R&D NOTE

Simple Approximate Rate Law for Both Short- and Long-Chain Rice Herzfeld Kinetics

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Many high-temperature hydrocarbon conversion processes are based on or contain an element of thermal reaction chemistry. The essential challenge in modeling these pyrolysis reactions stems from the complexity of the hydrocarbon feed. These are often multicomponent mixtures of molecules undergoing the elementary steps of bond fission, hydrogen transfer, β-scission and radical recombination/disproportionation. Mixture components will interact through the bimolecular steps of H-transfer and radical recombination/disproportionation. Quantitative modeling of these processes requires not only the kinetics of the elementary steps but also a formalism for their assembly into an analytical rate law or the calculation of a numerical scheme.

Toward this end, the elementary steps noted above can be organized into a general Rice-Herzfeld chain process comprising initiation, propagation, and termination components, as shown in Figure 1. In deriving a rate law for reactions such as shown in Figure 1, the nonlinearities arising from the bimolecularity (in radical concentration) of the termination step can present a serious mathematical burden when the combinatorial complexities of a mixture need be addressed. However, the chemistry will be such that frequently the disappearance of reactant is predominantly by the propagation cycle of Figure 1. Gavalas (1966) demonstrated the reduction of mathematical complexity that occurs under such a "long kinetic chain" condition. Essentially, the nonlinear problem becomes a linear one.

The appeal of this long-chain approximation (LCA), especially for modeling the reaction of mixtures, motivated the present scrutiny of its range of applicability. Limitations were expected because the LCA is more system-specific than, for example, the steady-state approximation, as the structure of the reacting molecule provides the critical balance of propagation vs. initiation rates. Thus, the application of the LCA appeared to require molecule-by-molecule, *a-priori* inspection. Moreover, because of the high activation energies of initiation, it seemed reasonable to suspect that a given system could shift away from long-chain conditions with increases in temperature. At extremely high temperatures, the highly activated initiation step could be expected to dominate.

$$\begin{array}{c}
\textit{initiation}\\
A \xrightarrow{\alpha} R_1 + R_2\\
R_1 + A \xrightarrow{\alpha_1} P_1 + \mu\\
R_2 + A \xrightarrow{\alpha_2} P_2 + \mu\\
\textit{propagation}\\
\mu \xrightarrow{k_1} P_3 + \beta\\
\beta + A \xrightarrow{k_{11}} P_4 + \mu\\
\textit{termination}
\end{array}$$

$$\begin{array}{rr}
R_1 + R_1 \xrightarrow{\omega_{11}} P_{11} & R_1 + R_2 \xrightarrow{\omega_{12}} A\\
R_1 + \beta \xrightarrow{\omega_{13}} P_{13} & R_1 + \mu \xrightarrow{\omega_{14}} P_{14}\\
R_2 + R_2 \xrightarrow{\omega_{22}} P_{22} & R_2 + \beta \xrightarrow{\omega_{23}} P_{23}\\
R_2 + \mu \xrightarrow{\omega_{24}} P_{24} & \beta + \beta \xrightarrow{\omega_{33}} P_{33}\\
\beta + \mu \xrightarrow{\omega_{34}} P_{34} & \mu + \mu \xrightarrow{\omega_{44}} P_{44}
\end{array}$$

Figure 1. Organization of pyrolysis elementary steps into the Rice Herzfeld chain formalism.

Approximate Rate Law

This line of reasoning suggested that the simple sum of the initiation plus the long-chain rates might approximate the exact kinetics of RH chains well (Eq. 1). Limiting-case accuracy seemed assured. A reactant with a highly unfavorable β-scission pathway would have a negligible contribution from the "long-chain rate," and may be well modeled by a simple initiation rate. Conversely, a reactant with a long chain would see a negligible contribution from the initiation rate. It is the goal of the present communication to show that the simple sum of Eq. 1 can be applied to predict the disappearance kinetics of a range of molecules without *a-priori* knowledge of the chain length. The value of this is that the exact solution of a nonlinear problem for disappearance kinetics can be replaced by the simple sum of the solution of two linear problems:

$$r_{AP} \simeq r_i + r_{LC} \tag{1}$$

The kinetics of heterogeneous catalysis provides a roughly parallel concept. Equation 1 may be viewed in a similar manner to the Langmuir-Hinshelwood-Hougen-Watson rate law derived by Aris (1968):

$$r(A) = \frac{C_t[A-(R/K)]}{\left[\left(\frac{1}{K_A k_{sr}} + \frac{1}{k_A} + \frac{1}{K k_R}\right) + \left(\frac{1}{K_A k_{sr}} + \frac{1+K_{sr}}{K k_R}\right) K_A A + \left(\frac{1}{K_A k_{sr}} + \frac{1+K_{sr}}{K_{sr} k_A}\right) K_R R\right]} \tag{2}$$

