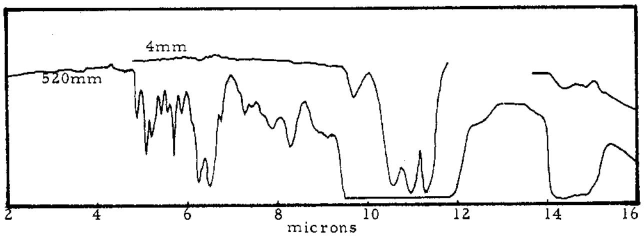

Fig. 1.—Infrared spectrum of $SF_5NF_2$.

monitoring a reaction using gas chromatographic analysis. Samples were taken at regular intervals over a 5-hr. period. The peak due to $SF_5NF_2$ gradually grew larger until the reaction mixture had been heated for 3 hr. After this time the peak size gradually diminished. Higher temperatures also gave decreased yields, possibly due to the tendency of $S_2F_{10}$ to decompose quite rapidly at 200° to $SF_4$ and $SF_6$.[4]

Difluoroaminosulfur pentafluoride also has been obtained as a product of the electric discharge reaction of tetrafluorohydrazine with $SF_4$, $SO_2$, $S_2F_{10}$, and thiophosgene. It also is formed in the reaction of fluorine and thiourea.

### Experimental

Disulfur decafluoride[5] (5.08 g., 0.02 mole) and tetrafluorohydrazine[6] (2.08 g., 0.02 mole) were condensed into an evacuated 300-ml. stainless steel autoclave and heated at 150° for 3 hr. The autoclave was cooled to −78° and the more volatile products (fraction A) were condensed into a cylinder in the vacuum line. The material (fraction B, 1.03 g.) remaining in the autoclave was separated by gas chromatography using a 40 ft. glass column (0.5 in. diameter) packed with the ethyl ester of Kel-F Acid 8114[7] on Chromosorb (35 g. of ester/100 g. of Chromosorb). Helium at a flow rate of 125 cc./min. was used as the carrier gas. Good separation of the products was obtained by this method, although the first components to be eluted ($SiF_4$, $SF_6$, and unreacted $N_2F_4$) could not be obtained in pure state without additional separation. Other peaks, in order of their elution, were due to $SOF_2$, $SF_2NF_2$, $SO_2$, $SF_5OSF_5$, $S_2F_{10}$, and a compound whose infrared spectrum is very similar to $SF_4(SO_3F)_2$. A total of 0.88 g. of pure $SF_2NF_2$ was recovered.

**Analysis.** (a) **Molecular Weight.**[8]—Calcd. for $SF_7N$: 179.0 Found: 178.2 (average of 7 determinations on 3 separate samples).

(b) **Nuclear Magnetic Resonance.**[9]—The n.m.r. spectrum showed three peaks as described below.

| Peak | Chemical shift, p.p.m. | Pattern and splitting | Rel. area | Assignment |
|---|---|---|---|---|
| A | −144.8 | Broad triplet | 1.00 | $NF_2$ |
| B | −127.0 | Multiplet | 0.5 | SF |
| C | −115.0 | Multiplet | 1.92 | $SF_4$ |

The spectrum for the $SF_5$ group was analyzed according to the methods of Merrill, Williamson, Cady, and Eggers.[10] The patterns were much as expected for this group. In addition, the four basal fluorines are coupled by 19 c.p.s. to the two fluorine atoms in the $NF_2$ group, and the apex atom is coupled by 4.5 ± 0.3 c.p.s. It will be noted that the apex fluorine atom is downfield from the basal atoms, which is the same relationship as that found[11] when the $SF_5$ substituent contains carbon attached to sulfur, and opposite to that usually found for oxygen attached to the sulfur atom.

(c) **Infrared.**—The infrared spectrum of $SF_5NF_2$ (Fig. 1) shows peaks at 9.72 (s), 10.58 (vs), 10.99 (vs), and 11.33 (vs) $\mu$. Although no specific assignments have been made, the peaks are in the general region usually assigned to N–F and S–F absorptions.

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[4] W. R. Trost and R. L. McIntosh, *Can. J. Chem.*, **29**, 508 (1951).

[5] A sample of this compound was generously supplied by Dr. James W. Dale, Monsanto Research Corp., Everett, Mass.

[6] 99% purity, obtained from E. I. du Pont de Nemours and Co., Wilmington, Del.

[7] Kel-F Acid 8114 was obtained from 3M Co., St. Paul, Minn.

