100 times lower than the experimental data. This enigma extends from the laboratory to interstellar space: Because the recombination process is the dominant destruction mechanism for H_3^+ in diffuse clouds, the uncertainty in the electron recombination rate translates to a large uncertainty in the size of the diffuse clouds where H_3^+ has been measured with the use of its infrared spectrum (*2*). The importance of reconciling theory and experiment and of reducing the present uncertainty in the value of the H_3^+ electron recombination rate cannot be overemphasized.

H_3^+ also plays an important role in planetary science. Ever since it was first spectroscopically detected in emission from Jupiter's aurora (*8*), the ion has served as a useful remote probe of Jupiter's upper atmosphere (*9*). Because the strongest spectral lines of H_3^+ are in a spectral region where few other molecules have lines, H_3^+ can be observed on Jupiter with only an infrared camera with a narrow filter. With this technique, Jupiter's aurora can be imaged with ground-based telescopes, and the images can be used to create and evaluate detailed models of the jovian magnetosphere and the interaction between Jupiter and its moon Io. As the only hydrogenic species in this environment with efficient spontaneous emission, H_3^+ is the dominant coolant of the jovian ionosphere. During the meeting, it was proposed that H_3^+ may also play a major role in the energy budget and the overall dynamics of the jovian magnetosphere. It was even suggested that H_3^+ emission might be detectable from Jupiter-like planets orbiting other stars such as τ Boötis.

In interstellar space, H_3^+ forms the basis for an extensive network of ion-molecule reactions that are responsible for the creation of most of the molecules observed in interstellar space (*10*). This scheme of interstellar chemistry was directly confirmed when the infrared spectrum of H_3^+ was observed in molecular clouds (*1*). Thanks to improvements in astronomical spectrometers, the detection of interstellar H_3^+ is now almost routine, and observations of H_3^+ can now be combined with those of other important molecules such as H_2 and CO to characterize the physical and chemical conditions in interstellar clouds. The observations of dense molecular clouds are generally in accord with theoretical models of interstellar chemistry.

The present understanding of the chemistry of diffuse clouds is, in contrast, quite primitive. In addition to the long-standing enigmas of the high abundance of CH^+ and the ubiquitous but unexplained diffuse interstellar bands, the H_3^+ ion presents a new mystery. Given the current experimental values of the H_3^+ electron recombination rate, the observations (*2*) suggest that H_3^+ in diffuse clouds extends for unreasonably long distances (over a thousand light years).

The physics and chemistry of H_3^+, combined with the low density and temperature of interstellar space, lead to interesting phenomena such as extraordinary deuterium fractionation, bistability of chemical models, and radiative thermalization through forbidden rotational transitions. The discussions between astronomers, physicists, and chemists about the various processes in which H_3^+ plays the pivotal role were inspiring, but, as expected, there are still more questions than answers. Hopefully, more astronomical observations and laboratory and theoretical studies will provide solutions to these problems in the coming years.

References and Notes

1. T. R. Geballe and T. Oka, *Nature* **384**, 334 (1996).
2. B. J. McCall, T. R. Geballe, K. H. Hinkle, T. Oka, *Science* **279**, 1910 (1998).
3. "Astronomy, Physics, and Chemistry of H_3^+," Royal Society Discussion Meeting, Royal Society, London, UK, 9 to 10 February 2000. See also h3plus.uchicago.edu. Proceedings will be published in the *Philos. Trans. R. Soc. London, Ser. A.*
4. J. J. Thomson, *Philos. Mag.* **21**, 225 (1911).
5. T. Oka, *Phys. Rev. Lett.* **45**, 531 (1980).
6. I. R. McNab, *Adv. Chem. Phys.* **LXXXIX**, 1 (1995).
7. M. Larsson, *Annu. Rev. Phys. Chem.* **48**, 151 (1997).
8. L. Trafton, D. F. Lester, K. L. Thompson, *Astrophys. J.* **343**, L73 (1989); P. Drossart *et al.*, *Nature* **340**, 539 (1989).
9. J. E. P. Connerney, R. Baron, T. Satoh, T. Owen, *Science* **262**, 1035 (1993).
10. E. Herbst and W. Klemperer, *Astrophys. J.* **185**, 505 (1973); W. D. Watson, *Astrophys. J.* **183**, L17 (1973).

