

HYDROXYLAMINE AS THE PARENT SUBSTANCE  
OF A SYSTEM OF ACIDS, BASES, AND SALTS

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Before the beginning of the twentieth century comparatively little thought was given to any other solvent except water. The property of forming solutions which possessed the ability to conduct the electric current was by tacit understanding restricted to water, and the old Lavoisian idea that acids, bases, and salts, owed their peculiar behavior to the presence of oxygen was regarded as an established fact. This idea has since been modified and extended, so that "not only oxygen, but also sulfur, nitrogen, the halogens, and to a recognizable extent even carbon," may be thought of as acid, base, and salt forming elements.<sup>1</sup>

What has heretofore been regarded as the oxygen series of acids, bases, and salts, may be considered as derived from water. To these the prefix aquo- has been applied. Thus, sodium hydroxide, nitric acid, and sodium nitrate may be considered as aquo-base, aquo-acid, and aquo-salt, respectively.

The nearest prototype of water, structurally and chemically, is liquid hydrogen sulfide. A great number of substances are known which bear the relationship of typical thio-acids, thio-bases, and thio-salts to it. As examples of these may be cited tri-thiocarbonic acid,  $H_2CS_3$ , potassium sulf-hydroxide, KSH, and potassium tri-thiocarbonate,  $K_2CS_3$ .

Ammonia has been studied extensively with respect to its solvent properties. However, it remained to Franklin<sup>2</sup> and his co-workers to recognize its true character as the parent substance of an ammonia system of acids, bases, and salts. It has been found to be the most water-like substance known, and actually does approach water very closely in all of its properties. Naturally the similarity between the corresponding compounds of the two systems is also very striking. Ammono-bases, such as sodium amide,  $NaNH_2$ , react readily in liquid ammonia with ammono-acids, such as cyanamide,  $H_2NCN$  (an ammono-carbonic acid), to yield ammono-

<sup>1</sup> Franklin, J., *Am. Chem. Soc.* 46, 2137 (1924).

<sup>2</sup> Franklin, *Am. Chem. J.* 20, 820 (1898); 23, 277 (1900); 47 285 (1912); also publications in the *Journal of the American Chemical Society* and the *Journal of Physical Chemistry*.

salts, as in this particular case, sodium cyanamide,  $\text{Na}_2\text{NCM}$  (sodium ammonio-carbonate).

A. W. Browne<sup>3</sup> and his students have shown hydrazine to be an excellent ionizing solvent comparable in scope with water and ammonia. The solubilities of many substances in it have been determined and reactions have been found to take place in it with facility. Compounds are known which bear a very definite relationship to hydrazine, viz., sodium hydrazide,  $\text{NaNHNH}_2$ , dihydrazo-sulfuric acid,  $(\text{NHNH}_2)_2\text{SO}_2$ , hydrazine dihydrazo-sulfate,  $(\text{N}_2\text{H}_4)_2(\text{NHNH}_2)_2\text{SO}_2$ . That hydrazine may be considered as the parent substance of a hydrazo-system of compounds is hardly disputable in light of these facts.

Many other substances have been studied with reference to their solvent properties. Among these may be included the halogen and halogenoid hydracids, sulfur dioxide, and hydrogen peroxide. Two others which have received extended consideration of late are carbonyl chloride<sup>4</sup> and glacial acetic acid.<sup>5</sup>

A cursory examination of the properties of hydroxylamine,  $\text{NH}_2\text{OH}$ , shows that it, too, may justly be considered the basis of a system of acids, bases, and salts. The striking similarity which this substance shows with water, its solvent properties, and the structural relationship which many substances bear to it, all point to this extremely interesting analogy. The peculiar position which it occupies intermediate between water and ammonia on the one hand, and between hydrogen peroxide and hydrazine on the other, makes its consideration from this point of view of highest theoretical interest. That this idea is not altogether new is attested to by the following quotation from the literature. "Even with respect to its solubilities may this substance be compared with water, as it is easily soluble in ethyl and methyl alcohol, and only barely so in the other common organic solvents. \* \* \* Numerous inorganic compounds combine with it in the manner of solvent of crystallization \* \* \*. It may, like water, be said to possess both basic and acid properties \* \* \* as exemplified by its ability to form salts \* \* \* and the easy replaceability of one of its hydrogen atoms by a metallic atom."<sup>6</sup>

Liquid anhydrous hydroxylamine has been found to dissolve<sup>7</sup> many substances quite readily, such as KI, KCN, and KBr in large

<sup>3</sup> Browne and others. *J. Am. Chem. Soc.* 48, 682 (1926). See also Welsh, *ibid.* 37, 497, 816, 825 (1915).

