

Application of PPSA to Chain Reactions

Many important types of reactions such as thermal cracking (pyrolysis), free radical polymerizations, liquid phase oxidations, photochlorinations etc involve free radicals in chain reactions. The Rice-Herzfeld [J. Am. Chem. Soc. 56, 284 (1934)] mechanism or its variation can often be used to explain the kinetics. This mechanism in thermal cracking consists of three basic types of steps:

1. Initiation or formation of free radicals by breaking a weak chemical bond

$$(\text{reactant}) \longrightarrow (\text{free radical})$$
2. Propagation by reaction of free radicals with reactants consisting of
 - a) Hydrogen abstraction

$$(\text{free radical}) + (\text{reactant}) \longrightarrow (\text{free radical} + \text{abstracted hydrogen}) + (\text{large free radical})$$
 - b) Large free radical decomposition

$$(\text{large free radical}) \longrightarrow (\text{product}) + (\text{free radical})$$
3. Termination by reaction of free radicals to form stable products

$$(\text{free radical}) + (\text{free radical}) \longrightarrow (\text{product})$$

The initiation step is usually first order if the reactant molecule is complicated, the temperature is low, the partial pressure of reactant is high. For opposite conditions the initiation step tends to be second order.

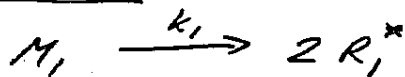
The termination step is governed by the relative rate constants of the propagation steps, magnitude of the rate constants for termination steps, complexity and size of the free radicals involved.

Consider for example the following free radical reaction



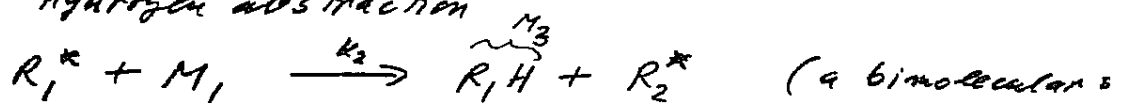
The hypothesized mechanism is:

Initiation



Propagation

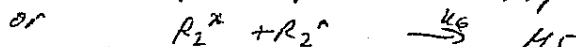
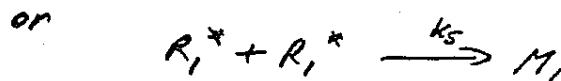
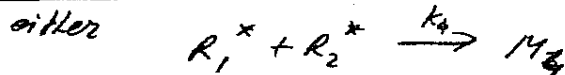
a) Hydrogen abstraction



b) Radical decomposition



Termination



Note: M_4, M_5 formed at all steps appears only in negligible quantities

The first thing to bear in mind is that propagation steps a) and b) occur ~~innumerable~~ uncountable times more frequently than the initiation and either of the termination steps which are very infrequent.

Thus when we write the net rate of disappearance of the starting reactant M_1 , we can safely ignore and neglect the contributions to the overall rate from the initiation and termination steps since almost all of M_1 reacts through the propagation step.

$$-R_{M_1} = k_1 \overset{\approx 0}{C_{M_1}} + k_2 C_{M_1} C_{R_1^*} - k_5 \overset{\approx 0}{C_{R_1^*}^2}$$

$$\text{since } k_2 C_{M_1} C_{R_1^*} \gg k_1 C_{M_1}$$

$$k_2 C_{M_1} C_{R_1^*} \gg k_5 C_{R_1^*}^2$$

Before we proceed further let us assume that only the first termination step occurs in the system. very like the test! Now we can set up the net rates of formation of both free radicals and since they are active intermediates by using PSSA we set them equal to zero.