PERSPECTIVES: HYDROCARBON CHEMISTRY

Conquering the Carbon-Hydrogen Bond

William D. Jones

Considering the vast quantities of liquid and gaseous hydrocarbons brought annually from beneath Earth's surface, it is a pity that the vast majority of these precious raw materials are burned as simple fuels for heating and transportation. Only a modest portion of these hydrocarbons—alkanes and aromatics—are converted into large-scale chemical intermediates for use in the chemical industry. But the controlled conversion of these hydrocarbons into the desired products remains a challenge. In this issue, Jia *et al.* on page 1992 (*1*) and Chen *et al.* on page 1995 (*2*) report important advances in the catalytic conversion of aromatic (*1*) and aliphatic (*2*) hydrocarbons into useful, reactive products.

Enhanced online at www.sciencemag.org/cgi/content/full/287/5460/1942

The reactions of saturated alkanes themselves are limited to partial oxidations, such as the conversion of butane and oxygen into acetic acid. Saturated alkanes (C_nH_{2n+2}) may be transformed into olefins (C_nH_{2n}) by way of a high-temperature process called cracking. The unsaturated olefins easily react with both electron-deficient reagents (electrophiles) and electron-rich reagents (nucleophiles). Similarly, aromatics, with their π electron systems, undergo a variety of reactions with Lewis or Bronsted acids to give substituted derivatives. The resulting derivatized hydrocarbons can be used to produce more desirable, value-added materials.

Many of the industrial processes used to derivatize hydrocarbons are based on heterogeneous catalysts. Homogeneous transition metal complexes have long been believed to also be capable of catalyzing these processes. Already in 1970, the strong C–H bonds of aromatics were found to undergo addition to metal complexes, followed by conversion to a product with a more reactive functional group (*3*). Similar addition reactions of alkanes to transition metal complexes (*4*, *5*) offered the hope of facile, selective conversion of the abundant alkanes into higher value products. These complexes typically contained electron-donating ligands and metals in low formal oxidation states. The hydrocarbon is effectively "reduced" upon cleavage of the C–H bond, whereas the metal is "oxidized," a process commonly referred to as "oxidative addition."

Despite this early progress in C–H activation, little progress toward catalytic hydrocarbon functionalization was not made until Waltz and Hartwig showed that linear alkanes could be reacted with a tungsten-borane complex ($L_nW\text{-}BR_2$) in a photochemical reaction to give a boron functionalized alkane ($R'\text{-}BR_2$) (*6*). The alkylboron products can be converted into a wide variety of derivatives with well-established properties. With a related rhenium complex,

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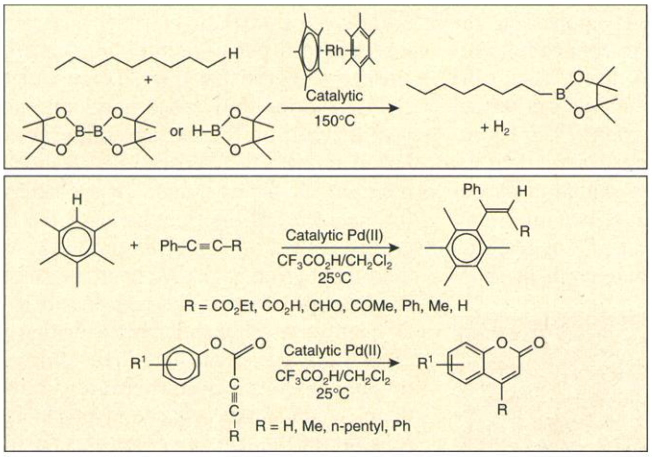
linear alkylborane products could be produced catalytically from alkanes and diboron reagents ($R_2B\text{-}BR_2$), but once again, light was required to drive the reaction (*7*). Chen *et al.* (*2*) now report a transition metal catalyst that can accomplish this same transformation at 150°C without the need for photochemical activation. This report represents a major advance in the ability to perform selective transformations of alkanes, as only terminal activation products are seen.



Catalytic functionalization of hydrocarbon C–H bonds. Both aliphatic and aromatic C–H bonds can be functionalized with the use of transition metal compounds. The alkylboron products (**top**) can easily be converted into a variety of derivatives, and the aromatic products (**bottom**) form in high regioselectivity and stereoselectivity.

The key to the reaction is the use of the catalyst ($(\eta^5\text{-}C_5Me_5)Rh(\eta^4\text{-}C_6Me_6)$). This species is believed to lose the hexamethylbenzene ligand under the reaction conditions and form the intermediate ($(\eta^5\text{-}C_5Me_5)RhH_2(Bpin)_2$). It is this intermediate that is believed to be responsible for the reaction with alkane to give H_2 and the organoborane product (see the figure). The catalytic reaction is characterized by high yields (80 to 90%) and high conversions (100%) of the diborane reagent, with low catalyst loadings (0.5 to 5%). The hydrocarbon substrate serves as the solvent, and both arenes and ethers appear to react in a similar manner. Exclusive selectivity is obtained for the straight-chain alkyl-borane products. The only other comparable metal-catalyzed chemistry of hydrocarbons that has been reported is the catalytic dehydrogenation of linear alkanes to alkenes and hydrogen, but selectivity for terminal alkenes has been a problem in this chemistry (*8*, *9*).