Equation 2 contains the flexibility to model reaction systems where any of adsorption, desorption or surface reaction is the controlling step. It can reduce to a limiting case when one of these steps is rate-determining, which, in general, is determined by the molecule type and the reaction conditions. Equation 1, similarly, contains the ability to model both initiation and long-chain controlling regimes, as dictated by the structure of the molecule and its reaction environment.

Analysis

The rate of disappearance of reactant is readily evaluated from the general pyrolysis mechanism of Figure 1.

$$-\frac{dA}{dt} = \alpha A + \alpha_1 A R_1 + \alpha_2 A R_2 + k_{11} A \beta - \omega_{12} R_1 R_2 \tag{3}$$

The standard kinetics tool of the steady-state approximation equates the rates of initiation and termination and allows derivation of the algebraic radical balance equations (Eqs. 4 and 5) for the β and μ radicals, respectively:

$$\frac{d\mu}{dt} \approx 0 \approx k_{11} A \beta - k_1 \mu + \alpha_1 A R_1 + \alpha_2 A R_2 - 2\omega_{33}\mu^2 - \sum_{j\neq 3} \omega_{3j} \mu R_j \tag{4}$$

$$\frac{d\beta}{dt} \approx 0 \approx -k_{11} A \beta + k_1 \mu - 2\omega_{44}\beta^2 - \sum_{j\neq 4} \omega_{4j} \beta R_j \tag{5}$$

A significant simplification may be obtained by invoking the reasonable approximation (for hydrocarbon pyrolysis) of statistical termination, which sets all termination rate constants equal except for the statistical factor of two for cross collision (Pryor, 1966). Defining R_T as the total radical concentration and $\omega = \omega_{ii} = (1/2)\omega_{ij}$, the equality of initiation and termination rates may be rearranged into the convenient form of:

$$R_T = \left(\frac{\alpha A}{\omega}\right)^{1/2} \tag{6}$$

The statistical-termination approximation leads directly to a linearization of the radical balances, since the source of termination for a given radical is the constant sum of all radicals, R_T. This may be lumped together with the rate constant for termination to give a pseudo-first-order termination rate constant according to:

$$2\omega_{ii} R_i^2 + \sum_{j\neq i} \omega_{ij} R_i R_j = 2\omega\left(\sum_j R_j\right) R_i = 2\omega R_T R_i = [2(\omega\alpha A)^{1/2}] R_i \tag{7}$$

Simple algebraic manipulation provides the steady-state radical concentrations which substitute into Eq. 3 to give the complex form of Eq. 8 for the rate of disappearance of the reactant. Note that while Eq. 8 also incorporates the simplification obtained from the statistical termination approximation, its complexity inhibits its use. This is especially compelling when it is remembered that Eq. 8 applies to pure component pyrolysis only. This motivated the search for a simple approximation of Eq. 8 in terms of the sum of the initiation and long-chain rates:

$$\begin{aligned} -\frac{dA}{dt} = {} & \alpha A + \frac{\alpha_1 \alpha A^2}{2(\omega\alpha A)^{1/2} + \alpha_1 A} + \frac{\alpha_2 \alpha A^2}{2(\omega\alpha A)^{1/2} + \alpha_2 A} \\ & - \frac{2\omega\alpha^2 A^2}{[2(\omega\alpha A)^{1/2} + \alpha_1 A][2(\omega\alpha A)^{1/2} + \alpha_2 A]} \\ & + \frac{k_1 k_{11} A \left(\frac{\alpha A}{\omega}\right)^{1/2} [(\alpha_1 + \alpha_2) A (\omega\alpha A)^{1/2} + \alpha_1\alpha_2 A^2]}{[k_1 + k_{11} A + 2(\omega\alpha A)^{1/2}][2(\omega\alpha A)^{1/2} + \alpha_1 A][2(\omega\alpha A)^{1/2} + \alpha_2 A]} \end{aligned} \tag{8}$$

