

Hydrogen, Ammonia-borane and Carbon Dioxide Activation by Phosphinoboranes

Mariano Mendez, David A. Dixon

The activation of CO₂ and further reduction to yield hydrogenated products such as methanol can be achieved by synergy between a strong Lewis acid (high capacity to accept electrons) and a strong Lewis base (high capacity to donate electrons) with the restriction that a steric effect due to their substituents precludes an optimal match for the formation of the adduct Lewis acid/Lewis base. Such frustrated Lewis pairs (FLP) containing main group elements meet these requirements and the scope of activation of inert molecules is opened beyond the use of compounds containing transition metals, with applications to hydrogen storage and the sequestration and further transformation of CO₂. Three different chemistries for the activation of H₂, H₃NBH₃ and CO₂ as well as their interaction between them were studied for Y = R₂P and X = R₂B. The global reaction between the four membered cyclic compound c-X₂Y₂ (1) in the presence of H₂/CO₂ to yield (OH)XYMe and water as a product is an exothermic reaction. The hydrogenation of the CO₂ through the activation of H₃NBH₃ is also studied. Global and local reactivity descriptors derived from density functional theory (DFT) are used to rationalize the results of the different reactions paths that are predicted. The electron density response to a change in the number of electrons, Fukui function, is compared to the frozen core approximation given by the frontier molecular orbitals. The calculations were performed with the B97x exchange-correlation functional and the DZVP2 basis set. The solvent is modelled as a continuum using self-consistent reaction field approaches with the dielectric constant of dichloromethane. This work was supported by the Department of Energy through Los Alamos National Laboratory.