

## KINETICS AND MECHANISMS OF HYDROCARBON OXIDATION BY THERMOCHEMICAL SULFATE REDUCTION

Geoffrey S. ELLIS<sup>1,2</sup>, Tongwei ZHANG<sup>1</sup>, Qisheng MA<sup>1</sup> and Yongchun TANG<sup>1</sup>

<sup>1</sup>*Power, Environmental, and Energy Research Center  
California Institute of Technology, Pasadena, California, USA*  
<sup>2</sup>*Present address: U. S. Geological Survey, Box 25046, MS 939  
Denver, CO 80225-0046 USA*

Although the process of thermochemical sulfate reduction (TSR) has been recognized by geochemists for nearly fifty years, it has proven extremely difficult to simulate in the laboratory under conditions close to those encountered in geologic settings. Published estimates of the kinetic parameters that describe the rate of the TSR reaction vary widely and are often inconsistent with geologic observations. Consequently, the prediction of the hydrogen sulfide generation potential of a reservoir prior to drilling remains a major challenge for the oil industry.

New experimental and theoretical evidence suggests that magnesium plays a significant role in controlling the rate of TSR in petroleum reservoirs. A novel reaction mechanism for TSR is proposed that involves the formation of contact ion-pairs between Mg and SO<sub>4</sub>. The formation of [MgSO<sub>4</sub>] contact ion pairs changes the symmetry of the sulfate ion [SO<sub>4</sub><sup>2-</sup>] from T<sub>d</sub> to C<sub>2v</sub> and consequently increases the S-O bond length making sulfate easier to be reduced. *Ab initio* quantum chemical calculations have been applied to this model in order to locate a potential transition state and determine the activation energy for this reaction pathway (56 kcal/mol). Detailed experimental work confirms previous reports that the presence of H<sub>2</sub>S is capable of catalyzing sulfate reduction and significantly increases the rate of reaction (Machel, 2001). These results suggest that TSR may proceed as a two-stage reaction initially involving the slow reduction of MgSO<sub>4</sub> to H<sub>2</sub>S followed by a more rapid sulfate reduction reaction catalyzed by H<sub>2</sub>S (Figure 1). The recognition that the overall TSR process may be the result of two different reaction mechanisms with very distinct kinetics may help to explain why previous estimates of TSR activation energies were so divergent.

While the details of the mechanisms of the H<sub>2</sub>S catalyzed reaction are still under investigation, preliminary experimental evidence suggests that this reaction involves the formation of sulfur radicals during the thermal decomposition of labile organic sulfur compounds (e.g., thiols and sulfides), which in turn enhance the formation of unsaturated hydrocarbons (C=C) that are more easily oxidized. A new conceptual model for understanding the process of TSR in geologic environments has been developed that does not

require the initial presence of reduced sulfur (e.g.,  $\text{H}_2\text{S}$  or  $\text{S}^\circ$ ) but rather invokes an  $\text{H}_2\text{S}$  threshold concentration in order to sustain rapid sulfate reduction rates. While this approach appears to be more consistent with field observations than previous mechanisms, further validation of this model will require detailed integration with other geologic data in basin models. These findings may explain the common association of  $\text{H}_2\text{S}$ -rich hydrocarbon deposits with dolomitic rocks ( $\text{CaMgCO}_3$ ), and have important implications for the maximum possible depth of oil occurrence within a sedimentary basin and estimates of global fossil fuel reserves.

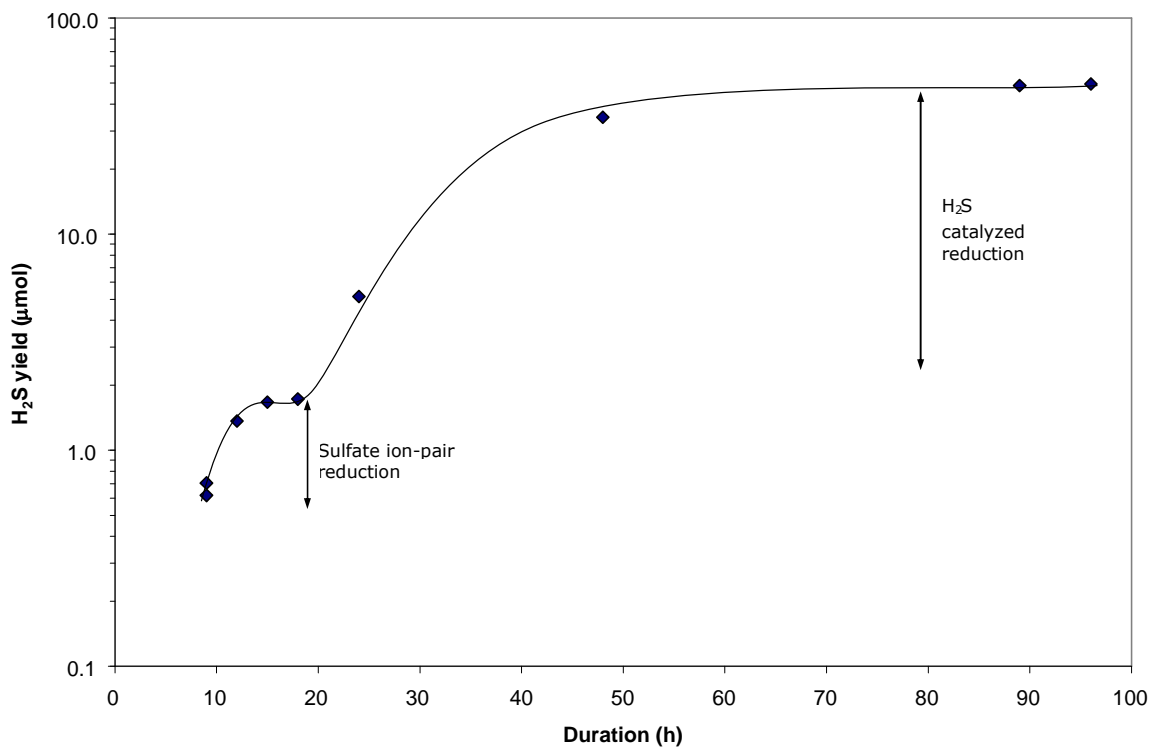


Figure 1. Hydrogen sulfide generation from TSR simulation experiments conducted in sealed gold-tubes containing a pure paraffin mixture +  $\text{MgCl}_2$  +  $\text{CaSO}_4$  +  $\text{H}_2\text{O}$  heated isothermally at  $360^\circ\text{C}$  with the *in situ* pH buffered to 3.0 using talc and silica. These results show an initial slower sulphate reduction reaction followed by the rapid  $\text{H}_2\text{S}$  catalyzed reaction.

## REFERENCES

Machel, H. G., 2001. Bacterial and thermochemical sulfate reduction in diagenetic settings - old and new insights. *Sedimentary Geology* **140**, 143-175.