$$R_{R_1^*} = 2k_1 C_{M_1} - k_2 C_{R_1^*} C_{M_1} + k_3 C_{R_2^*} - k_4 C_{R_1^*} C_{R_2^*} = 0$$

$$R_{R_2} = k_2 C_{R_1} C_{M_1} - k_3 C_{R_2} - k_4 C_{R_1} C_{R_2} = 0$$

The question may be asked as to why the terms $k_1 C_{M_1}$, $k_4 C_{R_1} C_{R_2}$ from initiation and termination steps appear in the above expressions while they were neglected earlier when setting up the rate of reaction for the reactant. One should bear in mind that these terms are negligibly small when compared to either $k_2 C_{R_1} C_{M_1}$ or $k_3 C_{R_2}$ individually. However, in the above expressions the difference $k_2 C_{R_1} C_{M_1} - k_3 C_{R_2}$ appears and this difference between two large quantities has to be small since all the other terms in R_{R_1} and R_{R_2} are small and since both of those rates must be zero, otherwise one or both radicals would form in appreciable quantities. Thus the terms $k_1 C_{M_1}$ and $k_4 C_{R_1} C_{R_2}$ cannot be neglected in the above expressions since they are of the same order of magnitude as the difference of the other two terms.

Solving the above two equations for the free radical concentrations one gets:

$$CR_2^* = \frac{k_1 CR_1}{k_4 CR_1^*}$$

$$CR_1^* = \frac{k_1}{2k_2} + \sqrt{\left(\frac{k_1}{2k_2}\right)^2 + \frac{k_1 k_3}{k_2 k_4}}$$

If the initiation rate constant, k_1 , is really very, very small then terms with k_1^2 are much smaller than terms with k_1 , which are smaller than $\sqrt{k_1}$. Thus

$$CR_1^* \approx \sqrt{\frac{k_1 k_3}{k_2 k_4}}$$

Substituting this into the rate of disappearance of the reactant leads to a first order rate expression

$$-r_{M_1} = \sqrt{\frac{k_1 k_2 k_3}{k_4}} C_{M_1} = k C_{M_1}$$

However, if we assume that the second termination reaction is the faster of the two then we would have to delete the last term in the expression for CR_1^* and to replace the last term in the form for CR_1^* by $k_5 CR_1^{*2}$. Note that since the termination reaction occur in parallel (not in series) it is the fastest (not the slowest) that determines the overall termination rate.

Now we get the following expressions for the free radical concentrations:

$$CR_2^* = \frac{k_2}{k_3} C_{M_1} C_{R_1^*} \quad C_{R_1^*} = \sqrt{\frac{2k_1}{k_3}} C_{M_1}^{1/2}$$

This yields a rate expression of order $3/2$ for the rate of disappearance of M_1 :

$$-R_{M_1} = k_2 \sqrt{\frac{2k_1}{k_3}} C_{M_1}^{3/2}$$

Obviously the type of the termination step will profoundly affect the form of the overall rate and it is to be expected that the form of the initiation step will have a similar effect.

One can then make the following generalization for the various combinations of the different types of initiation and termination steps.

Let μ - a radical involved as a reactant in a unimolecular propagation step (R_2^* in our example)

β - a radical involved as a reactant in a bimolecular propagation step (R_1^* in our example)

Various termination steps may be labeled

$\mu\mu$ - involving two μ radicals

$\beta\mu$ - involving a μ and a β radical (first termination step in our example)

$\beta\beta$ - involving two β radicals (2nd termination step in our example)

In addition all of the previous three types may require a presence of a third body M and become $\mu\mu M$, $\beta\mu M$, $\beta\beta M$ types.

Since μ radical is larger than the β one the magnitude of the termination step rate constant usually follows the following pattern

$$k_{\mu\mu} < k_{\beta\mu} < k_{\beta\beta}$$

where $k_{\mu\mu}$ is the termination constant for a $\mu\mu$ step etc.

The initiation step may be 1st or 2nd order as mentioned previously. The following table is ~~then~~ useful:

Overall Reaction Orders for Free Radical Reactions

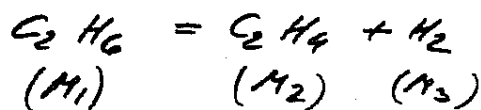
First Order Initiation		Second Order Initiation		Overall order
Simple Termination	Third Body	Simple Termination	Third Body	
		$\beta\beta$		2
$\beta\beta$		$\beta\mu$	$\beta\beta M$	3/2
$\beta\mu$	$\beta\beta M$	$\mu\mu$	$\beta\mu M$	1
$\mu\mu$	$\beta\mu M$		$\mu\mu M$	1/2
	$\mu\mu M$			0

In the first part of our example we dealt with 1st order initiation and a simple $\beta\beta$ termination which led to 1st order overall behavior. In the 2nd part of the example we had 1st order initiation and a $\beta\beta$ termination step which led to a $3/2$ order behavior. Our table correctly predicts these orders.