<sup>4</sup> Germann and Timpany, *J. Am. Chem. Soc.* 47, 2275 (1925).

<sup>5</sup> Conant, J. B., *J. Am. Chem. Soc.* 49, 3097, 3062 (1927).

<sup>6</sup> Kohlschütter and Hofmann, *Ann.* 307, 314 (1899).

<sup>7</sup> Lobry de Bruyn, *Rec. trav. chim.* 11, 18 (1892).

amounts and  $\text{NaNO}_3$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{NaCl}$ , and  $\text{KCl}$  in lesser quantities. Sodium hydroxide, crystallized barium hydroxide, and ammonia are also very soluble. Peculiarly enough, solutions of barium nitrate and potassium sulfate in hydroxylamine are said to give no precipitate when mixed. Many other substances react chemically with hydroxylamine and it is not at all improbable that the solvent in such cases exerts a solvolytic effect upon the solute comparable to the hydrolytic action of water upon certain dissolved salts.

With many substances hydroxylamine combines to form compounds containing hydroxylamine of crystallization. A large number of such hydroxylamates<sup>8</sup>, analogous to hydrates, ammonates, and hydrazinates, has been isolated. Furthermore, a whole series of hydroxylamino-basic mercury salts<sup>9</sup>, similar to the ammono-basic and aquo-basic compounds, has been prepared. These facts lead to a clearer conception of what have previously been considered as abnormal salts of hydroxylamine, salts in which the ratio of base to acid is greater than would normally be expected. Thus, compounds of the type  $(\text{NH}_2\text{OH})_2 \cdot \text{HX}$  and  $(\text{NH}_2\text{OH})_3 \cdot \text{HX}$  (where  $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ ) should be considered as hydroxylamates of the normal salts, just as there are ammonium salts with ammonia of crystallization.

Just as sodium hydroxide is called an aquo-base, sodium amide an ammono-base, sodium hydrazide a hydrazo-base, so sodium hydroxylamate,  $\text{NaNHOH}$ <sup>7</sup>, may be considered as a hydroxylamino-base, derivable by the replacement of one of the hydrogen atoms of hydroxylamine by sodium. This compound is actually prepared by the action of metallic sodium upon hydroxylamine in ethereal solution and presents an extremely unstable and explosive substance. Other metallic derivatives of hydroxylamine simulate the sodium compound in reactions and properties.

As in the case of ammonia where the negative  $\text{NH}_2$  radical may take the place of a hydroxyl group in uniting with non-metallic elements to form ammono-acids, so the  $\text{NHOH}$  residue enters into combination with metalloids or acidic groups to form hydroxylamino-acids. Due to the fact that there are three replaceable hydrogen atoms in hydroxylamine, six types of acids are possible. Examples of all of these are known, viz., (1)  $\text{XNHOH}$ , (2)  $\text{H}_2\text{NOX}$ , (3)  $\text{X}_2\text{NOH}$ , (4)  $\text{XNHOX}$ , (5)  $\text{X}_2\text{NOX}$ , (6)

<sup>8</sup> Crismer, Bull. soc. chim. (3) 3, 114 (1890); Antonow, J. russ. phys. chem. Ges. 37, 479 (1905); Feldt, Ber. 27, 401 (1894).

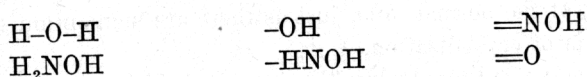
<sup>9</sup> Adams, Am. Chem. J. 28, 199 (1902).

$X_3NO$ . Among the inorganic compounds only the analogues of sulfurous, sulfuric, carbonic, nitrous and nitric acid are known. The aryl hydroxylamino-acids of the type  $RCONHOH$  and  $RSO_2NHOH$  (where R represents an aromatic residue) are characterized by well-defined acidic properties, whereas the alkyl hydroxamic acids react neutral in aqueous solution. In this respect they behave like the alkyl ammono-acids (acid amides) which are also neutral in aqueous solution, but which yield well-defined salts when treated with an ammono-base in the parent solvent, liquid ammonia.

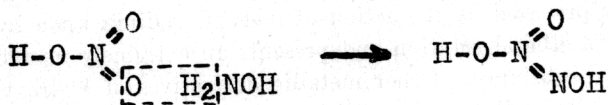
A consideration of several typical acids which are related to hydroxylamine in much the same way as ordinary aquo-acids are to water will serve to bring out the analogy between water and hydroxylamine more clearly.

Of the possible hydroxylamino-sulfuric acids only one, mono-hydroxylamino-sulfuric acid,  $SO_3H.NHOH$ , has been obtained in the free state. Several others are known in the form of their salts.

