Hydrogen isotope equilibria in C1-C5 alkanes

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C1-C5 alkanes are the dominant constituents of natural gases, and are both an economically important and relatively clean fossil fuel energy resource. The stable isotope composition of these compounds can constrain their origins, transport and fates.[1][2] Isotopic equilibrium is a useful and common phenomenon; when observed it indicates reversible chemical processes, and can be used to constrain the temperature of the equilibrating system. Violation of equilibrium isotope distributions provides evidence for kinetically limited reactions. Defining the equilibrium isotope distributions among these alkanes is therefore a critical foundation for interpreting measured stable isotope compositions of natural gases.

Little prior experimental work has addressed the equilibrium hydrogen isotope effects in C1-C5 hydrocarbons. We present the first experimental effort to exchange and equililibrate hydrogen isotope structures (including intermolecular and intramolecular effects) of mixtures of these hydrocarbon molecules. We conducted laboratory experiments at 100°C and 200°C in the presense of metal catalysts. A GC-Pyrolysis-irMS is used for the analysis of compound-specific D/H ratios. We find that the catalytic activities of metal catalysts has the following order: $Rh/Al_2O_3 > Pd/C > Pd/Al_2O_3$, and that methane is much less susceptible to hydrogen isotope exchange than the higher alkanes. The hydrogen isotopic exchange of C2 to C5 molecules occurs on time scales of hours in the presence of Rh/Al_2O_3 at 100°C. Every intermolecular isotopic fractionation pair at that stage matches well with our theoretical prediction of equilibrium isotope effects, calculated with the B3LYP/aug-cc-pvtz basis set and Urey-Bigeleisen-Meyer theory. At thermodynamic equilibrium, the order of D-enrichment in these molecules is: *n*-pentane > *n*-butane > iso-pentane > propane > iso-butane > ethane > methane. We will also present results for the intramolecular isotopic equilibria (clumping and site-specific differences) in these compounds. [1] Whiticar (1999), *Chemical Geology* [2] Valentine and Reeburgh (2000), *Environmental microbiology*