[8] Determined by the vapor density method.

[9] These spectral results were obtained on a Varian High-Resolution nuclear magnetic resonance spectrometer Model V-4300-2, provided with field homogeneity control, magnet insulation, and superstabilizer. Chemical shifts were determined by side-bands applied with an audio oscillator for which the frequency is continuously monitored by an electronic counter. A tube of $CF_3COOH$ was used as a reference. The frequency was 56.4 Mc.

(10) C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, *Inorg. Chem.*, **1**, 215 (1962).

(11) N. Muller, P. C. Lauterbur, and G. F. Svatos, *J. Am. Chem. Soc.*, **79**, 1043 (1957).

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## The Dissociation Constants of α-Oxyhyponitrous Acid[1]

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Sodium α-oxyhyponitrite, $Na_2N_2O_3$, has been titrated with HCl at 1°. Experimental values of $pK_1$ and $pK_2$ have been extrapolated to infinite dilution to give the thermodynamic values, $pK_1 = 2.51$ and $pK_2 = 9.70$. These data have been interpreted as excluding the structure HO–NON–OH for α-oxyhyponitrous acid.

### Experimental

Sodium α-oxyhyponitrite was prepared as previously described[2] by a modification of the procedure of Addison, *et al.*[3] Baker analyzed reagent potassium chloride was used to adjust the ionic strength.

The titration was carried out at 1° under a nitrogen atmosphere using a Beckman Model G pH meter standardized against NBS buffers of pH values of 4.01 and 6.97 at 1°. The pH meter and temperature compensator were calibrated against a Leeds and Northrup Type K-2 potentiometer.

The weighed sample of sodium α-oxyhyponitrite was introduced and dissolved under a nitrogen atmosphere. In most experiments 1 ml. of 1 *N* NaOH (carbonate-free) was introduced before the titration with 1 *N* HCl. In the later experiments the titrant was changed to 0.01 *N* HCl just on the alkaline side of the end point for the titration of $N_2O_3^{-2}$ to $HN_2O_3^-$. This allowed increased accuracy in evaluation of the fraction titrated just past this end point.

The values of $pK_2$ were obtained from the titration data by interpolation of the point where $N_2O_3^{-2}$ was half-titrated to $HN_2O_3^-$.

Values of $pK_1$ were calculated at each point past the end point by the procedure outlined below. The average number of

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(1) Presented in part before the Division of Physical Chemistry at the 141st National Meeting of the American Chemical Society, March, 1962, in Washington, D. C.

(2) H. R. Hunt, Jr., J. R. Cox, Jr., and J. D. Ray, *Inorg. Chem.*, **1**, 938 (1962).

(3) C. C. Addison, G. A. Gamlen, and R. T. Thompson, *J. Chem. Soc.*, 338 (1952).

hydrogens bound to the $N_2O_3^{-2}$ ion at each point was calculated by the equation

$$\bar{n} = \frac{aC_N - [H^+]}{C_N} = a - [H^+]/C_N \qquad (1)$$

where $C_N$ is the analytical concentration of α-oxyhyponitrite in all forms (after correction for dilution), $a$ is the number of equivalents of hydrogen ion added per mole of α-oxyhyponitrite, $[H^+]$ is the concentration of free hydrogen ions in solution. $C_N$ was calculated from the weight of sodium α-oxyhyponitrite and the total volume and was verified by the volume of titrant needed to reach the end point, $a$ was calculated from the titration volumes, and $[H^+]$ was obtained from the pH and the activity coefficients of Harned and Hamer.[4] The values of $K_1$ were calculated from the values of $\bar{n}$ and $K_2$ by use of eq. 3 which was derived from eq. 2 by substituting the mixed acid constant expressions for the concentrations of the various species.

$$\bar{n} = \frac{[HN_2O_2^-] + 2[H_2N_2O_3]}{[N_2O_3^{-2}] + [HN_2O_3^-] + [H_2N_2O_3]} \qquad (2)$$

$$K_1 = \frac{[2 - \bar{n}](H^+)^2}{\bar{n}K_2 + [\bar{n}^- - 1](H^+)} \qquad (3)$$

In eq. 3 molar concentrations are indicated by brackets, while activities are indicated by parentheses.

