

THE ROLE OF SECOND ORDER REACTIONS IN GAS GENERATION AT HIGH MATURITIES

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Immature terrigenous organic matter or mixtures of terrigenous and marine organic matter can be thermally stabilised during maturation by second order recombination reactions (Schenk and Horsfield, 1998). The recombination process can lead to a significant dry gas potential at very high maturity levels ($R_o \sim 2\%$) and geological temperatures ($>200^\circ\text{C}$) (Erdmann and Horsfield, 2006; Dieckmann et al., 2006). This is in contrast to many organic-rich marine type II source rocks which generate mainly secondary gas at lower levels of thermal stress ($R_o > 1.2\%$; $T > 150^\circ\text{C}$). In this study we investigate potential bimolecular (second order) reactions by performing pyrolysis experiments on synthetic mixtures of three immature source rock samples stemming from different sedimentary environments. We show that phenolic/aromatic moieties in immature terrigenous organic matter play an important role in second order recombination reactions.

The three immature source rock samples used in the study originated from Brazil (lacustrine type I kerogen concentrate), Norway (mixed marine-terrigenous type II/III kerogen concentrate, Spekk Formation) and Canada (fluvio-deltaic coal, Kugmallit Sequence).

Two sample series were produced by preparing synthetic mixtures of two original source rock samples at a time. The first series was made up of two mixed samples consisting of type I and type II/III kerogens with defined mixing ratios (weight-%) of 3:1 and 1:3, three mixed samples consisting of type II/III kerogen and coal with defined mixing ratios of 3:1, 1:1 and 1:3 and two mixed samples consisting of type I kerogen and coal with defined mixing ratios of 3:1 and 1:3. Non-isothermal open system pyrolysis (bulk kinetics) and non-isothermal closed system micro scale sealed vessel (MSSV) pyrolysis were performed on this sample series. The second sample series was made up of three mixed samples consisting of type II/III kerogen and coal with defined mixing ratios of 3:1, 1:1 and 1:3. Preparative non-isothermal closed system (MSSV) pyrolysis was applied to perform non-isothermal open system pyrolysis (bulk kinetics) on the artificially matured pyrolysis residues of this sample series.

For the first sample series no second order reactions are detectable by open system pyrolysis. The TOC, S₂- and S₃-yields of mixed samples depend linearly on yields of their original source rock samples (Rock-Eval 6) and generation rate curves (temperatures) of

mixed samples lie between those of the according parent material (bulk kinetics). This can be explained by the immediate transport of thermal extractable compounds out of the hot reaction zone by an inert gas flow inhibiting possible second order recombination reactions of first formed products with the residual organic matter.

In contrast, closed system pyrolysis reveals second order reactions during artificial maturation in both samples series. The bulk kinetics of the pyrolysis residues in which terrigenous derived organic matter is present display second order reactions by a shift of generation rate curves out of the envelope of the corresponding immature sample to higher temperatures. This phenomenon indicates the formation of a thermal stable pyrobitumen due to recombination reactions of C₆₊ primary products with the kerogen in a closed system (Erdmann and Horsfield, 2006). For the first sample series second order reactions are made visible by the single chemical compound yields of coal-containing mixed samples which do not linearly depend on the yields of their corresponding source samples (MSSV to 440°C). Reduced yields of long (*n*-C₁₅₊) and short (*n*-C₆₋₁₄) alkyl-chains could be explained by the integration of those compounds into a thermal stable pyrobitumen (Erdmann and Horsfield, 2006). In addition, strongly increased yields of phenolic compounds are generated by coal-containing mixed samples relative to the pure coal sample. This may be explained by a partial suppression of recombination reactions in which phenolic and also aromatic compounds take part. Aliphatic hydrocarbons provided by the lacustrine or marine organic matter enhance the solvating properties of the reaction medium which improves the hydrogen transfer efficiency in the closed system inhibiting recombination of free radicals (Mansuy et al., 1995).

The prediction of significant charges of late dry gas from source rocks in which terrigenous derived organic matter is present has important implication for petroleum exploration in regions where eligible sediments are sufficiently buried.

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