

REAÇÕES DE RADICAIS LIVRES

(FREE RADICAL REACTIONS)

REAÇÕES EM CADEIA SIMPLES E RAMIFICADA

(CHAINS AND BRANCHED CHAINS)

CONCEITO DE QUEBRA DE LIGAÇÃO

"BOND CLEAVAGE"



HOMOLÍTICA

≠ RADICAIS



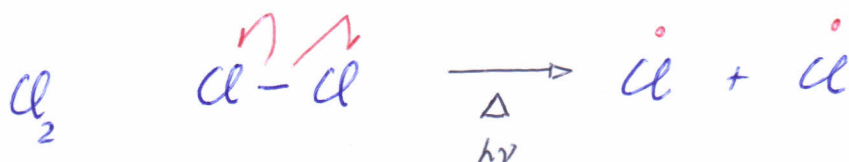
ELÉTRONS DO PAR LIGANTE
EM DIREÇÃO OPUSTA



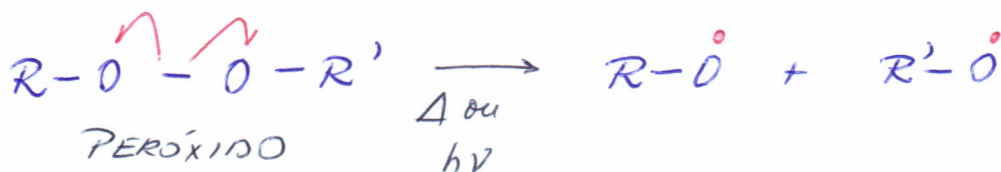
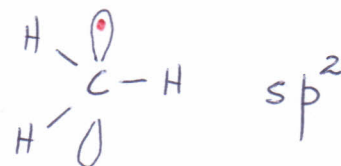
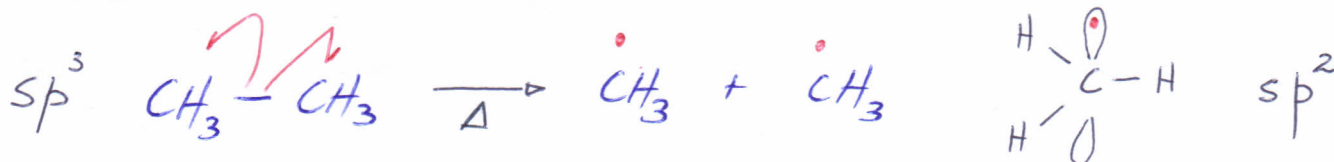
HOMOLÍTICA

MESMO RADICAL

EXEMPLOS

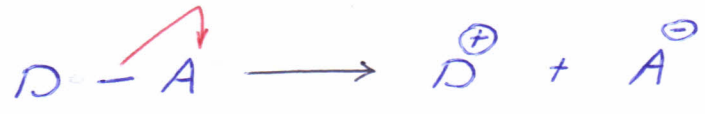


MUDANÇA SPIN
E
GEOMETRIA



PERÓXIDO

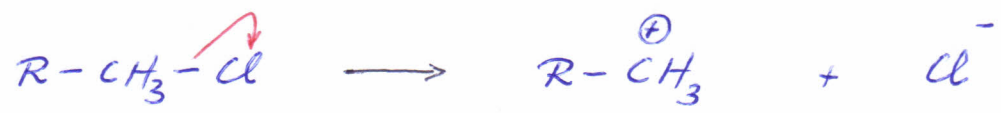
HETEROLÍTICA



"DOADOR" "ACEPTOR"

POSSIBILIDADE
 CÁTION E
 ÂNION RADICAL
 FORMADO PELO
 MOVIMENTO DO
 PAR ELETRONS
 LIGANTE

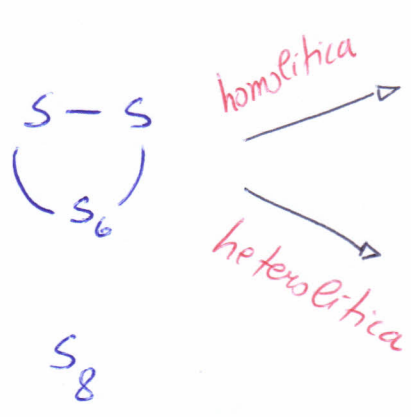
EXEMPLOS



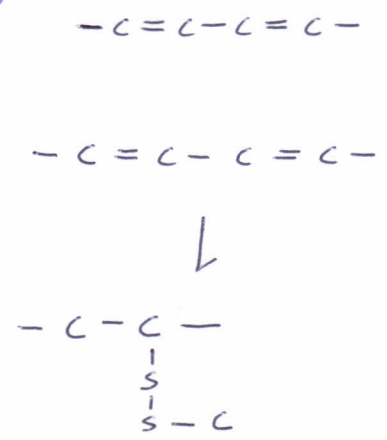
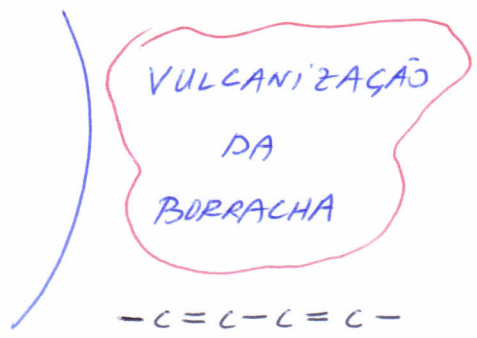
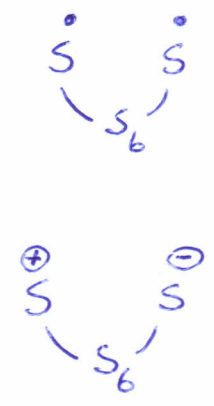
CARBOCATION



