Structural and Chemical Similarities of Hydrogen Peroxide, Hydroxylamine and Hydrazine

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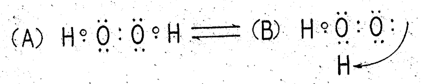
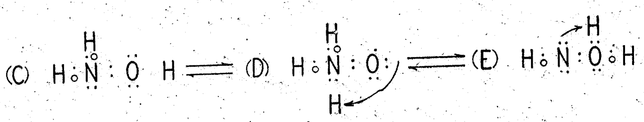
A comparison of the nitrogen and the oxygen systems of compounds leads to the conclusion that hydrogen peroxide, hydroxylamine, and hydrazine are related structurally, since the -OH and -NH_2 radicals are isosteric. Chemically, each of these compounds behaves both as an oxidizing and a reducing agent; hydrogen peroxide, primarily as an oxidizing agent, while hydroxylamine and hydrazine find application chiefly as reducing agents.

Hydrogen peroxide tends to behave as a strong oxidizing agent in neutral and alkaline solution, but in acid solution does exhibit the properties of a reducing agent. This observation is explained readily by application of the Bronsted concept, since it may be assumed that removal or wandering of a proton must take place before the hydrogen peroxide molecule can release oxygen readily. Two tautomeric structural formulas have been proposed.



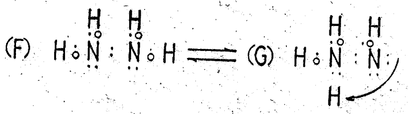
The compound with structure (B) should act more readily as an oxidizing agent since the second oxygen atom is held by a coordinate link. In this state it may be represented by the formula: $H_2O \rightarrow O$. The molecule (B) would form only if the proton were permitted to wander, a tendency which would be suppressed in a solution containing acid. In aqueous solution hydrogen peroxide is a very weak acid and practically any base will remove the proton with formation of the OOH^- ion, which is evidently a strong oxidizing agent.

In the case of hydroxylamine several structures are possible:



Of these (D) is more probable than (E) as nitrogen has a higher proton affinity than oxygen. However, (E) is not necessarily ruled out. Structure (D) is known in the amine oxides, where the oxygen is held by a coordinate covalency: $R_3N \rightarrow O$. The ability of hydroxylamine to act as an oxidizing agent in water solution is not great, due to the fact that it is more basic than water. There is little or no tendency on the part of water to remove a proton from the hydroxylamine molecule to give an ONH_2^- ion. The reverse tendency is so great that solutions of NH_2OH in water contain an appreciable concentration of $NH_2OH \cdot H^+$ ions. A much stronger base than water would be required to remove the proton, or even to permit proton migration in the molecule to give the tautomeric amine-oxide structure. Hence, hydroxylamine acts primarily as a reducing agent in aqueous solution, since it exists overwhelmingly in the molecular form depicted by structure (C).

In the case of hydrazine, two forms are possible:



Theoretical considerations indicate that N_2H_4 may exist in the ammonium imide $(NH_3 \rightarrow NH)$ (G) form in the vapor state. That this tautomer (G) is capable of existing in any quantity in aqueous solution is highly improbable, since the hydrazine molecule is a strong base and may even add two protons, as in the formation of the dihydrochloride. Hence, in aqueous solution an exceptionally strong base would be required to effect the proton removal or migration necessary to allow hydrazine to act as an oxidizing agent.

There thus appears to be a qualitative relationship between the pH of the solution and the ability of these compounds to act as oxidizing or reducing agents. To act as oxidizing agents proton migration, or proton removal is necessary. As the basicity of the molecules increases in the order $H_2O_2 < NH_2OH < N_2H_4$ the east with which proton removal or migration is effected decreases correspondingly. While these considerations define the general behavior of these three related compounds, it should be pointed out that the redox equilibrium is a relative one and exceptions may occur depending upon the oxidizing or reducing strength of the other reactant.

Application of the Bronsted concept suggests that both hydroxylamine and hydrazine may act more effectively as delectronators (augmenting or oxidizing agents) in more basic solvents such as ammonia and the amines; whereas all three compounds will presumably act only as reducing agents in acid solvents such as glacial acetic acid. Coexistence of both tautomers may in turn be expected in amphiprotic or aprotic non-aqueous solvents.