The Stability of Gaseous Nitrous Acid

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Summary From the observation of appreciable pressures of nitrous acid in the products of reaction of hydrogen peroxide with nitric oxide it is concluded that nitrous acid is much more stable at 550K than expected from previous work.

GASEOUS nitrous acid has been suggested as a minor product in many reactions involving nitrogen dioxide[1] but there is little information on its stability or on the reactions responsible for its removal. At room temperature the equilibrium

$$2\,HNO_2 \rightleftharpoons H_2O + NO + NO_2;\ \Delta H^0_{298} = 38\text{ kJ};\quad (K_p)_{298} = 8{\cdot}0 \times 10^5\text{ N m}^{-2}$$

is rapidly established.[2] At higher temperatures it is usually assumed that nitrous acid will not be formed in measurable quantity. We report evidence from a study[3] of the gas-phase reaction of hydrogen peroxide with nitric oxide that nitrous acid may be formed in concentrations far greater than the equilibrium value for the above reaction, and that it is more stable than expected from rate measurements at room temperature.[4]

The major products found from reaction of H_2O_2 and NO at 550K are water and NO_2, and there is little change in pressure during the reaction unless a large excess of NO is used. The pressure drop observed under such conditions indicates that some other product species must also be formed. As the occurrence of higher nitrogen oxides can be discounted on kinetic and thermodynamic grounds[3] the only likely species are nitric or nitrous acid. Indirect evidence that it is HNO_2 that is present can be obtained from the stoicheiometries for NO_2, HNO_2, and HNO_3 formation. Thus in an experiment at 550K using initial partial pressures of H_2O_2, NO, and N_2 of 0·89, 5·9, and 33·3 kN m^{-2} respectively the pressure decrease after 70 s reaction, corrected for thermal effects, was 0·30 kN m^{-2}, and the partial pressure of NO_2 was 0·33 kN m^{-2}. The stoicheiometries giving the greatest pressure decreases are,

$$H_2O_2 + NO \rightarrow H_2O + NO_2$$

$$H_2O_2 + 2NO \rightarrow 2HNO_2 \qquad \text{giving } \Delta P = \Delta(H_2O_2)$$

$$3H_2O_2 + 2NO \rightarrow 2HNO_3 + 2H_2O \text{ giving } \Delta P = \Delta(H_2O_2)/3.$$

It can be seen that the initial pressure of H_2O_2 is insufficient to account for the observed pressure drop and NO_2 formation if HNO_3 is the additional product, but is quite adequate if the pressure drop is due to HNO_2 formation. Other experiments with different initial reactant pressures from that quoted above require the same explanation.

Direct evidence for the presence of HNO_2 has been obtained from the u.v. absorption spectrum of the reaction products, recorded *in situ* using an Optica CF4 scanning monochromator. Using a reaction mixture of 0·27 kN m^{-2} of H_2O_2 with 53 kN m^{-2} of NO at 550K (half-life of mixture less than 10 s) the spectral region from 340 to 400 nm was scanned at 0·5 nm s^{-1}. The scan was started as soon as the reactants had been mixed. Comparison with a blank scan and with the spectrum for NO_2 showed small additional absorption peaks at 355·0, 368·5, and 384·5 nm. Nitric acid does not absorb in this region but nitrous acid has a diffuse absorption spectrum[5] with peaks at 341·9, 354·2, 368·3, and 384·2 nm. The correspondence of three of these peaks with those we observe confirms the presence of HNO_2.

The amount of HNO_2 formed and its rate of decomposition were estimated from an experiment where the spectral region 363·0 to 373·0 nm was scanned at 30 s intervals. The reaction mixture was 0·33 kN m^{-2} of H_2O_2 with 53 kN m^{-2} of NO, and the strongest absorption peak of HNO_2 at 368·5 nm was observed for 10 min. An example of the observed spectrum is shown in the Figure. From the absorption spectrum of HNO_2 at 298K given by King and Moule[5] the extinction coefficient of HNO_2 at 368 nm was estimated to lie between 50 and 150 l mol^{-1} cm^{-1}. Using a value of 100 l mol^{-1} cm^{-1} and correcting for the absorption due to NO_2 we calculate the maximum pressure of HNO_2 present in this experiment as 0·15 kN m^{-2} between 30 and 60 s, falling to less than 0·07 kN m^{-2} at 10 min. These figures are to be compared with a calculated equilibrium value of 0·006 kN m^{-2} under our experimental conditions and a predicted half-life of 25 s based on the room temperature data of Wayne and Yost.[4] Clearly the low temperature kinetic data cannot be applied in the temperature range we used, and nitrous acid must be treated as a species of moderate stability at these temperatures, due to its slow rate of decomposition. The rate of removal observed in the above experiment is not greatly faster than that of HNO_3 under similar conditions.[3,6]

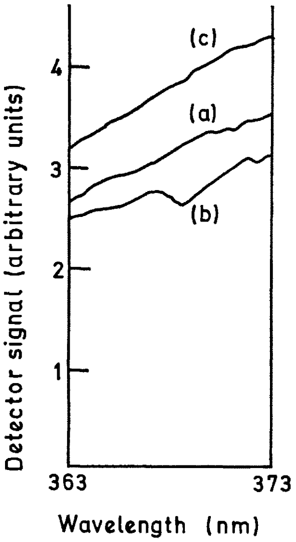

FIGURE. *Absorption spectra for* (a) 0·13 kN m^{-2} *nitrogen dioxide and* (b) *for reaction products after* 70 s. *Trace* (c) *shows the baseline obtained with an evacuated vessel.*

The mechanism of formation of HNO_2 in our system is thought[3] to be in the initiation and termination steps of a short chain reaction.

$$H_2O_2 + NO \rightarrow HNO_2 + OH$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2$$

$$HO_2 + NO \rightarrow NO_2 + OH$$

$$OH + NO + M \rightarrow HNO_2 + M$$

We do not have sufficient data to suggest a mechanism for the removal of HNO_2.

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[1] J. H. Thomas, *Oxidation and Combustion Rev.*, 1965, **1**, 137.
[2] P. G. Ashmore and B. J. Tyler, *J. Chem. Soc.*, 1961, 1017.
[3] P. L. Asquith, Ph.D. thesis, University of Manchester, 1969.
[4] L. G. Wayne and D. M. Yost, *J. Chem. Phys.*, 1951, **19**, 41.
[5] G. W. King and G. Moule, *Canad. J. Chem.*, 1962, **40**, 2057.
[6] H. S. Johnston, L. Foering, and J. R. White, *J. Amer. Chem. Soc.*, 1955. 77, 4208.