# Organosulfur radical acceleration and D/H isotope exchange effects during petroleum decomposition

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The influence of chemical constituents other than hydrocarbons on the thermal decomposition of petroleum in reservoirs is not well understood. In this investigation, we examine the individual effects of organic sulfur (a putative accelerant [1]) and subcritical water (a potential retardant or accelerant) on the decomposition of a model heavy oil analog (phenyldodecane, PDD), using a confined pyrolysis approach in sealed gold capsules. Following Lewan [1], experiments were performed on liquid PDD and PDD-diethyldisulfide (DEDS, an organosulfur analog) mixtures with and without subcritical $H_2O$ or $D_2O$ as a minor fluid phase at 250–350°C (35 MPa). Remnant PDD and products were analyzed by gas chromatography-mass spectrometry (GC/MS), isotope-ratio MS, and comprehensive two-dimensional GC-ToF-MS.

Our observations indicate DEDS does not significantly accelerate anhydrous PDD decomposition relative to PDD in isolation at 350°C. Substantial acceleration (~5-fold), however, was observed at 250°C with DEDS present, along with expected PDD decomposition products (*e.g.* short-chain alkylbenzenes). Hydrous experiments at 350°C indicate a moderate retarding effect of water on PDD decomposition rates, with trace undecanone products forming only with DEDS present. DEDS decomposition products also differed in the presence of water, yielding $CO_2$ and $CH_4$ in addition to $H_2S$ and ethane, implying $H_2O$ acted as a source of H and O. In the absence of DEDS, $D_2O$ had a minimal effect on the D/H isotope ratio of PDD. Experiments with $D_2O$ and DEDS, however, resulted in extensive D incorporation into PDD, implicating $H_2S$ or $D_2S$-derived radicals (originating from DEDS) in D/H isotope exchange between PDD and water.

Overall, these experiments support the hypothesis [1, 2] that organosulfur compounds could accelerate hydrocarbon decomposition under geologic conditions. Furthermore, our results suggest a novel potential role for $H_2S$-derived radicals in mediating water-hydrocarbon D/H isotope exchange.

[1] Lewan *et al.* (1998), *Nature* 391, pp164-166.
[2] Dominé *et al.* (2002), *Org. Geochem.* 33, pp1487-1499.