Let us take a look now at a straight forward extension of this mechanism in treating the pyrolysis of ethane

Example Thermal Cracking of Ethane

Overall Reaction:



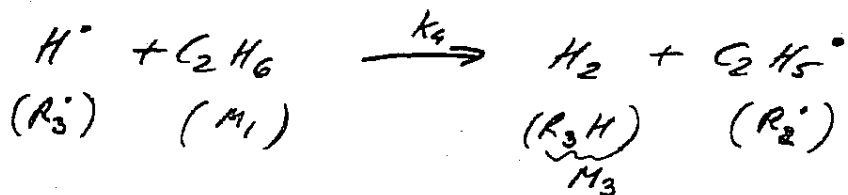
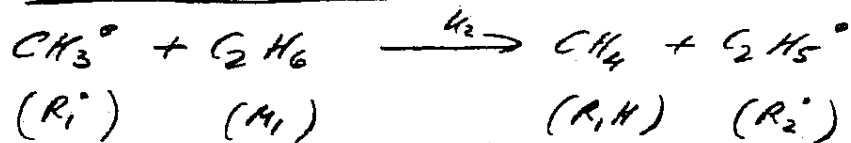
Mechanism

Initiation

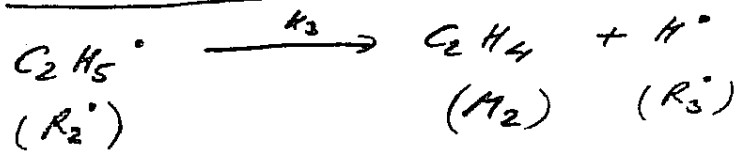


Propagation

Hydrogen Abstraction



Radical Decomposition



Termination

- either a) $C_2H_5^\cdot + H^\cdot \xrightarrow{k_5} C_2H_6$ (β/μ)
 $\mu \qquad \beta$
- or b) $2 C_2H_5^\cdot \xrightarrow{k_5} C_4H_{10}$ (μ/μ)
- or c) $2 H^\cdot \xrightarrow{k_5} H_2$ (β/β)
- or d) $CH_3^\cdot + H^\cdot \xrightarrow{k_5} CH_4$ (β/β)

Since ethane can be considered a moderately complex molecule a first order initiation step was assumed a the (β/μ) termination step (step leading to the observed first order behavior

$$r_{C_2H_4} = k_3 (C_2H_5^\cdot) = \sqrt{\frac{k_1 k_3 k_4}{k_5}} C_{C_2H_6}$$

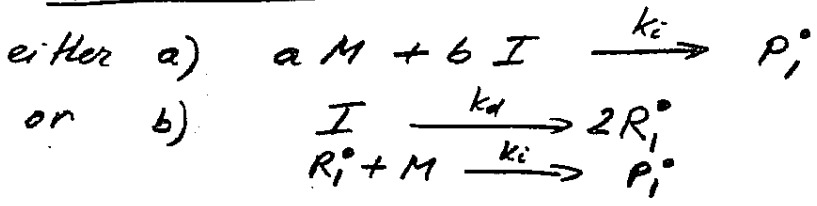
Experimental evidence shows that the following table of free radical concentrations are found

Temp. K	$C_{CH_3^\cdot} / C_{C_2H_5^\cdot}$	$C_{H^\cdot} / C_{C_2H_5^\cdot}$	$C_{C_2H_5^\cdot} \text{ (mol/at)}$	$P_{C_2H_6}$ (at)
850	0.03	0.0014	6×10^{-9}	1
850	0.3	0.14	6×10^{-10}	0.01
900	0.12	0.0041	2.5×10^{-8}	1
900	1.2	0.41	2.5×10^{-9}	0.01

