HCN-Synthesis from Methane and Ammonia: Mechanisms of Pt^+-Mediated C–N Coupling

M. Diefenbach, M. Brönstrup, M. Aschi, D. Schröder, and H. Schwarz

Institut für Chemie der Technischen Universität,
Straße des 17. Juni 135, D-10 623 Berlin, Germany.
email: `Helmut.Schwarz@www.chem.tu-berlin.de`

The Pt^+-mediated coupling of methane and ammonia has been studied both experimentally and computationally. This system serves as a model for the DEGUSSA process for the industrial production of the valuable feedstock hydrogen cyanide. Mass spectrometric studies demonstrate that C–N bond formation is catalysed efficiently by Pt^+. Details of the experimentally observed reaction channels have been explored computationally using the B3LYP hybrid DFT/HF functional. In the first reaction step, Pt^+ dehydrogenates CH_4 to yield $PtCH_2^+$; in contrast, dehydrogenation of ammonia by Pt^+ is endothermic and does not occur experimentally. Starting from $PtCH_2^+$ and NH_3, C–N bond formation, which constitutes the crucial step in making HCN from CH_4 and NH_3, is achieved via two independent pathways. The major pathway is found to be exothermic by 23 kcal mol^{-1} and yields neutral PtH and $CH_2NH_2^+$. The second pathway involves a dehydrogenation to yield the aminocarbene complex $PtC(H)NH_2^+$ ($\Delta_r H = -36$ kcal mol^{-1}); dehydrogenation of $PtC(H)NH_2^+$ to $PtCNH^+$ is exothermic with respect to $PtCH_2^+ + NH_3$ ($\Delta_r H = -8$ kcal mol^{-1}), but hindered by kinetic barriers. A comparison of Pt^+ with other transition metal cations (Fe^+, Co^+, Rh^+, W^+, Os^+, Ir^+, and Au^+) shows that Pt^+ is unique with respect to its ability to activate one equivalent of CH_4 *and* to mediate C–N-bond coupling.