Jia *et al.* (*1*) present another remarkable demonstration of hydrocarbon functionalization in the form of the addition of a two-carbon unit from an acetylene to an aromatic ring. They have found that the simple Lewis acid palladium(II)acetate in trifluoroacetic acid/dichloromethane solution serves to catalyze the facile insertion of electron-deficient acetylenes into the C–H bonds of electron-rich aromatics (see the figure). Catalyst loadings of only 1 to 5% are required, and the reactions proceed at ambient temperatures to give selectively the trans-insertion products. An intramolecular version of the acetylene insertion reaction leads to the formation of bicyclic coumarins in good yield (70 to 90%). The study builds on the work by Sen with acidic solutions of Pd(II) for alkane functionalization (*10*) and shows vast improvement over any known alkyne/C–H insertion reactions (*11*). It provides many strong examples of how reactive small molecules such as alkynes can be incorporated into C–H cleavage reactions to generate products with a high degree of functional complexity.

The two reports described here extend hydrocarbon functionalization by homogeneous transition metal complexes to include facile thermal reactions with substrates that introduce reactive groups in high yields and selectivities. The work will stimulate others to find even more useful hydrocarbon functionalization schemes, with strong potential for industrial applications.

References

1. C. Jia *et al.*, *Science* **287**, 1992 (2000).
2. H. Chen, S. Schlecht, T. C. Semple, J. F. Hartwig, *Science* **287**, 1995 (2000).
3. G. W. Parshall, *Acc. Chem. Res.* **3**, 139 (1970).
4. With iridium: A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.* **105**, 3929 (1983).
5. With rhodium: W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.* **106**, 1650 (1984).
6. K. Waltz and J. F. Hartwig, *Science* **277**, 211 (1997).
7. H. Chen and J. F. Hartwig, *Angew. Chem. Int. Ed. Engl.* **38**, 3391 (1999).
8. F. Liu and A. S. Goldman, *Chem. Commun.* **1999**, 655 (1999).
9. C. M. Jensen, *Chem. Commun.* **1999**, 2443 (1999).
10. A. Sen, in *Activation of Unreactive Bonds and Organic Synthesis*, S. Murai, Ed. (Springer-Verlag, Berlin, 1999), chap. 4, pp. 81–96.
11. F. Kakiuchi and S. Murai, in *Activation of Unreactive Bonds and Organic Synthesis*, S. Murai, Ed. (Springer-Verlag, Berlin, 1999), chap. 3, pp. 56–58.

PERSPECTIVES: NEUROSCIENCE

Strengthening Visual Connections

Max Cynader

It has long been known that the environment in which the mammalian cerebral cortex finds itself early in postnatal life has the potential to alter its structure, function, and its connections with other parts of the brain. The strongest evidence in support of experience-dependent modification of brain circuitry during a well-defined critical period of postnatal development comes from studies of vision. The Nobel Prize-winning work of Hubel and Weisel in the 1960s (*1*) established that preventing one eye of a kitten from seeing during the first 3 to 6 weeks of life resulted in a series of anatomical and functional changes throughout the visual pathways of the brain. The eye that was not used developed a markedly reduced visual capacity relative to the other eye. Rather than being a simple consequence of disuse, this appears to be the result of competition between the two eyes because when both eyes are covered the degree of cortical disconnection is not as great as when one eye is covered. Since the 1960s, we have sought to understand how and where in the brain this competition between the two eyes takes place. A report by Trachtenberg *et al.* (*2*) on page 2029 of this issue, presents new and surprising evidence that the primary location of binocular competition is not in granular layer IV of the visual cortex as originally thought but rather is located in the extragranular layers above and below it.

The cerebral cortex has six layers that are all interconnected, each layer having its own set of connections and a specific function. Layer IV is the major input layer of the cortex, receiving the bulk of neuronal projections from the lateral geniculate nucleus of the thalamus. The other five layers are referred to as the extragranular layers. Layer V sends connections to downstream output pathways and layer VI (which has a strong connection to layer IV) is an important feedback center, sending outputs back to structures from which cortical inputs have arisen.

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