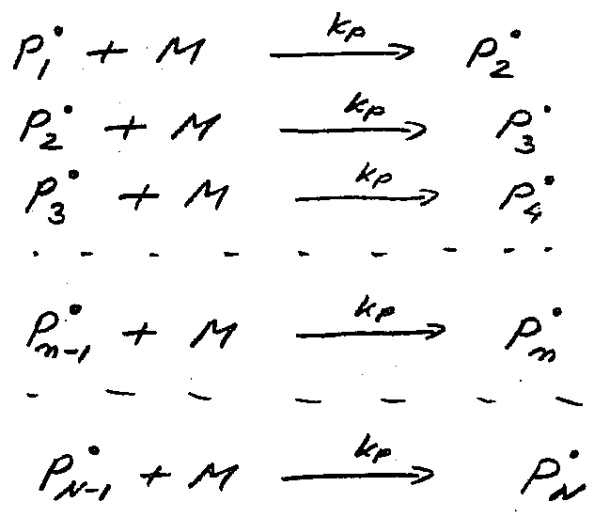
Free Radical (Chain) Polymerization

Many polymers such as polyethylene or polystyrene are made by addition polymerization reactions which occur via ~~the~~ free radical mechanism. The general reaction scheme consists again of three basic steps: initiation, propagation and termination.

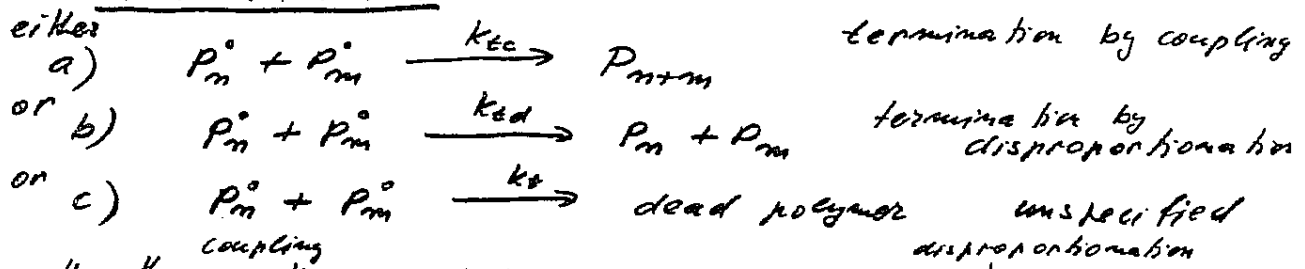
Initiation



Propagation



Termination



Typical termination constants are in the range $10^6 - 10^8 \left(\frac{\text{lit}}{\text{mole s}}\right)$ and are even order of magnitudes larger than the propagation constants.

It is an experimental fact that the concentrations of free radicals rise during a very short time (order of one second) and then stay at a steady level of $10^{-8} \text{ (mole/lit)}$ throughout the polymerization process. This shows that PSSA is applicable.

If we set the net rates of formation of all free radicals equal to zero and sum them all up we get:

$$0 = R_i - k_t \sum_{j=1}^N C_{P_j} \sum_{m=1}^N C_{P_m}$$

Thus

$$0 = R_i - k_t \left(\sum_{m=1}^N C_{P_m} \right)^2$$

which leads to

$$\sum_{m=1}^N C_{P_m} = \left(\frac{R_i}{k_t} \right)^{1/2}$$

The rate of polymerization then is

$$-R_M = k_p C_M \sqrt{\frac{R_i}{k_t}}$$

Notice that the polymerization rate is directly proportional to the square

root of the initiation rate. ~~and~~ ^{if} we double the initiation rate the polymerization rate only increases by $\sqrt{2}$. To increase the polymerization rate 4 times we would have to increase the initiation rate 16 times.

The order ~~of~~ of reaction with respect to monomer is one (this may change if the initiation rate depends on monomer concentration).

Several types of initiation reactions are possible:

- A) Thermal, homolytic dissociation of initiators leads to thermal catalyzed polymerizations (commercially ^{very} important).
The ~~primary~~ ^{first} step in the initiation reaction is much slower than the second one thus it controls the initiation rate

$$R_i = 2fk_d C_I$$

f - initiator efficiency is the fraction of the radicals R_i produced in the dissociation reaction which initiate polymer chains.

The polymerization rate becomes:

$$-R_M = R_{pol.} = k_p C_M \sqrt{\frac{2fk_d C_I}{k_t}}$$

order with respect to I : $\frac{1}{2}$

This rate form has been confirmed for a wide variety of systems.

