Aqueous Active Nitrogen

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ALTHOUGH the high chemical reactivity of active nitrogen was first reported in 1911[1] and has been the subject of hundreds of published Papers,[2] investigation of the reactions of this reagent in aqueous solution has been almost completely neglected; the literature includes only one fragmentary study.[3] We report initial results which demonstrate that aqueous active nitrogen is a versatile reagent.

Experiments employed equipment, procedures, and nitrogen which have been described elsewhere[4] and which included activation of the nitrogen by glow discharge supported by 2450 Mc./sec. microwaves. The gas stream was introduced 50—90 cm. downstream from the discharge, a few cm. below the surface of the chilled (0—10°c) magnetically stirred liquid. That reaction was due to active nitrogen rather than to adventitious oxygen, ions, or photochemical effects originating in the discharge emission was determined by experiments in which the nitrogen was not passed through the discharge, argon was used in place of nitrogen, with and without the discharge, and geometrical parameters were varied. Spectral data were obtained with a Cary model 14 spectrophotometer.

The following transformations have been identified by the indicated criteria: $Fe^{II} \rightarrow Fe^{III}$ in $0{\cdot}8$N-H_2SO_4, identified by appearance of the absorption of Fe^{III} at 304 mμ; $Fe^{III} \rightarrow Fe^{II}$ in $0{\cdot}8$N-H_2SO_4, identified by absorption at 512 mμ and a pH of 4 of the 1,10-phenanthroline complex; $I^- \rightarrow I_3^-$ in netural solution, identified by the absorption of the product at 287 mμ; $Ce^{IV} \rightarrow Ce^{III}$ in 1N-H_2SO_4, identified by diminution of absorption at 320 mμ; MnO_4^- is reduced in $0{\cdot}05$N-H_2SO_4, identified by diminution of absorption at 525 mμ; fumaric acid is converted with similar efficiency in $0{\cdot}8$N-H_2SO_4 and in 10^{-3}M-solution in neutral water (pH approx. 3) into as yet unknown products shown by diminution of absorption at 208 mμ. The yield of oxidation of 10^{-2}M-Fe^{II} in acid solution was found to be linear with time of passage of active nitrogen up to about 2% conversion (as far as was determined). A negligible induction period was observed. According to the older literature active nitrogen does not react with gaseous[5] or liquid[3] water or with aqueous sulphuric acid.[3] We have, however, found that a substance which was determined[6] as H_2O_2 is formed on reaction with $0{\cdot}8$N-H_2SO_4 in yields comparable to those observed in the oxidation of Fe^{II}. Reaction with neutral water provides barely detectable amounts of product determinable[6] as H_2O_2, less than one tenth the yields observed in the oxidation of I^- under essentially identical conditions. It can be concluded tentatively that there is direct reaction with iodide and possibly with fumaric acid in neutral solution but evaluation of the relative roles of direct as against indirect action in acid solutions awaits work now in progress.

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