Alternate Pathway Model

Sometimes reactions do not go directly from starting material to final product. A common example from fossil fuel research is the formation of a soluble but nonvolatile product prior to complete breakdown to oil or tar and gas. Similarly, some polymers might have medium molecular weight products are their way to volatile products. This model is intended to treat these situations.

The alternate pathway model consists of three reactions, (1) A $\rightarrow$ C, (2) A $\rightarrow$ B, and (3) B $\rightarrow$ C. Reactions (1) and (2) are in parallel and reactions (2) and (3) are in series. Each reaction can be a first or nth-order reaction and have a Gaussian distribution of activation energies. Data to be fitted can be either the intermediate (B) or the final product (C), but not both simultaneously. Neither can the model be fitted to the disappearance of the starting material (A).

The serial reaction model is nearly as good as the nucleation model for analyzing narrow reaction profiles (Burnham et al., 1996). In this case, just reactions (2) and (3) should be used. This is done by setting A_1 small and/or E_1 large for reaction (1) and not refining them. This model is also useful for more general analysis of serial and competing reactions. For the most general model, the A's and E's for all three reactions can be refined simultaneously. Again, initial A's that are equal will be tied together during their least squares refinement.

The alternate pathway feature of the model becomes necessary when one considers that most kerogens appear to have a bitumen intermediate, yet the maximum rate of oil and gas production occurs at initial time, which is inconsistent with a serial reaction. Furthermore, the bitumen concentration does not achieve the concentration required by s strictly serial reaction. The most logical explanation is that the bitumen is formed by the breakdown of weak links in the kerogen, but oil and gas can form at roughly the same rate from either kerogen or bitumen by breaking stronger bonds. This would suggest that the A and E for reactions (1) and (3) be determined initially from the disappearance of (A) or the appearance of (C). (If from the disappearance of A, it would have to be done with the standard Gaussian/nth order option, because the serial model can't fit the disappearance of (A).) With those parameters then frozen, the A and E for reaction (B) might be determined from the rise and fall of (B). The use of the complete alternating pathway model is difficult without either external constraints or this sequential type of fitting of the reaction parameters.

REFERENCES

Burnham A. K., Braun R. L., Coburn T. T., Sandvik E. I., Curry D. J., Schmidt B. J., and Noble R. A. (1996) An appropriate kinetic model for well-preserved algal kerogens. *Energy & Fuels* **10**, 49-49.