Deviations are found ~~mainly~~ in that sometimes the order with respect to I appears to be less than $\frac{1}{2}$ at high C_I .

This maybe simply explained by the fact that usually f is presumed constant and is at fixed temp. incorporated in the constants, yet at higher C_I f may rise. The rise in f would raise the constant term but since this was kept at the previous level the apparent order with respect to (w.r.t.) C_I becomes less than $\frac{1}{2}$.

In addition even in thermal initiation initiation steps of type a) are not excluded which may lead to the following polymerization rate

$$R_{pol} = k_p \sqrt{\frac{k_i}{k_t}} C_M^{3/2} C_I^{1/2}$$

The above rate form would also result if the initiator efficiency varies linearly with C_M i.e. $f = f' C_M$

where f' is constant at fixed temp. Then

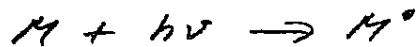
$$R_{pol} = k_p \sqrt{\frac{k_i f'}{k_t}} C_M^{3/2} C_I^{1/2}$$

Polymerization of styrene in chloroform initiated

with *t*-butyl peresters shows such rate form.

B) Photochemical polymerization
(commercially not that important at present)

a) photolysis of the monomer



$$\boxed{R_i = \phi I_a = \phi \epsilon I_0 C_M}$$

ϕ - quantum yield for radical production

I_a - intensity of absorbed light in einsteins (moles of light quanta per liter and second)

ϵ - molar absorptivity (extinction coefficient of the monomer for the particular wave length of radiation absorbed)

I_0 - light intensity in einsteins incident on the monomer

The polymerization rate then is:

$$\boxed{R_{pol} = k_p \left(\frac{\phi \epsilon I_0}{k_t} \right)^{1/2} C_M^{3/2}}$$

The above formula is valid only if all the monomer is exposed to the same light intensity i.e. if the monomer is exposed in a thin slot. For larger vessels

Notice that this polymerization scheme represents an example of mixed reactions with respect to species P_n^\bullet . The reactions take place in series but with respect to the monomer M they take place as competitive reactions.

If the rate of the initiation reaction (rate of formation of P_1^\bullet) is denoted by R_i (we will worry later about its form)

then:

$$R_{P_1} = R_i - k_p C_{P_1} C_M - k_t C_{P_1} \sum_{n=1}^N C_{P_n}$$

$$R_{P_2} = k_p C_{P_1} C_M - k_p C_{P_2} C_M - k_t C_{P_2} \sum_{n=1}^N C_{P_n}$$

$$\dots$$

$$R_{P_n} = k_p C_{P_{n-1}} C_M - k_p C_{P_n} C_M - k_t C_{P_n} \sum_{n=1}^N C_{P_n}$$

$$\dots$$

$$-R_{P_N} = -k_p C_{P_{N-1}} C_M - k_t C_{P_N} \sum_{n=1}^N C_{P_n}$$

The rate of polymerization is the rate of monomer disappearance:

$$-R_M = \cancel{a R_i} + k_p C_M \sum_{n=1}^N C_{P_n}$$

However the first term resulting from monomer depletion in the initiation step can be neglected in comparison to the rate of consumption in the propagation steps.

Note that in the proposed mechanism

The same propagation rate constant was assumed in every propagation step. Partial experimental evidence for this exists, however when one deals with steps involving large long molecules it may be that the apparent propagation constant will change (decrease) due to diffusional effects. This is to say that in highly viscous solution containing large polymer radicals and monomer the ~~propagation~~ ^{propagation} constant may not be any more a measure of probability of successful reaction between a long polymer radical and monomer (which is what a true kinetic constant measures) but rather it becomes a partial measure of probability that the monomer and active group on the polymer will find each other in their random motion during a certain time interval (which is a measure of diffusion). Briefly the propagation constant may show diffusion or viscosity effects. However, as shown later these effects are ~~more~~ ^{more} dramatic for the termination constant, thus k_p remains in comparison a constant.

The typical order of magnitude for k_p is $10^2 - 10^4 \left(\frac{\text{lit}}{\text{mol s}} \right)$ which is much larger than typical 2nd order rate constants in other reactions.