NEWS

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Amidation of Light Alkanes

- High-end Derivatives directly from Natural Gas

Methane and higher alkane analogues constitute Natural gas, a by-product from oil well. If not converted to fuel, these gases are released to the atmosphere as such and are wasted. A path-breaking technology has been developed to convert these alkanes into useful chemical intermediates.

The carbon–hydrogen bonds in alkanes, particularly those at the terminal carbon having 3 hydrogen atoms, are very hard to “crack” if you want to replace the hydrogen atoms with other atoms. Methane (CH4) and ethane (CH3CH3) are made up, exclusively, of such tightly bound hydrogen atoms. In the journal Angewandte Chemie, a team of researchers has now described how they break these bonds while forming new carbon–nitrogen bonds (amidation).

Although there has been some success in the functionalization of heavy hydrocarbons, even at the end positions, the particularly strong C–H bonds of light alkanes, especially methane, can hardly be split at all. The use of these primary components of natural gas as synthetic building blocks is especially desirable, as it would allow for the use of this often-wasted side-product of oil extraction.

A team comprised of scientists at Universidad de Huelva, Spain, and University of California, Berkeley, USA, has now successfully coupled amides (nitrogen-containing organic compounds) to light alkanes with loss of a hydrogen atom. The products of these dehydrogenative amidations are known as N-alkyl amides.

Propane, n-butane, and iso-butane gave similar results. In the light alkanes, reactivity correlates significantly more strongly with the dissociation energy of the C–H bonds than in higher alkanes.

And methane? Even the toughest candidate—amidation of methane has never previously been observed—could be coupled to the amide. Isotopic experiments were used to prove that methane reacts to form N-methylbenzamide.

If this technology is commercially exploited, it would be possible to synthesize complex organic molecules much more conveniently and directly from petroleum gases. This strategy could also provide more pathways for recycling plastic waste. The formation of carbon–nitrogen bonds is of particular interest because these also play an important role in natural products.

Reference:
Angew. Chemie, 2021, 133, 1-6
https://www.chemeurope.com/en/news/1172006