

Gas Phase Organometallic Chemistry: Alkane C-H and C-C Bond Activation

Wenbin Lin

Literature Seminar

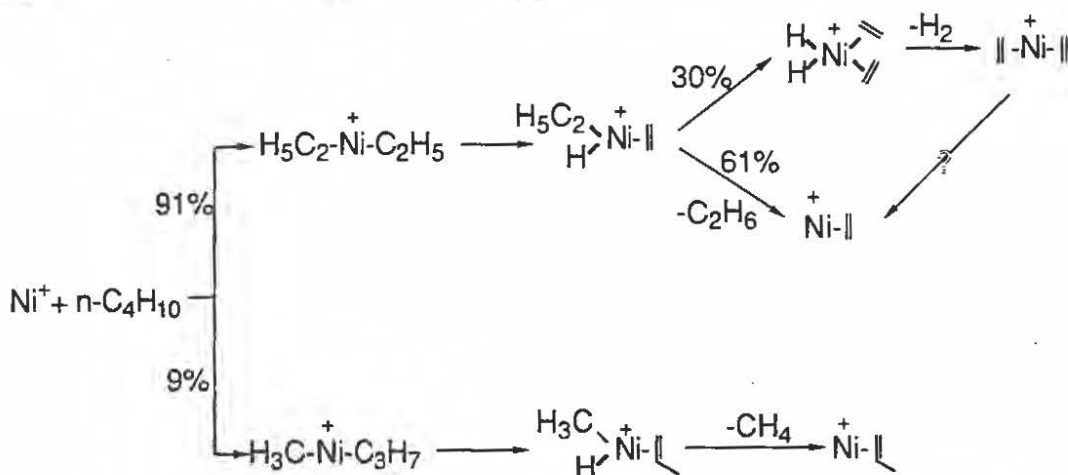
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The activation of alkanes by homogeneous transition metal complexes has been a very active area of interest in recent years [1]. The mechanistic and thermodynamic details of these reactions have been explored in some depth [2]. Gas phase organometallic chemistry offers an alternative chemical approach to the investigation of organometallic reactions in the absence of complicating factors such as solvent effects and ion pairing [3]. The activation of alkanes by transition metal ions in the gas phase has proven to be a rich and informative field of study [4].

In 1979, by using Ion Cyclotron Resonance mass spectrometry, Ridge found that the naked Fe^+ ion could not only break C-H but also C-C bonds in n-butane and isobutane [5]. Co^+ and Ni^+ were found to react in a similar way in a study utilizing Fourier Transform mass spectrometry. The activation of C-C bonds by M^+ ($\text{M} = \text{Fe}, \text{Co}, \text{and Ni}$) in the gas phase is of interest because activation of C-C bonds of hydrocarbons in solution is usually observed only if the C-C bond is highly strained or if aromatization occurs [6]. Reactions of Ni^+ with deuterium labeled alkanes showed that Ni^+ dehydrogenates n-butane exclusively in a 1,4-manner [7]:



More strikingly, Ni^+ completes this 1,4-dehydrogenation of linear alkanes via initial C-C bond cleavage followed by two β -H shifts and dihydrogen elimination. Molecule-ion reactions and Collision Induced Dissociation (CID) studies of four different $\text{Ni}(\text{C}_4\text{H}_8)^+$ isomers further confirmed the proposed bis(ethylene) structure, and a mechanism was proposed to account for the reaction of Ni^+ with n-butane [8]:



Fe^+ and Co^+ dehydrogenate alkanes by both a 1,4- and a 1,2-mechanism; the latter mechanism involves initial attack of the metal at an alkane C-H bond rather than a C-C bond. Fe^+ reacts in the 1,4-fashion 30% of the time, and in the 1,2-fashion 70% of the time; while for Co^+ , the percentages are 90% and 10% respectively [9]. Similar reactivity has been found for M^+ ($\text{M} = \text{Fe}, \text{Co}, \text{and Ni}$) towards larger alkanes: Co^+ and Ni^+ predominantly cleave C-C bonds of alkanes and preferentially insert into interior C-C bonds, while Fe^+ reacts with alkanes less selectively.

Armentrout found that the Ion Beam technique could be used to study the translational energy dependence of reactions of M^+ with alkanes. A variety of M^+ -L bond dissociation energies have been derived by studying the translational energy dependence of endothermic reactions [10]. The M-C bond strengths of M^+ -CH₃ cations were found to be about 6 kcal/mol higher than those of the hydride species M^+ -H in the gas phase; in contrast, the L_nM -H bond is much stronger than the L_nM -CH₃ bond in solution. These experimental values are in good agreement with theoretical values derived from Generalized Valence Bond Plus Configuration Interactions calculations [11]. The product distributions of reactions of M^+ with alkanes can be rationalized fairly successfully by using these thermochemical data, while Allison proposed that initial electrostatic interactions might control the reaction product distribution [12]. More elegant experiments were designed to probe the reactivities of different electronic states of transition metal ions, and for the reaction of M^+ with H₂, good agreement with theoretical calculations has been found [13].

Studies on other transition metal ions showed even more diverse and striking results: Ru⁺, Rh⁺, Pd⁺, Ti⁺, V⁺, Nb⁺, and Mo⁺ predominantly activate C-H bonds of alkanes in a 1,2-fashion leading to dehydrogenation [14]; Os⁺ and Ta⁺ are so reactive that they even dehydrogenate methane [15]; Sc⁺, Y⁺, La⁺, and Gd⁺ show both C-H and C-C activation, a unique 1,3-dehydrogenation, and formation of dialkyl complexes [16]. Interestingly, Cr⁺, Mn⁺, Cu⁺, Pr⁺, and Eu⁺ are unreactive towards alkanes [17]. Electronic state arguments have been used to rationalize the different reactivities of transition metal ions.

The effects of ligands on the reactivity of gas-phase metal ions have also been studied. For late first row metal ions, attachment of a ligand such as -CH₃, -CH₂, -H, and -Cp increases the preference for C-H insertion over C-C insertion [18]. In contrast, attachment of an alkene ligand to Nb⁺ or Ta⁺ increases the preference for C-C insertion [15b].

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