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Isotopic analysis of atmospheric hydrocarbons from CH4 to H2, CO and CO2
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Methane is a key greenhouse gas and a main component of the atmospheric carbon cycle. The oxidation of methane is the starting point for a chain of reactions producing important radical and molecular species that control the oxidation capacity of the atmosphere. An overview of this chemistry is shown in Figure 1; as methane breaks down in the atmosphere it is converted into trace gases such as CO, CO2, H2 via the stable intermediate formaldehyde, HCHO.1,2 The sources of methane are of both natural and anthropogenic origin; wetlands, rice paddies, natural gas and livestock. The dominant sink is the tropospheric oxidation by OH. We know accurately how much methane there is in the atmosphere and where it goes, but there are significant uncertainties in its sources and this makes it difficult to predict its future concentration. While the atmospheric concentration of methane has doubled since preindustrial times, its rate of increase has slowed and stopped during the years 1984 to 2006, as shown in Figure 2.2 The reasons for this trend are not known with certainty, and recent data from NOAA show that during 2007 methane concentration has again increased, see inset in Figure 2. The IPCC report of 2007 concludes that an improved knowledge of trace gas budgets, including methane, will significantly reduce uncertainties in climate projections. Another motivation for investigating the reaction mechanism in Figure 1 is the potential use of molecular hydrogen as an energy carrier. High pressure H2 would leak into the atmosphere from the distribution system and act as an indirect greenhouse gas. This is since there will be a competition between methane and H2 for the oxidizing hydroxyl radicals, OH, inducing a perturbation to the natural chain of reactions oxidizing methane.

Isotope effects are a tool for studying the steps in the oxidation of methane.1,3-10 The idea is to use isotopic mass balance, equating the isotopic signatures of trace gas sources (Si) and sinks (Li) with the atmospheric composition. Since the distribution of stable isotopes in samples from the atmosphere is known, establishing the isotopic signature of the photochemical loss processes in the laboratory constrains the sources of the gas. This method, called inverse analysis, has been applied to the global budgets of N2O, CH4, H2 and CO2, among others.9

We report the results of isotopic studies of several steps in the methane oxidation mechanism. These results link the isotopic composition of methane and molecular hydrogen in the atmosphere. Our results include the discovery of extreme deuterium enrichment in the formaldehyde produced in the reaction of CH2DO with O2, and extreme deuterium depletion in the photolysis of formaldehyde. Experimental studies has been conducted at several laboratories; the European Photoreactor Facility (EUPHORE) in Valencia, Spain, Ford Motor Company, Dearborn, Michigan, and Copenhagen Center of Atmospheric Research, University of Copenhagen, Denmark.

FIGURES

Simplified overview of the atmospheric photochemical oxidation linking methane to formaldehyde, molecular hydrogen and carbon monoxide. Stable molecules indicated with bold text.
Figure 2. Concentration of methane in the atmosphere from 1984 to 2006. The insert shows the latest data from NOAA.

References