The derivation of the r_{LC} component of Eq. 1 follows the time-honored procedure. For long kinetic chains, initiation and termination become mathematically insignificant compared to propagation reactions. This leads directly to the linear relationship of Eq. 9 between the two chain-carrying radicals β and μ. In fact, for pure-component pyrolysis, one of Eqs. 4 and 5 is mathematically redundant.

$$k_{11} A \beta = k_1 \mu \tag{9}$$

Equation 9 and the long-chain reactant balance equation provide the convenient long-chain rate, given as Eq. 10 for a single component:

$$r_{LC} = \frac{k_{11}\left(\frac{\alpha A}{\omega}\right)^{1/2}}{1 + \frac{k_{11} A}{k_1}} \tag{10}$$

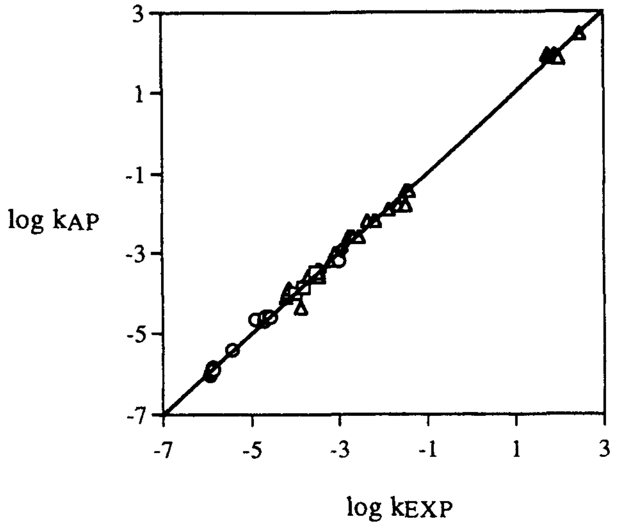

Figure 2. Comparison of approximate apparent first-order rate constant with experimental values.

□ dibenzylether, △ ethane, ○ bibenzyl, ◇ benzylphenylamine.

Returning to Eq. 1, the approximate rate law is obtained simply by adding the rate of reactant consumption by initiation to the long-chain rate as:

$$r_{AP} = 3\alpha A + \frac{k_{11}\left(\frac{\alpha A}{\omega}\right)^{1/2}}{1 + \frac{k_{11}A}{k_1}} \tag{11}$$

The peculiar coefficient of three in the approximate solution arises because the "short-chain" limit consumes one A in the initiation step that produces two radicals that each, in turn, consume an A molecule. In any event, the coefficient of three is not mathematically significant since this coefficient would be adsorbed into α for any regression using Eq. 11. Much like the Aris equation relies on a conservation of catalyst sites, Eq. 11 similarly depends on the steady-state approximation. Outside the applicable range of the steady-state approximation, Eq. 11 may still provide a convenient form; however, the coefficient in the initiation term varies depending on the relative magnitude of the elementary-step rate constants.

The flexibility of Eq. 11 is demonstrated in Figure 2 which shows a parity plot of regressed pseudo-first-order rate constants from Eq. 11 (r_{AP}/A) vs. the experimental result. The molecules presented span a range of approximately 10 orders of magnitude in rate constant and chain lengths from approximately 10^3 for dibenzylether (DBE) (LaMarca, 1992), 10^2 for ethane (Frey and Smith, 1928; Marek and McCluer, 1932; Hepp et al., 1949; Quinn, 1963; Pratt, 1966) and at most 0.1 for bibenzyl (BB) (Poutsma, 1980; Miller and Stein, 1981; Petrocelli and Klein, 1984; Petrocelli, 1985) and benzylphenylamine (BPA) (Abraham and Klein, 1985; Abraham, 1987). The strong correlation in Figure 2 shows the versatility of Eq. 11. In short, the simple approximation of Eq. 11 captures the kinetics of reactant disappearance without *a-priori* knowledge of the chain length.

Conclusions

The mathematical convenience of the long-chain approximation can be retained at conditions where it is a poor representation of the exact solution of RH kinetics by constructing an approximate solution as the sum of the initiation and long-chain rates. This simple strategy obviates the need for the full solution of a problem *nonlinear* in radical concentrations by adding the trivial initiation rate to the solution of a problem *linear* in radical concentrations. This approximation is expected to be quite useful in the analysis of complex pyrolysis mixtures.

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