It was found that if the solution becomes more acidic than about pH 4.60, α-oxyhyponitrite is unstable and decomposes to form NO gas, eq. 4 and 5, while the pH of the solution increases.

$$H^+ + HN_2O_3^- \rightleftarrows H_2N_2O_3 \qquad (4)$$

$$H_2N_2O_3 \longrightarrow 2NO + H_2O \qquad (5)$$

Figure 1 shows the increase of pH with time. It was concluded that significant experimental measurements could not be made below pH 4.60. Unfortunately, at this pH $\bar{n}$ is approximately 1.005 rather than 1.50 where $K_1$ could be evaluated most accurately.

The calculated values of the constants are summarized in Table I.

TABLE I

| Ionic strength | $pK_1$ | $pK_2$ |
|---|---|---|
| 1.02 | 2.32 ± 0.01 | 9.18 ± 0.01 |
| 0.38 | 2.30 ± 0.01 | 9.30 ± 0.01 |
| 0.12 | 2.40 ± 0.05 | 9.43 ± 0.01 |
| 0 02 | 2.46 ± 0.05 | 9.56 ± 0.01 |
| 0.00 extrapolated | 2.51 | 9.70 |

All values except for $pK_1$ at $\mu = 0.38$ are the results of at least two separate experiments. The errors indicated for $pK_1$ are the average deviations of the calculated $pK_1$ values of all experimental points for the region $\bar{n} = 1.001$ to $\bar{n} = 1.005$. The errors for $pK_2$ represent the limits of the values obtained by interpolation of the titration curves.

## Discussion

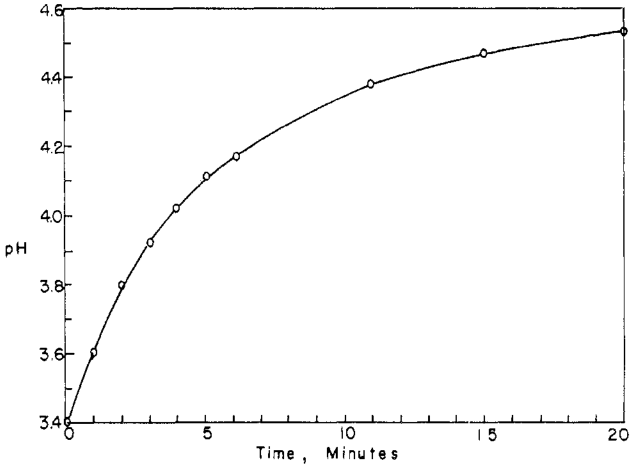
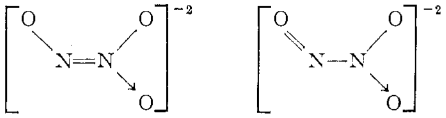


Fig. 1.—Change of pH as a function of time resulting from decomposition of $H_2N_2O_3$.

In general when a molecule has two acid groups of the same type the two pK values become closer as the distance between the acid groups increases. This is seen in a comparison of the last two pK values of chain polyphosphates where (at $\mu = 1$) these pK values for pyrophosphate are 8.93 and 6.13[5]; for tripolyphosphate, 8.81 and 5.83[6]; for tetrapolyphosphate, 8.38 and 6.59[7]; and for a long chain polyphosphate, $HO_2P(HPO_3)_{58(av)}PO_2H$, they are 8.17 and 7.22.[8] The spacing between the groups in HO–NON–OH would be similar to that in pyrophosphate. Furthermore, in dicarboxylic acids the two pK values are separated by about 3 pK units or less except in cases like maleic acid where conjugated unsaturation may occur. From these analogies it is concluded that in the case of α-oxyhyponitrous acid the structure HO–NON–OH is improbable since the two pK values are separated by 7.19 units.

Several structures have been suggested for α-oxyhyponitrous acid.[3] The calorimetric experiments of Hunt, Cox, and Ray[2] have excluded the peroxide structure. The remaining structures all have in common a nitrogen to nitrogen bond with two oxygen atoms bonded to one nitrogen and the third oxygen to the other nitrogen. Thus the resonance structures



are possible for the α-oxyhyponitrite ion. The remaining question, the location of the protons in the monohydrogen α-oxyhyponitrite ion and the free acid, will be discussed in terms of Hammett σρ relationships in a future paper.

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[6] J. I. Watters, E. D. Loughran, and S. M. Lambert, *ibid.*, **78**, 4855 (1956).

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[8] R. R. Irani and C. F. Callis, *J. Phys. Chem.*, **65**, 934 (1961).

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## The Chemistry of Alane. I. Some Observations on the Effect of the Coördinating Base on the Aluminum-Hydrogen Absorption in the Infrared[1]

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The infrared spectra of solutions of various alane–

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