ACTIVATION OF ALIPHATIC C-H AND C-C BONDS

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ABSTRACT

Alkyl C-H bonds are generally resistant to attack by soluble transition metal complexes. Nevertheless, alkane reactions are catalyzed by [PtCl_4]^{2-} and activated methanes form C-H oxidative addition products with Fe^{0}(dmpe)_2 and [Ir(dmpe)_2]^+. The iridium system is especially interesting because it reacts with CH_3X compounds (X = CN, Ac, NO_2) even though it is inert to aryl C-H bonds which are often more reactive. The iridium complex brings about reaction of acetonitrile with carbon dioxide to form cyanoacetic acid derivatives.

Methylene complexes, analogous to those postulated as intermediates in H-D exchange in methane, have been isolated for niobium and tantalum. Even more reactive methylene complexes of titanium have been prepared as alkylaluminum adducts. The methylene titanium compounds react with vinyl and allyl C-H bonds in propylene and isobutylene:

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\begin{align*}
\text{CH}_3\text{CH}=&\text{CH}_2 + [\text{CH}_2] & \rightarrow & (\text{CH}_3)_2\text{C}=&\text{CH}_2 \\
(\text{CH}_3)_2\text{C}=&\text{CH}_2 + [\text{CH}_2] & \rightarrow & \text{CH}_3\text{CH}_2\text{C}=&\text{CH}_2 \\
& & & \text{CH}_3
\end{align*}
\]

The mechanisms of some of these reactions involve metalallocycles like those implicated in olefin metathesis. Similar intermediates may also occur in heterogeneous catalytic reactions such as alkane isomerization. These relations between homogeneous and heterogeneous catalysis are being explored with alkane and cycloalkane substrates.

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The isomerization and hydrogenolysis reactions collectively known as catalytic reforming are among the largest processes in a modern industrial economy. The sophisticated catalysts that make and break the C-H and C-C bonds of alkanes in these processes are largely oxide-supported platinum metals. Homogeneous catalysts play no role in these operations, both because heterogeneous catalysts have engineering advantages and because the ability to manipulate alkanes with soluble catalysts is scarcely in its infancy.

The chemistry that I shall discuss simply begins to lay the groundwork for development of soluble catalysts for alkane reactions. I am not optimistic that soluble catalysts have any future in refining of petroleum, but I hope that our studies may contribute in two respects. One is the development of more selective catalysts for transformation of hydrocarbons to high value organic compounds (rather than fuels). The other is to contribute to our understanding of the chemical processes that occur on the surfaces of heterogeneous catalysts.

Despite the contributions of new instrumentation to understanding the structures of metallic catalysts, our knowledge of the reactions which occur on the surface of reforming catalysts is very limited. Study of soluble catalysts can contribute to understanding detailed surface processes. Despite the limitations of surface vs. solution analogies, solution chemistry can define possible reaction courses.

The surface-solution analogy leads to an attractive mechanistic description of alkane isomerization. This reaction does not occur with known soluble catalysts, but many of the individual steps are known in transition metal organic chemistry. Apparently, soluble mononuclear metal complexes lack sufficient reaction sites to effect all the necessary steps simultaneously. A metal surface, on the other hand, can supply a large number of sites on adjacent metal atoms.

These points are illustrated in the isomerization of neopentane to 2-methylbutane. This reaction is unknown with soluble catalysts and occurs only with highly active metal catalysts such as a well-dispersed platinum on alumina. The generally accepted mechanism [1] is illustrated in Figure 1 in which the steps are written in the semantics of homogeneous catalysis. The first and perhaps most difficult step is C-H activation. In this instance, it represents cleavage of a methyl C-H bond and attachment of the resulting hydrogen and neopentyl ligands to adjacent surface platinum atoms. In organometallic chemistry, the process would be termed oxidative addition and the two ligands would attach to the same metal atom. In doing so, they would probably fill the only free coordination