CCXLVIII.—*The Decomposition of Nitrous Acid in Aqueous Solution.*

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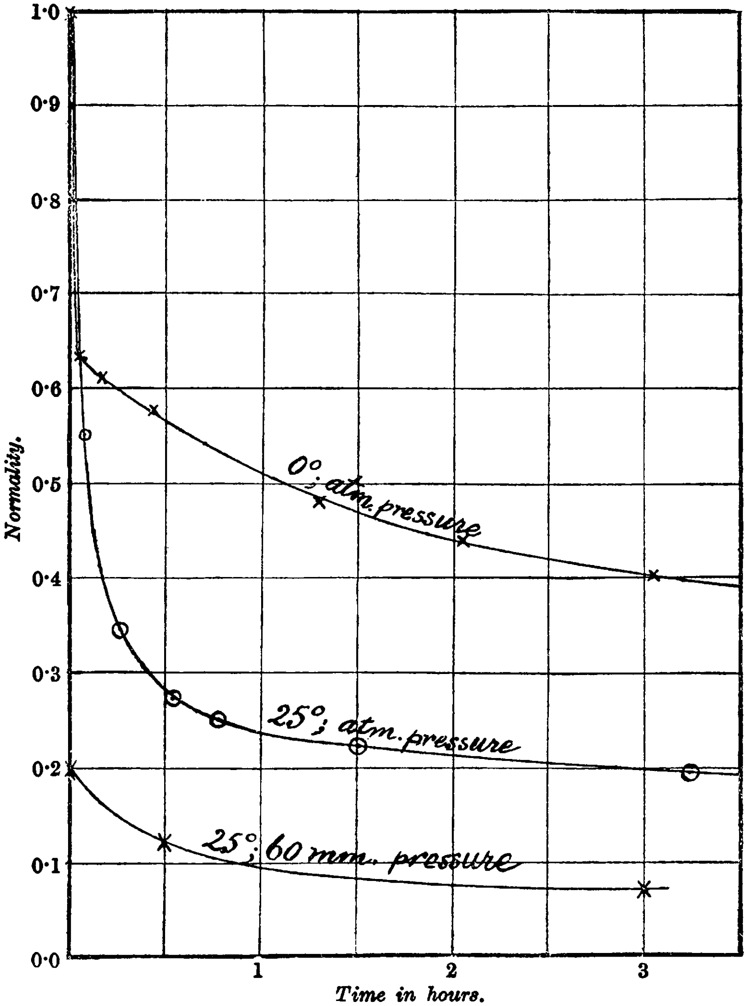
The decomposition of nitrous acid in aqueous solution is a complex phenomenon. The more important facts already known can be summarised as follows: (1) In contact with air, there is a certain amount of oxidation; if an inert gas replaces air, the reaction $3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$ takes place (Montemartini, *Atti R. Accad. Lincei*, Rendiconti, 1890, **6**, ii, 263). (2) The rate of decomposition follows approximately a unimolecular law, in contact either with air (Ray, Dey, and Ghosh, J., 1917, **111**, 413) or with carbon dioxide (Montemartini, *loc. cit.*). (3) The rate is reduced by adding nitric oxide to the gas above the solution, and is slower the greater the pressure of nitric oxide (Montemartini, *loc. cit.*; Klemenc and Pollak, *Z. physikal. Chem.*, 1922, **101**, 150). (4) The rate is much increased by bubbling an inert gas through the solution (Knox and Reid, *J. Soc. Chem. Ind.*, 1919, **38**, 105T) and apparently reaches no limit as the speed of bubbling is increased (Klemenc and Pollak, *loc. cit.*). (5) The reaction is reversible (Veley, *Chem. News*, 1892, **66**, 175), but the reverse reaction proceeds extremely slowly with dilute solutions of nitric acid (Saposhnikov, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 375; 1901, **33**, 306).

In an attempt to find conditions under which solutions of nitrous acid would be sufficiently stable for investigation of its reactions, the effect of reducing the area of surface of the solution in contact with the gas phase was tried. This can be done most simply by floating a layer of an immiscible liquid on the top of the solution; most liquids which might be used, however, such as benzene or ligroin, dissolve nitrogen trioxide from fairly strong solutions of nitrous acid, but the solubility of the trioxide is smaller in the mixture of higher paraffins sold as " medicinal paraffin," and this liquid has the added advantage that its high viscosity makes it possible to stir the lower aqueous layer without breaking up the paraffin layer.

Dilute solutions of nitrous acid prepared beneath a layer of this paraffin from a solution of pure barium nitrite (Witt and Ludwig, *Ber.*, 1903, **36**, 4384) and the equivalent of dilute sulphuric acid, and thus containing barium sulphate in suspension, are considerably more stable than similar solutions under nitrogen and very much more stable than those in contact with air. For example, equal volumes of a solution in identical vessels were kept at 25°, the one under paraffin and the other in contact with air; after 3 hours, the first showed 5% decomposition and the second 53%. Quite dilute solutions, *i.e.*, 0·1*N* and less, could be kept at 0° for 5 hours without the decomposition exceeding 4%. The solutions were stirred during these experiments by a small stirrer passing through the paraffin, but not at such a rate as to draw gas bubbles into the solution; the concentration of acid was determined by Veley's method (*Proc. Roy. Soc.*, 1893, *A*, **52**, 28).

