Energetics

General Equation

\[ k = Ae^{\frac{-E}{RT}} \]

\[ \ln k = \ln A - \frac{E}{RT} \]

For thermal decomposition of initiator

\[ R_p = k_p [M][M] = k_p \left( \frac{k_d}{k_t} \right)^{\frac{1}{2}} f\frac{1}{2} [M]^2 I^2 \]

net rate constant

"fudge factor"

Arrhenius expression:

\[ \ln \left( \frac{k_p}{k_t} \right)^{\frac{1}{2}} = \ln \left( \frac{A_d}{A_t} \right)^{\frac{1}{2}} \frac{E_p + \frac{E_d}{2} - \frac{E_t}{2}}{RT} \]

constant w.r.t. Temp

\[ E_p = \text{activation energy for propag. step} \]

\[ \left[ E_p + \frac{E_d}{2} - \frac{E_t}{2} \right] \text{is activation energy for polymerization} \]

\[ E_R = E_p + \frac{E_d}{2} - \frac{E_t}{2} \]

Overall:

\[ \ln R_p = \ln \left( \frac{A_d}{A_t} \right)^{\frac{1}{2}} + \ln \left( f[I] \right)^{\frac{1}{2}} [M] \frac{E_R}{RT} \]
Sample Values of $E_p$ and $E_t$ in kJ/mol

<table>
<thead>
<tr>
<th>Monomers</th>
<th>$E_p$ (kJ/mol)</th>
<th>$E_t$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl chloride</td>
<td>16</td>
<td>17.6</td>
</tr>
<tr>
<td>Methyl acrylate</td>
<td>29.7</td>
<td>22.2</td>
</tr>
<tr>
<td>Methyl metacrylate</td>
<td>26.4</td>
<td>11.9</td>
</tr>
<tr>
<td>Styrene</td>
<td>26.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Initiator</th>
<th>$E_d$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIBN</td>
<td>123.4</td>
</tr>
<tr>
<td>Acetyl Peroxide</td>
<td>136</td>
</tr>
<tr>
<td>Benzoyl Peroxide</td>
<td>124.3</td>
</tr>
</tbody>
</table>

On Average: $E_p \sim 20 - 30$
$E_t \sim 10 - 15$
$E_d \sim 100 - 150$
$\Rightarrow E_R = E_p + E_d/2 - E_t/2$

is dominated by $E_d$
$E_R \sim 80 - 90$ kJ/mol

Because $R_p$ is a positive number $\rightarrow$ positive activation energy

If $T \uparrow$, $k \uparrow$

e.g. if $T \uparrow \sim 10^\circ C$, $R_p \uparrow$ by 2-3x
(rate of polymerization increases by 2 or 3 times)

What about $\overline{p_n}$?

(assume no chain transfer)

$\overline{p_n} = 2a \nu$

let $a = 1$ (coupling)

$\overline{p_n} = 2\nu = \frac{k_p[M]}{(k_d k_i[I])^{1/2}}$

Large value

$\ln \overline{p_n} = \ln \left[ \frac{A_p}{(A_d A_i)^{1/2}} \right] + \ln \left[ \frac{[M]}{([I])^{1/2}} \right] + \frac{E_p - E_d/2 - E_t/2}{RT}$

$\Rightarrow$ on average, get negative value for $[\ ]$ E term

$\Rightarrow \frac{E_p - E_d/2 - E_t/2}{RT}$ is negative

10.569, Synthesis of Polymers, Fall 2006
Prof. Paula Hammond

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT
OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
Thermodynamics

\[ \Delta G = \Delta H - T \Delta S \]
should be negative for polymerization to take place

1. \( \Delta H \) → strongly exothermic rxns
   \( \Delta H_p \) (enthalpy of propagation) → ~ -160 to -60 kJ/mol

2. \( \Delta S \) → lose entropy with polymerization
   \( \Delta S \rightarrow -90 \text{ to } -120 \text{ J/(mol} \cdot \text{K}) \)
   or -0.09 to -0.12 kJ/(mol·K)

Usually \( \Delta H \) is much larger than \( T \Delta S \) term

⇒ negative \( \Delta G \) (thermodynamically favorable to polymerize)

At certain Temp range, it's possible for \( \Delta G \rightarrow 0 \)
⇒ get near equilibria conditioning

\[ \underset{\text{depagation rate constant}}{\text{+}} \]

At equilibrium (or near):

\[ -\frac{d[M]}{dt} = (k_p[M] - k_{dp})[M-] \]

at equilibrium = 0

\[ K_{eq} = \frac{[M_{n+1}]}{[M_n]} \text{ and } [M_{n+1}] \text{ and } [M_n] \text{ approx. equal} \]

\[ = \frac{1}{[M]} = \frac{k_p}{k_{dp}} \]
\[ [M_{\text{eq}}] = \frac{k_d}{k_p} = \frac{1}{K_{\text{eq}}} \]

Equilibrium monomer concentration at a given temp

Will always define with respect to monomer conc or temperature.

**Standard States Defns:**

\[ \Delta G^o = \Delta H^o - T\Delta S^o = -RT \ln K_{\text{eq}} \]
\[ \Delta G = \Delta G^o + RT \ln K_{\text{eq}} = 0 \]
\[ \Delta H^o - T\Delta S^o = -RT_c \ln \left[ \frac{[M]_{\text{eq}}}{[M]^o} \right] = RT_c \ln [M]_{\text{eq}} \]

Solve for \( T_c \):

\[ T_c = \frac{\Delta H^o}{\Delta S^o + R \ln [M]_{\text{eq}}} \]

"ceiling temp" \([M]_{\text{eq}}\) defined as ratio: \( \frac{[M]_{\text{eq}}}{[M]^o} \)

Equilibrium monomer conc

Standard state monomer conc

= highest \( T \) for polymerization to occur \( [M]^o_s = 1 \) M soln

(or bulk conc'n)

\[ \Rightarrow \ln \left[ \frac{[M]}{[M]^o} \right] = \ln [M]_{\text{eq}} = \frac{\Delta H^o}{RT_c} - \frac{\Delta S^o}{R} \]

Determine \([M]_e\) from \( T \)

Ceiling temperature term when no monomer conc is specified, is usually assuming that \([M]_e = [M]_{\text{bulk}}\)
<table>
<thead>
<tr>
<th>Examples</th>
<th>([M]_c) (M)</th>
<th>(T_c) (assuming bulk monomer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl acetate</td>
<td>1x10^-4</td>
<td>--</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>--</td>
<td>220°C</td>
</tr>
<tr>
<td>(\alpha)-methyl styrene</td>
<td>2.2</td>
<td>61°C</td>
</tr>
</tbody>
</table>