ula for the calculation of the ammonia equilibrium constant over a range of temperatures. Probably the value for the free energy of ammonia at 800° A., 9220 cal. as calculated by its use, is not greatly in error.

These data lead to the value 28,400 cal. for the free energy of hydrogen cyanide gas at 800° A. Combining this with the heat data mentioned we obtain for the free energy of this gas as a function of temperature: $F = 30{,}600 + 0.60T \ln T - 0.00068T^2 + 0.00000011T^3 - 6.3T$. This leads to the special value 29,700 cal. at 298° A. Lewis and Randall give the fairly concordant value 28,910 cal., but this was obtained very indirectly through the combination of results on a series of equilibria.

Summary

A study of the equilibrium of the reaction between ammonia and carbon, yielding as products hydrogen cyanide and hydrogen, has been described; and the free-energy decrease attending the reaction at 800° A. has been calculated. By the use of data on the ammonia dissociation and of heat data, the free energy of hydrogen cyanide gas has been expressed as a function of temperature, and the special values at 800° and 298° A. have been given.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

HYPONITRITES[1]

BY LAUDER W. JONES AND ALFRED W. SCOTT

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Experiments which required silver hyponitrite in considerable quantities compelled us to seek a satisfactory method for its preparation.

The various preparative methods employed in the making of hyponitrites may be classified into two major groups: first, those which employ compounds whose molecules contain one atom of nitrogen; second, those which use substances with two atoms of nitrogen in their molecules.

In the first group, we may place all of the methods based upon the reduction of nitrates, nitrites[2] or nitric oxide and upon the direct[3] or indirect[4] oxidation of hydroxylamine.

The second group of methods shows considerable diversity also. Many of the proposed syntheses depend upon the interaction of nitrous acid and

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[1] The experiments described in this article were undertaken jointly by the authors at Princeton University. They were completed at the University of Georgia.

[2] (a) Divers and Haga, *J. Chem. Soc.*, **47**, 623 (1885); **75**, 87, 95 (1899). (b) Hantzsch and Kaufmann, *Ann.*, **292**, 317 (1896). (c) Raschig, *Ann.*, **241**, 230 (1887). (d) Divers and Haga, *J. Chem. Soc.*, **55**, 765 (1889). (e) Kirshner, *Z. anorg. Chem.*, **16**, 424 (1898).

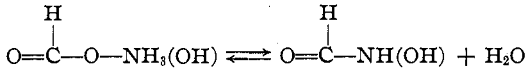
[3] Ref. 2 b. Thum, *Wien. Monatsh.*, **14**, 294 (1893).

[4] Piloty, *Ber.*, **29**, 1559, 2324 (1896). Angeli, *Gazz. chim. ital.*, **26**, 17 (1896); **30**, 593 (1900). Angeli and Angelico, *ibid.*, **31**, 15 (1901); **33**, 245 (1903).

hydroxylamine, or its derivatives. A theory may be advanced to correlate all such methods, if we assume that hydroxylamine combines primarily with nitrous acid to form an unstable salt, which decomposes as follows.

$$\underset{A}{O{=}NONH_3(OH)} \longrightarrow \underset{B}{O{=}N{-}NH(OH)} + H_2O \longrightarrow \underset{C}{O{=}NN} + 2H_2O \qquad (1)$$

When the hydroxylamine salt of an organic acid loses one molecule of water in this fashion, an hydroxamic acid results.[5]



$$O{=}\overset{\displaystyle H}{\overset{|}{C}}{-}O{-}NH_3(OH) \rightleftharpoons O{=}\overset{\displaystyle H}{\overset{|}{C}}{-}NH(OH) + H_2O \qquad (2)$$

So, by analogy, Formula B may be said to represent the *hydroxamic acid of nitrous acid.* It will be apparent that the formula usually assigned to hyponitrous acid bears a tautomeric relation to Formula B.

$$O{=}N{-}NH(OH) \rightleftharpoons HO{-}N{=}N{-}OH \qquad (3)$$

Hyponitrous acid, therefore, may be regarded as the *hydroximic acid of nitrous acid.* Organic derivatives of both types exist; the formula, $RON{=}NOR$, is assigned to the esters obtained by the action of halogen alkyls or aryls upon silver hyponitrite, while nitroso-hydroxylamines, such as nitroso-β-phenylhydroxylamine, $O{=}N{-}N(C_6H_5)OH$, are derivatives of the hydroxamic type (B).[6]

In view of these relations, several methods described in the literature become plausible. Thus Wislicenus[7] prepared silver hyponitrite from the product obtained by mixing an aqueous solution of hydroxylammonium sulfate with sodium nitrite. Paal[8] varied the reaction by using hydroxylammonium chloride and silver nitrite in water solution at 0°. Hantzsch[9] reports that Kaufmann allowed free hydroxylamine dissolved in methyl alcohol to react with nitrous acid; that is, he "diazotized" hydroxylamine. In all of these reactions the amount of hyponitrite obtained was exceedingly small; nitrous oxide was the chief product.

In our search for a more practical method, these formal relations of hyponitrous acid to hydroxamic acids suggested that, among the general methods used to synthesize hydroxamic acids, we might find one especially suited to the preparation of hyponitrites. Organic hydroxamic acids are most frequently made by the action of hydroxylamine upon esters. This method proved to be applicable to the preparation of pure sodium

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[5] Jones and Oesper, *Am. Chem. J.*, **42,** 518 (1909).

[6] Acyl derivatives have been used to prepare hyponitrites. Thus, Hantzsch and Sauer [*Ann.*, **299,** 67 (1898)] treated dimethyl-hydroxyurea with nitrous acid to prepare dimethylnitroso-hydroxyurea which they hydrolyzed with alkali at 0°: $(CH_3)_2NCO.\text{-}NH(NO) + 4KOH = (CH_3)_2NH + K_2CO_3 + KON = NOK + 2H_2O$.

