40.0 hours. Hydrolysis was assumed to be complete in both instances.

The hydrolytic process goes as shown in the equation

$$H_2NNHSO_3H + HOH \longrightarrow N_2H_5^+ + HSO_4^-$$

The observed increase in acidity is obviously due to the formation of the hydrogen sulfate ion. Any method of measuring the $[N_2H_5^+]$ concentration should make possible the determination of the extent of hydrolysis at any given time interval.

The curve obtained for the titration of hydrazine hydrogen sulfate with sodium hydroxide solution reveals a sharp, vertical portion at *p*H 3.5–6.5 and a second inflection point in the *p*H range 9.5–10.5. Thymolphthalein, which changes from colorless to blue over the *p*H range 9.3–10.5, was selected as an indicator for titration of the $N_2H_5^+$ ion. However, check analyses using pure hydrazine hydrogen sulfate solutions gave low values for the hydrazinium ion concentration. The *p*H change is apparently not rapid enough, thus causing a premature and gradual change in color of the indicator. Accurate results were obtained for the $[N_2H_5^+]$ concentration by first titrating with standard base to the appearance of a pale blue color (*p*H 9.3) followed by titration with a Beckman Model G glass electrode *p*H meter. The equivalence points were calculated from the titration curves. "Acculate" carbonate-free sodium hydroxide standardized against potassium acid phthalate was used as the titrant.

Sample solutions of hydrazinosulfuric acid were prepared in 100-ml. volumetric flasks and maintained at 45°; 5-ml. aliquot portions were withdrawn periodically for analysis. Each titration was conducted in a chilled beaker containing 10 ml. of water in order to cool the sample to room temperature (25°). A 5-ml. aliquot portion was withdrawn from the freshly prepared solution and titrated to the thymolphthalein end-point. The number of milliliters of sodium hydroxide required for this "zero time" titration was then subtracted from the total amount of base required for each subsequent titration. The increase in total acidity is directly attributable to the formation of $N_2H_5^+$ ions. The data are represented graphically in Fig. 2.

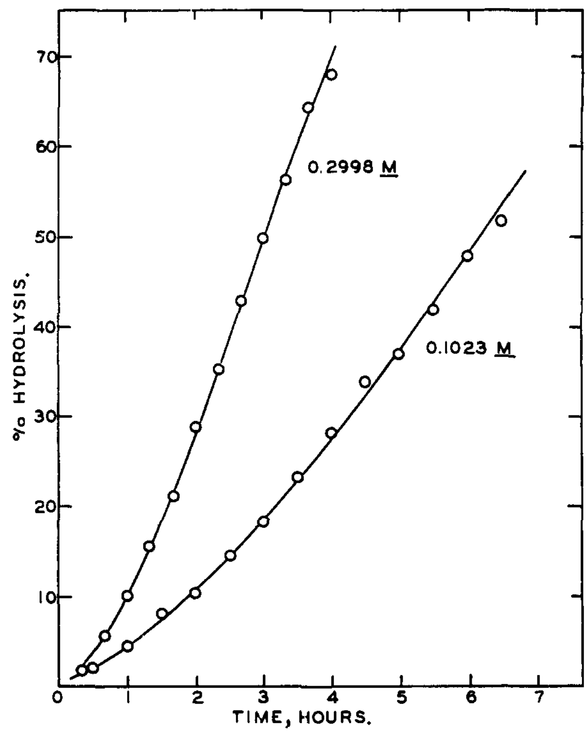

Fig. 2.—Percentage hydrolysis of solutions of hydrazinosulfuric acid *vs.* time at 45 ± 0.5°.

Structure of the Crystalline Form.—The infrared spectra of Nujol suspensions of both sulfamic acid and hydrazinosulfuric acid were obtained for comparison purposes on a Perkin–Elmer automatic recording spectrometer. Both substances were found to give absorptions characteristic of NH_3^+ deformation vibrations.

	H_2NSO_3H	H_2NNHSO_3H
Frequency, cm.$^{-1}$	1638(w), 1541(m)	1598(w), 1521(m)

Absorptions in this region characterize all amino acids capable of possessing the NH_3^+ structure and are commonly designated as "amino acid bands," 1 and 2 [1660–1610 cm.$^{-1}$ (w), 1550–1485 cm.$^{-1}$ (m)]. Although the origin of these bands is not clear, Bellamy[12] concludes that they are probably associated with the NH_3^+ deformation, since they are absent in salts and in N-substituted amino acids but present in the hydrochlorides. The presence of both of these absorptions in the acids under consideration would thus appear to justify the assumption that $H_3N^+NHSO_3^-$ more properly describes crystalline hydrazinosulfuric acid.