CARBANION



homolítica
 heterolítica



REAÇÕES EM CADEIA

i) FASE GÁS \Rightarrow RADICALAR NEUTRA

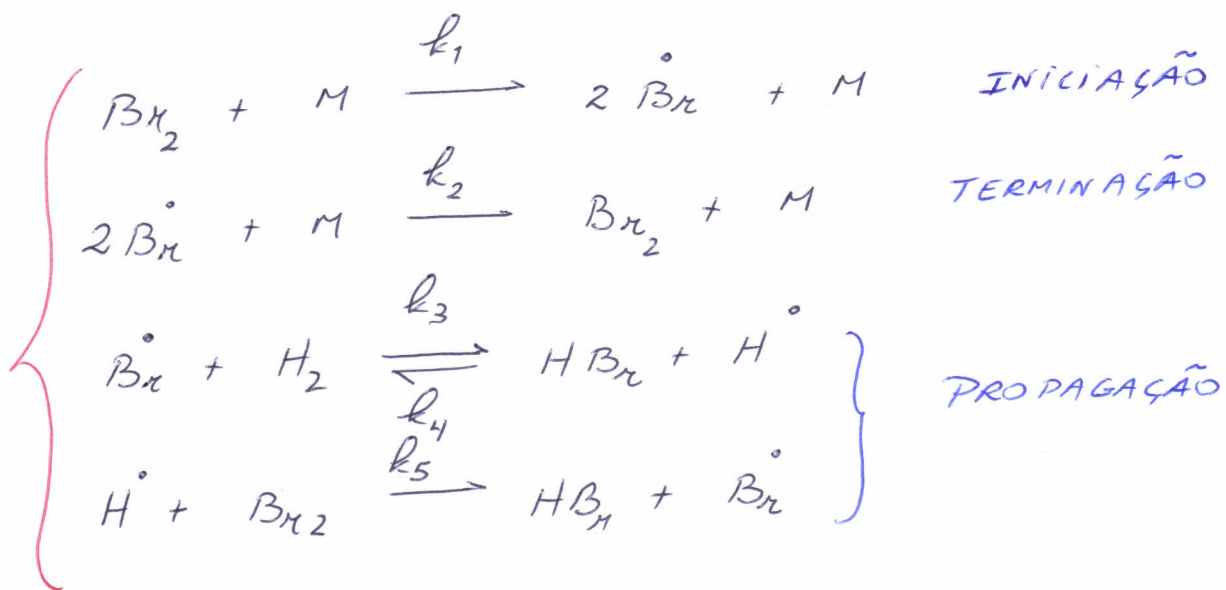
ii) FASE LÍQUIDA
POLAR \Rightarrow IÔNICAS

FASE GÁS RADICALAR



$$\text{VELOCIDADE FORMAÇÃO } v_{HBr} = \frac{k [H_2] [Br]^{1/2}}{1 + k' [HBr] / [Br_2]}$$

MECANISMO (PROPOSTO CHRISTIANSEN, HERZFELD
POLANYI)



APLICANDO A HIPÓTESE DE ESTADO ESTACIONÁRIO
 PARA OS RADICAIS INTERMEDIÁRIOS \dot{H} e \dot{B}_x

$$\frac{d[\dot{B}_x]}{dt} = 2k_1[B_{x2}][M] - k_2[\dot{B}_x]^2[M] - k_3[\dot{B}_x][H_2] + k_4[HB_x][\dot{H}] + k_5[H][B_{x2}] \approx 0$$

$$\frac{d[\dot{H}]}{dt} = k_3[\dot{B}_x][H_2] - k_4[HB_x][\dot{H}] - k_5[H][B_{x2}] \approx 0$$

$$[\dot{H}] = \frac{k_3[\dot{B}_x][H_2]}{k_4[HB_x] + k_5[B_{x2}]} \quad ; \quad [\dot{B}_x] = \left(\frac{2k_1[B_{x2}]}{k_2} \right)^{1/2}$$

AGORA:

$$\frac{d[HB_x]}{dt} = k_3[\dot{B}_x][H_2] - k_4[HB_x][\dot{H}] + k_5[H][B_{x2}]$$