[7] Wislicenus, *Ber.*, **26,** 771 (1893).

[8] Ref. 7. Paal, *Ber.*, **26,** 1026 (1893).

[9] Hantzsch and Sauer, *Ann.*, **299,** 98 (1898).

hyponitrite with yields comparatively satisfactory, and with fairly simple manipulations.[10]

$$O{=}N{-}O{-}C_2H_5 + H_2NOH = O{=}NH(OH) + HOC_2H_5$$
$$2O{=}NH(OH) + 2C_2H_5ONa = NaON{=}NONa + 2C_2H_5OH \qquad (4)$$

Pure sodium hyponitrite is a fairly stable compound. We have observed that it may be kept in tightly stoppered vessels for several years without appreciable decomposition. From the sodium salt prepared by this method, it is easy to make pure silver hyponitrite.

Experimental Part

Ethyl nitrite was prepared according to the method described by Wallach and Otto.[11]

The only modification of this method consisted in the introduction of an efficient purifying train which contained two U-tubes filled with calcium chloride and a third tube filled with solid sodium hydroxide. The gas obtained by dropping dil. sulfuric acid into an alcoholic solution of sodium nitrite was passed through this train and condensed in a vessel surrounded by a freezing mixture. To purify the ethyl nitrite still further, it was redistilled and, after passing through the train once more, it was led directly into the reaction mixture.

The Preparation of Sodium Hyponitrite.—A solution of sodium ethylate made by the action of 6.62 g. of sodium upon absolute alcohol was added to a solution of 20 g. of hydroxylammonium chloride in absolute alcohol. This mixture was cooled and filtered to remove sodium chloride. Then a solution of sodium ethylate made from 15.4 g. of sodium was poured into it. Finally, this solution was cooled by a freezing mixture and the calculated amount of pure ethyl nitrite was distilled directly into it. Sodium hyponitrite was precipitated.

An excess of sodium ethylate seems to be favorable. Several experiments were performed in which sodium ethylate was added gradually and in sufficient amounts to keep the solution alkaline; this procedure appeared to diminish the yield of hyponitrite materially. If the ethyl nitrite was not distilled into the reaction mixture but added to it all at once or in several portions, the amount of hyponitrite was decreased.

A few minutes after all of the ester had been added, the salt was col-

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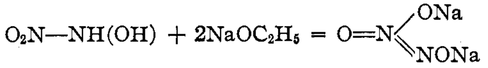
[10] In a similar manner, Angeli prepared the sodium salt of his "nitrohydroxylaminesäure," $Na_2N_2O_3$; he used ethyl nitrate, sodium ethylate and hydroxylamine.

$$O_2N{-}OC_2H_5 + H_2NON = O_2N{-}NH(OH) + C_2H_5OH$$



$$O_2N{-}NH(OH) + 2NaOC_2H_5 = O{=}N\begin{matrix}\diagup ONa\\ \diagdown NONa\end{matrix} \qquad (5)$$

The unstable acid, $H_2N_2O_3$, would be the hydroxamic acid of nitric acid, and its salt, the disodium salt of the hydroximic acid of nitric acid.

[11] Wallach and Otto, *Ann.*, **253**, 251 (1889). Vanino's "Handbuch der präparativen Chemie," F. Enke, Stuttgart, **1921**, vol. I.

lected on a filter and washed with cold absolute alcohol and with ether; yield, 4.1 g., or about 13.5%.

If the products of reaction are allowed to stand for some time before the hyponitrite is separated, sodium nitrite may form and contaminate the salt.

Silver Hyponitrite.—The calculated amount of a 5% solution of silver nitrate in water was added to a cold, dilute aqueous solution containing 4 g. of sodium salt. Silver hyponitrite was precipitated at once; it was collected, washed with water, then with absolute alcohol and with ether. Dried in a desiccator, it weighed 10.3 g. A sample was analyzed by the Volhard method.

Anal. Subs., 0.2899: cc. of 0.1208 *N* KSCN, 17.36. Calc. for $Ag_2O_2N_2$: Ag, 78.24. Found: 78.04.

Summary

1. Various methods of preparing hyponitrites have been described.
2. The preparation of sodium hyponitrite from hydroxylamine, sodium ethylate and ethyl nitrite is described.
3. Sodium hyponitrite is quite stable and is a source from which silver hyponitrite may be prepared easily.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE PREPARATION OF FLUORINE

BY JOSEPH SIMONS

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An unusual interest attaches to the chemistry of fluorine and its compounds on account of the extremely electro negative character of the element. Comparatively little attention has been paid to this field, however, due to the experimental difficulties involved, so that further investigations are very important. A necessary preliminary to such work is the development of the technique for the preparation of elementary fluorine in large quantities.

The electrolysis of anhydrous hydrofluoric acid, used by Moissan[1] in the first isolation of the element, is difficult and expensive, and like the decomposition of lead tetrafluoride described by Argo, Mathers, Humiston and Anderson[2] is not promising as a method of preparing large quantities of fluorine. The most satisfactory method for this purpose is the electrolysis of fused potassium acid fluoride as described by the authors just mentioned. Their cell consists of an electrically heated copper vessel which serves both as cathode and as a container for the electrolyte. In

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[1] Moissan, *Compt. rend.*, **102**, 1543 (1886); **103**, 202, 256 (1886).

[2] Argo, Mathers, Humiston and Anderson, *Trans. Am. Electrochem. Soc.*, **23**, 348 (1919).