Hydrogen isocyanide (HNC) has been proposed as an important intermediate in oxidation of hydrogen cyanide (HCN) in combustion, but details of its chemistry are still in discussion. At higher temperatures, HCN and HNC equilibrate rapidly, and being more reactive than HCN, HNC offers a fast alternative route of oxidation for cyanides. However, in previous modeling, it has been required to omit the HNC subset partly or fully in the reaction mechanisms to obtain satisfactory predictions. In the present work, we re-examine the chemistry of HNC and its role in combustion nitrogen chemistry. The HNC + O₂ reaction is studied by ab initio methods and is shown to have a high barrier. Consequently, the omission of this reaction in recent modeling studies is justified. With the present knowledge of the HNC chemistry, including an accurate value of the heat of formation for HNC and improved rate constants for HNC + O₂ and HNC + OH, it is possible to reconcile the modeling issues and provide a satisfactory prediction of a wide range of experimental results on HCN oxidation. In the burned gases of fuel-rich flames, HCN and the CN radical are partially equilibrated and the sequence HCN → HNC → HNCO is the major consumption path for HCN. Under lean conditions, HNC is shown to be less important than indicated by the early work by Lin and co-workers, but it acts to accelerate HCN oxidation and promotes the formation of HNCO.