

THE REDUCTION OF HYDRONITRIC ACID. I. A PRELIMINARY NOTE ON THE STRUCTURE OF HYDRONITRIC ACID.

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Following experiments by E. Fischer,¹ which, in the light of our fuller knowledge of the behavior of hydrazine upon oxidation, could at least

be given a different interpretation—the structural formula, $\text{H}-\text{N} \begin{array}{l} \diagup \text{N} \\ \parallel \\ \diagdown \text{N} \end{array}$,

has been given to hydronitric acid; this formula has no parallel among the other nitrogen compounds or inorganic acids, and places that acid structurally in a quite isolated position.

Heretofore, hydronitric acid has been regarded as an analog of the halogen hydracids, and it is possible to construct a sort of analogy between them. It may be observed, however, that this analogy is based almost entirely on solubilities and not on reactions.²

In a study of the reduction of hydronitric acid, it was found that many metals below magnesium in the electrochemical series, when acted upon by hydronitric acid, led to the formation of ammonia and free nitrogen as reduction products (Equation 1). No hydrogen was evolved. In one instance hydrazine appeared as an additional reduction product.

In the reduction of the acid by oxidizable metallic compounds, the action resulted in a compound of the metal in which the latter possessed a higher valence, and in ammonia and nitrogen as the reduction products of the acid (Equation 3).

With certain oxidizable, non-metallic compounds the acid was reduced with the formation of ammonia and nitrogen, again, as the reduction products, and with the negative element of the reducing agent appearing in a higher state of oxidation (Equation 5).

Certain metals lying near the bottom of the electrochemical series do not displace the hydrogen of acids because of the large difference between the electrode potentials of those metals and hydrogen. The reaction may be regarded as a reversible one, the reverse action taking place at a much greater rate than the direct one. A substance able to reduce the active mass of the hydrogen—a depolarizer—prevents the reverse action and enables the direct action to take place to completion.

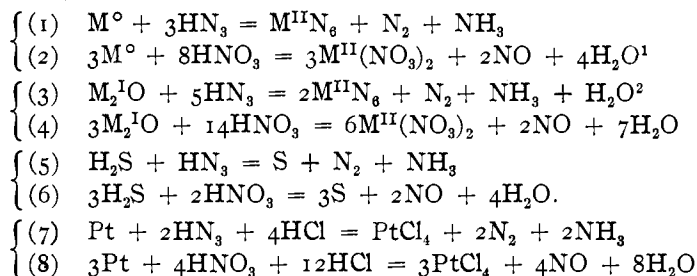
Hydronitric acid was found to be an efficient depolarizer. In its presence hydrochloric acid dissolved platinum. Ammonia and nitrogen were among the reduction products (Equation 7).

When we consider the behavior of hydronitric acid in the reactions mentioned and attempt to bring it into line with that of other inorganic acids under like conditions, we are struck at once with the parallelism

¹ "Ueber die Hydrazinverbindungen," *Ann.*, 190, 67 (1878), see p. 92.

² THIS JOURNAL, 33, 803 (1911).

between the chemical properties of this acid and those of nitric acid. This analogy is brought out when we examine the equations representing the reactions of the two acids with the respective reducing agents, as follows:



An inspection of the first two equations brings out the following points: In neither reaction is hydrogen evolved. In both cases a portion of the acid radicle appears as a gaseous product, in one instance consisting chemically of a nitrogen atom united to a nitrogen atom, and in the other, a nitrogen atom united to an oxygen atom. In the one case ammonia results, and in the other, the strictly analogous substance, water, is produced. That the same analogy holds throughout the series of equations is perfectly evident.

Assuming that an analogous reaction implies an analogous structure, the formula $H-N=N\equiv N$ is proposed for hydronitric acid, which is a parallel formula to $H-O-N \begin{smallmatrix} =O \\ =O \end{smallmatrix}$, commonly accepted as representing the structure of nitric acid. In the one instance a pentavalent nitrogen, the nucleus of the molecule, is united to nitrogen, and in the other, to oxygen.

When we review the structure of the inorganic acids, such as cyanic, thiocyanic, nitrous, etc., we see that the various positions in the molecules are occupied in turn by the negative atoms to form the various acids. In hydronitric acid all the positions are occupied by nitrogens. Furthermore, the hydroxyl group of nitric acid is replaced in hydronitric acid by the analogous imide group.

Hydronitric acid, then, must be regarded as a nitridizing agent, analogous to nitric acid, an oxidizing agent; and just as nitric acid is a hydrated oxide of nitrogen, hydronitric acid may come to be regarded as an ammoniated nitride of nitrogen.

These conclusions are supported by and are derivable from numerous

¹ While it is recognized that other products may, and do, result from the action of nitric acid on metals, those represented above are regarded as the most typical.

² Two reactions are represented by this equation, one the action of an acid on an oxide to form a salt and water, and the other the nitridation of the metal to a higher valence.

other considerations to be presented subsequently. In a recent article Thiele¹ has assigned hydronitric acid the same structure as that advanced in this note. While the conclusions are similar, the one was arrived at through organic considerations, while the other was reached through a study of the inorganic chemistry of the acid. That the conclusions were arrived at quite independently may be further attested by the fact that the matter here presented was communicated by correspondence, and otherwise, to various members of the chemical profession almost a year ago, and months before the appearance of the article in the *Berichte*.

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SOLUBILITY OF WROUGHT TUNGSTEN AND MOLYBDENUM.

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Since the production of tungsten and molybdenum metals in a malleable and ductile form,² various interesting applications have been found for these metals. Probably the most extensive use for tungsten at present is in metal filament lamps, but this metal, combining the physical properties of high melting point (3000°), high specific gravity (19.3), low vapor pressure and high heat conductivity, has found use as a contact metal in numerous current interrupting devices, as a target in Röntgen tubes, and as a possible projectile material.³

It is the purpose of this paper to point out some of the chemical properties of these wrought metals, which, combined with their physical properties already described, may broaden the field of application of these two interesting metals.

Tungsten.

In the following experiments the samples of metal used were all of the same surface and shape. They were discs, of sheet tungsten, such as are now being used for X-ray targets, and are 18 mm. in diameter and about 2.5 mm. thick. The surface area was $510 + 140 = 650$ sq. mm. on the average. The weight, according to thickness, varied from 9 to 12 grams.

Solubility in Hydrochloric Acid.—Wrought tungsten is insoluble in hydrochloric acid of any concentration at room temperature and only very slightly so at 110°. After 45 hours the hot, concentrated acid (sp. gr. 1.15) showed no effect upon the tungsten. After 175 hours, however, a black coating of oxide formed and the metal lost 0.5% in weight.

In dilute acid, at 110°, it lost 0.05% after 22 hours but showed no further loss after 50 hours. After 175 hours the metal was coated with tungstic oxide and there was a gain in weight of 1% due to oxidation. This

¹ *Ber.*, 44, 2522 (1911).

² Fink, *Trans. Am. Electrochem. Soc.*, 17, 229-234. Coolidge, *Proc. Am. Inst. E. E.*, 29, Part II, 961-965.

³ Coolidge, *J. Ind. Eng. Chem.*, 4, 2 (1912).