Catalytic Reduction of Nitrous Oxide with Nitrogentris(triphenylphosphine)cobalt Hydride

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As an extension of our study on the reactions of $H(N_2)Co(PPh_3)_3$ with H_2, C_2H_4, and CO_2,[1] we have studied its reaction with nitrous oxide. Nitrous oxide has been considered as very inert under mild conditions, but a recent communication reports its reactivity toward some transition-metal complexes.[2] Nitrous oxide is known as a competitive inhibitor of nitrogen fixation by biological systems, and a correlation has been found between the nitrogen fixing and the N_2O reducing activity of these systems.[3] We thought it interesting to study the reaction of nitrous oxide with the N_2–cobalt complex which can be regarded as a model of the nitrogen binding site in biological systems.

The reactions of nitrous oxide with $H_3Co(PPh_3)_3$ and

$H(N_2)Co(PPh_3)_3$ were carried out in hydrocarbon solvents both in the presence and absence of triphenylphosphine. The reaction of N_2O with $H(N_2)Co(PPh_3)_3$ in benzene at room temperature caused the rapid change of original red colour through yellowish green to pale blue and was accompanied by effervescence of the solution. The loss of the co-ordinated nitrogen from the complex was shown by the rapid disappearance of the $\nu(N_2)$ band[1a,b] at 2088 cm.$^{-1}$ in the i.r. spectrum.

When a similar reaction was carried out in the presence of triphenylphosphine, the catalytic oxidation of triphenylphosphine to triphenylphosphine oxide was observed.

In the reaction of nitrous oxide with $H_3Co(PPh_3)_3$[1a] for a short period in the presence of triphenylphosphine, the appearance of the $\nu(N_2)$ band at 2088 cm.$^{-1}$ as well as $\nu(PO)$ at 1200 cm.$^{-1}$ were observed in the i.r. spectrum. Mass spectrometric examination of the gas phase revealed the evolution of H_2 and N_2 from the solution.

These results may be interpreted as follows: nitrous oxide can expel nitrogen or hydrogen molecules from $H(N_2)Co(PPh_3)_3$ or $H_3Co(PPh_3)_3$ and an N_2O-co-ordinated intermediate may be formed. The co-ordinated N_2O may be split to N_2 and oxygen which attacks Ph_3P and oxidizes it to Ph_3PO. The formation of the N_2 complex by the reaction of $H_3Co(PPh_3)_3$ with N_2O suggests the recapture of the split-off N_2 by the cobalt complex. Thus, the system will catalytically reduce N_2O to N_2 and oxidize triphenylphosphine to triphenylphosphine oxide.

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