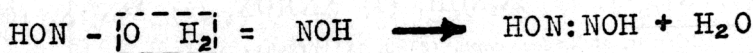
Nitro-hydroxylamic acid,  $HO(NO)NOH$ , may be looked upon as nitric acid in which one of the oxygen atoms has been replaced by its hydroxylamine equivalent, the  $NOH$  radical.



Its preparation by the action of ethyl nitrate upon hydroxylamine in alcoholic solution in the presence of alkali lends credence to this conception. The acid is known only in the form of its salts.

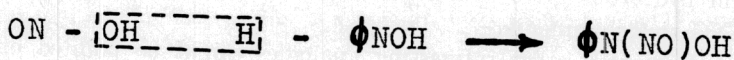


That hyponitrous acid may be regarded as a hydroxylamino-nitrous acid is indicated by the fact that its salts may be prepared by the action of hydroxylamine hydrochloride upon nitrites. The acid itself is formed as the result of the decomposition of hydroxylamine nitrite.<sup>10</sup> Both of these reactions consist essentially in the replacement of an oxygen atom in nitrous acid by the hydroxylamine equivalent, the  $NOH$  radical.

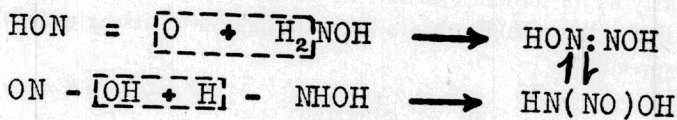


<sup>10</sup> Paal, Ber. 26, 1026 (1893).

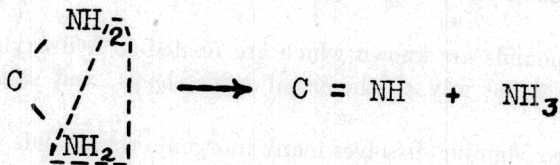
In this connection it is interesting to note that the interaction of phenylhydroxylamine with nitrous acid yields phenylnitrosohydroxylamine, a substance which is very stable towards alkalis reacting with the latter to form stable salts. The hypothetical parent substance, nitroso-hydroxylamine, may most certainly be regarded as a tautomer of hyponitrous acid, the hydroxyl group in nitrous acid in this case having been replaced by the hydroxylamine equivalent.



In line with the above considerations two possible structures may be assigned to hyponitrous acid, depending upon where the solvolytic action of hydroxylamine has taken place. Both forms undoubtedly exist in equilibrium with each other.

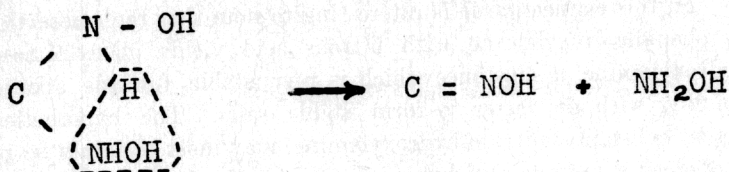


Another interesting deduction which can be made using the conception of hydroxylamine as the parent substance of a system of compounds it concerns itself with fulminic acid. In reactions and properties it resembles hydrocyanic acid very closely. Both substances are believed to contain a divalent or unsaturated carbon atom. Franklin<sup>11</sup> has shown that HNC may be regarded as an ammono-carbonous acid derivable by deammonation of the ortho-carbonous acid, as illustrated by the following equation.



The same reasoning may be applied to fulminic acid, a hydroxylamino-carbonous acid.

<sup>11</sup> Franklin, J. Phys. Chem. 27, 167 (1923).



That such a structural formulation of fulminic acid is in accord with its chemical behaviour is indicated by the fact that acid hydrolysis gives hydroxylamine, much as acid hydrolysis of HNC yields ammonia.

Numerous other interesting analogies might be pointed out to show the logicity of the idea of a hydroxylamine system of compounds. The value of any such generalization lies largely in that it may serve to clarify structural relationships which obtain among hydroxylamine compounds and at the same time aid in the classification of hydroxylamine derivatives. As a solvent, particularly as an ionizing solvent in chemical reactions, its great instability will probably always act as a barrier to its extended and widespread use.

#### SUMMARY

Evidence from the chemical literature has been adduced to show that hydroxylamine may be looked upon as the parent substance of a hydroxylamino-system of acids, bases, and salts.

That such a behavior might be expected is suggested by the peculiar position which it occupies between water and ammonia on the one hand and hydrazine and hydrogen peroxide on the other—to all of which it bears a close resemblance both in physical and chemical properties. All four of these substances have been shown to be ionizing solvents and parent substances of systems of compounds.

Compounds are known which are related to hydroxylamine in much the same way as the usual acids, bases, and salts are to water.

Hydroxylamine dissolves many inorganic compounds and combines with others in the manner of solvent of crystallization.