Discussion

The *p*H concentration curves comparing hydrazinosulfuric acid (HSA) with sulfamic and other acids[13] illustrated in Fig. 3 emphasize the decrease of acid strength in the series $HO–SO_2–OH > HO–SO_2–NH_2 > HO–SO_2–N_2H_3$. From the observed basicities of ammonia, hydrazine, amines and N-substituted hydrazines in general, where ammonia and amines are more strongly basic than the corresponding hydrazine compounds, one might have expected hydrazinosulfuric acid to be more strongly acidic than sulfamic acid. Any explanation of the decrease in acidity of these solvo sulfuric acids must

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[12] L. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

[13] M. E. Cupery, *Ind. Eng. Chem.*, **30**, 627 (1938).

obviously take into account steric effects on the relative acidity of products formed by the successive replacement of OH by NH_2 and of the latter group by N_2H_3.

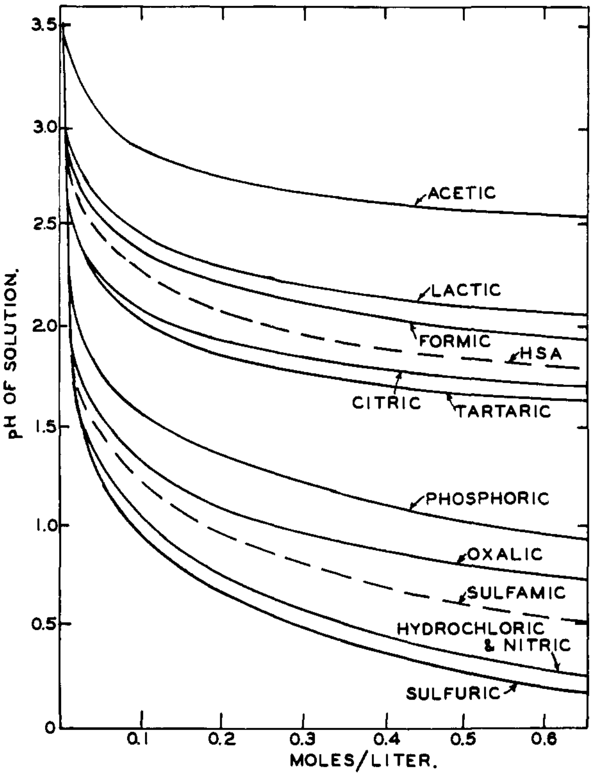

Fig. 3.—*p*H–concentration curves comparing hydrazinosulfuric acid (HSA) with other acids.

Hydrazinosulfuric acid is surprisingly susceptible to hydrolysis. Sulfamic acid is far more stable under comparable conditions. Oberhauser and Urbina[14] have reported that 1, 10 and 30% aqueous solutions of sulfamic acid were hydrolyzed to the extent of 16.86, 28.28 and 27.49% after 5 hours at 80°. The hydrolysis of sulfamic acid yields ammonium hydrogen sulfate; the acidity of such solutions does not change significantly during the course of the decomposition. The hydrolysis of hydrazinosulfuric acid, however, yields a more acidic solution, and the decomposition appears to be autocatalytic.

The salts of sulfamic and hydrazinosulfuric acids are stable in neutral or alkaline media. Such salt solutions may be boiled without appreciable decomposition whereas solutions of the acids hydrolyze extensively under the same conditions. After an investigation of the properties of imidodisulfamide and its derivatives Kirsanov and Zolotov[15] postulated that the enhanced stability toward hydrolysis of those species capable of existing as ions in solution is due to the shorter S–N distance in the ions. Such a picture could well account for the difference in ease of entry and cleavage of the S–N link by the water molecule.

Hydrazinosulfuric and sulfamic acids both apparently exist as zwitterions in the crystal. Though evidence is lacking for the presence of such species in solution, the momentary existence of such ions in acidic media is not improbable. X-Ray studies have shown that the S–N distance in the sulfamate ion (1.56 Å.) is far less than the observed distance in the sulfamic acid molecule (1.73 Å.).[7] Although no interatomic distances are yet available for the $H_2NNHSO_3^-$ and H_3N^+ $NHSO_3^-$, it seems safe to assume that the S–N distance is shorter in the anionic species. The relative distances involved in the S–N links in these species could thus account for the comparative ease of hydrolytic cleavage of the acids. Acidic solutions undoubtedly contain acid molecules as well as anionic species. Salt solutions, however, contain only sulfamate or hydrazinosulfate ions and are thus more stable.

The greater observed length of the S–N bond in sulfamic acid is in keeping with the extensive hydrogen bonding known to exist in this substance. Intermolecular attraction apparently causes a partial separation of charges with a stretching of the S–N link

$$H_2N—SO_3^-H^+ \ldots \longrightarrow H_2N—SO_3H$$

URBANA, ILLINOIS

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[14] F. Oberhauser and H. E. Urbina, *C. A.*, **41**, 1944d (1947).

[15] A. V. Kirsanov and Y. M. Zolotov, *J. Gen. Chem. U. S. S. R.*, **22**, 185 (1952) (English translation).