When stronger solutions were investigated under paraffin, it was found that critical concentrations existed above which the rate of decomposition was very rapid and below which it was much slower. The critical concentration depends on the temperature, being higher the lower the temperature, and on the pressure of air above the paraffin, increasing with the pressure. Fig. 1 shows the rate of decomposition in two solutions, originally of *N* concentration, at 25° and at 0°, and also the effect at 25° of reducing to 60 mm. the pressure above a 0·2*N*-solution, *i.e.*, one which at atmospheric pressure would decompose but slowly. Ray, Dey, and Ghosh (*loc. cit.*) noted this critical phenomenon and could not obtain a solution stronger than 0·185*N* which did not evolve nitric oxide rapidly when at 0° and in contact with air.

FIG. 1.



The velocity of the "slow" reaction at 25° was measured, and the results of any one experiment roughly agreed with the unimolecular law, although the velocity coefficient slowly decreased as the reaction proceeded; but the reaction is in no sense truly unimolecular—even well below the critical concentration the value of the velocity coefficient depends on the initial concentration and on the shape of the vessel in which the solution is kept, and thus has no absolute significance.

The velocity of the reaction under paraffin is also influenced by the presence of other substances in the solution; in $5N$-sulphuric acid it is markedly smaller, and in $7N$-acid smaller still. This result disagrees with that found by Klemenc and Pollak, who used solutions through which nitrogen was bubbling, but agrees with that of Knox and Reid (*loc. cit.*), whose solutions were in contact with air. The velocity is also much reduced by the presence of sodium sulphate, which at $0{\cdot}65M$ concentration has an effect equivalent to $5N$-sulphuric acid.

The presence of barium sulphate in suspension during these experiments had no appreciable influence on the stability of the acid, since similar experiments were carried out using nitrous acid prepared from pure sodium nitrite (Divers, J., 1899, **75**, 80) and sulphuric acid, and the rates of decomposition were those to be expected from the previous experiments, account being taken of the effect of the sodium sulphate.

These results show that, by using paraffin and sodium sulphate, solutions of nitrous acid the strengths of which do not exceed certain maximum values ($0{\cdot}4N$ at 0° and $0{\cdot}2N$ at 25°, at atmospheric pressure) can be conveniently stabilised to a considerable extent. The complicated character of the decomposition has, however, not yet been satisfactorily explained. Klemenc and Pollak advance the improbable hypothesis that nitrous acid spontaneously breaks up into nitric oxide and the hydroxyl radical, and attribute its existence in solution to mutual action between molecules of the acid and of the solvent; they suggest that the rate of decomposition depends upon the rate of escape of nitric oxide from the solution. This, although accounting for the sensitiveness of a solution to its method of treatment, scarcely accounts for the sudden change in rate of decomposition shown in the figure.

The fact that the reaction is reversible does not come into play, because of the extremely slow rate of the reverse reaction at the dilutions investigated [see (5), p. 1924]. The critical phenomenon and its dependence on temperature and pressure must arise from the existence of some kind of equilibrium in which one of the substances involved is a gas of limited solubility in water; this equilibrium must be established with great rapidity to account for the observations of Klemenc and Pollak [(4), p. 1924].

The view advanced here is that in a solution of nitrous acid the equilibrium $2HNO_2 \rightleftharpoons N_2O_3 + H_2O$ is set up, and that the complicated nature of the decomposition arises from the behaviour of the anhydride; that this latter exists in solution is supported by the observations of Saposhnikov (*loc. cit.*) on the ease with which organic solvents will dissolve it from solutions of the acid. It is not the anhydride itself which escapes as gas from the solution, for, if this were so, the solution would contain eventually less nitric acid than the quantity corresponding to the equation of decomposition [(1), p. 1923], and experiment showed that in every case under paraffin the theoretical amount of nitric acid remained. If, however, the further equilibrium $N_2O_3 \rightleftharpoons NO + NO_2$ tends to be set up in solution, the facts receive an intelligible explanation. In a completely stable solution, the concentration of water being assumed to be constant, the function $[NO][NO_2]/[HNO_2]^2$ would have a fixed value at any one temperature; but the concentration of nitric oxide cannot exceed a certain limit because of its slight solubility, and the limit will depend on the pressure. The existence of the "rapid" decomposition is accounted for. No completely stable solution, however, can exist, even in a sealed bulb where the pressure of nitric oxide can become high (Montemartini, *loc. cit.*), since the nitrogen peroxide is continually hydrated and removed from the equilibrium. During the "slow" decomposition two factors come into play: the rate of escape of nitric oxide and the rate of hydration of the peroxide. The concentration of the latter is probably extremely small and thus the quantity hydrated in unit time is small, and consequently the second factor under normal conditions is of less importance. Any factor tending to facilitate the escape of the nitric oxide, such as increased area of contact with the gas phase, addition of sand or charcoal (Frémy, *Compt. rend.*, 1870, **70**, 63), or reduction of pressure, will increase the rate of decomposition. The escape of a gas from solution has a rapid stage, followed by a slower stage (Perman, J., 1895, **67**, 868; Bohr, *Ann. Physik*, 1899, **68**, 507; Findlay and King, J., 1913, **103**, 1170) which follows a logarithmic law, thus agreeing with the behaviour of nitrous acid. The effect of added substances in reducing the rate of decomposition can be compared with the result found by Bohr that carbon dioxide escapes less rapidly from a solution of sodium chloride than from pure water.

Work is in progress on various reactions of nitrous acid stabilised in the manner described in this paper.

Our thanks are due to Dr. W. H. Mills for his helpful criticism and to Messrs. Brunner Mond & Co., Ltd., for their generosity in making a grant which has covered part of the expenses of this work.

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[*Received, May 9th*, 1927.]