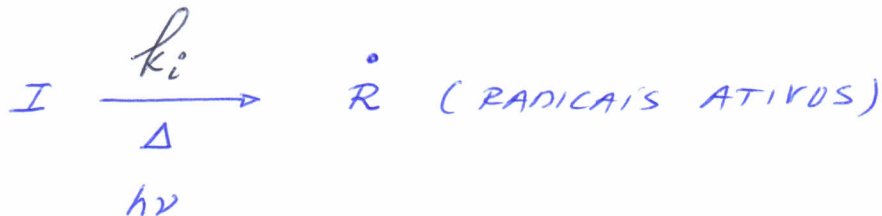
CONCLUINDO:

$$v = \frac{d[HB_x]}{dt} = \frac{2k_3 k^{1/2} [H_2][B_{x2}]^{1/2}}{1 + (k_4/k_5)[HB_x]/[B_{x2}]}$$

POLIMERIZAÇÃO VINÍLICA RADICALAR

CINÉTICA É COMPOSTA DE 4 ETAPAS

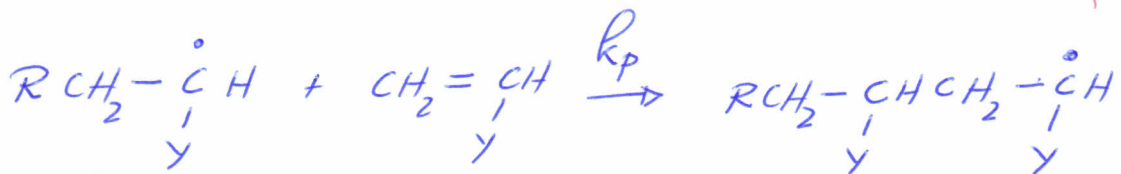
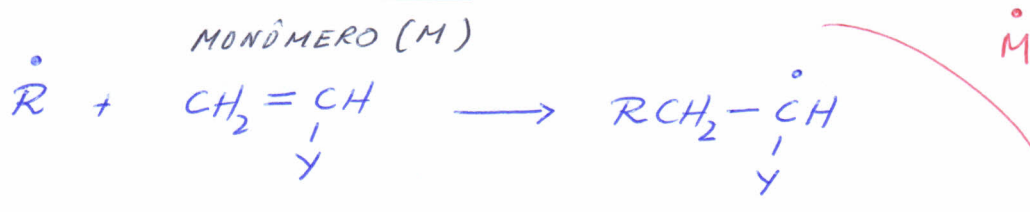
1) INICIAÇÃO: INICIADOR I



VELOCIDADE DE INICIAÇÃO (v_i)

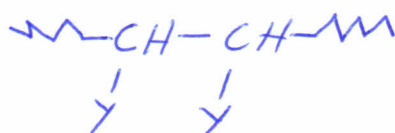
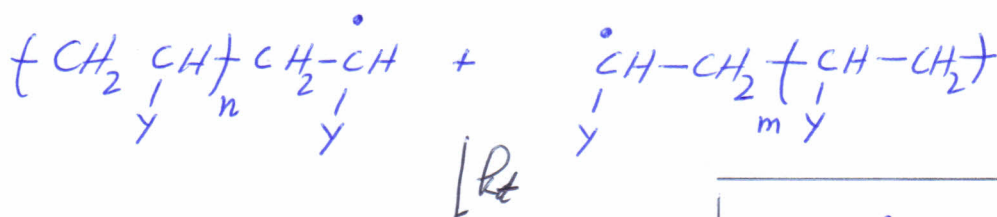
$$(1) \quad \boxed{v_i = k_i [I]} \quad 1^\circ \text{ ORDEM}$$

2) ADICÃO / PROPAGAÇÃO



$$\boxed{v_p = -\frac{d[M]}{dt} = k_p [M][\dot{M}]} \quad (2) \quad 2^\circ \text{ ORDEM}$$

3) TERMINAÇÃO



$$\boxed{-\frac{d[\dot{M}]}{dt} = k_t [\dot{M}]^2} \quad (3)$$

CONDIÇÃO DE ESTADO ESTACIONÁRIO PARA OS RADICAIS IMPLICA EM

$$v_i = v_t$$

ASSIM: $k_i [I] = k_t [\dot{M}]^2$

$$[\dot{M}] = \left(\frac{k_i [I]}{k_t} \right)^{1/2} \quad (4)$$

(4) \rightarrow (2) CONCLUIMOS:

VELOCIDADE DE POLIMERIZAÇÃO v_p

$$v_p = - \frac{d[M]}{dt} = k_p [M] \left(\frac{k_i [I]}{k_t} \right)^{1/2}$$

CONSUMO DE MONÔMERO PRODUZINDO POLÍMERO

LINEAR c/ M

RAIZ QUADRADA DA CONC. I

GRAU DE POLIMERIZAÇÃO DP

$$DP \approx \left(\frac{v_p}{v_t} \right) = \frac{k_p [M] [\dot{M}]}{k_t [\dot{M}]^2} = \frac{k_p [M]}{k_t [\dot{M}]}$$

por (4)

$$DP \approx \frac{k_p [M]}{(k_t k_i [I])^{1/2}}$$

ASSIM DP \uparrow \Rightarrow BAIXAR [I]