Chain Reaction Mechanisms

A chemical pathway characterized by the following distinctive steps:

- a) Initiatiation
- b) Propagation
- c) Inhibition
- d) Termination

Chain Reaction Mechanisms - cont'd.

- + Initiation: A step in which a stable molecular species (not necessarily a reactant in the overall reaction) reacts to generate one or more reactive intermediates
- + Propagation: A reactive intermediate attacks a reactant in the overall reaction to generate a new reactive intermediate
- + Inhibition: A reactive intermediate attacks a product in the overall reaction to generate a new reactive intermediate
- + Termination: Reactive intermediates combine with one another to form a stable molecular species

Example of a Chain Reaction Mechanism

Overall rxn:
$$1 \text{CH}_4 + 1 \text{Cl}_2 \xrightarrow{\Delta} 1 \text{CH}_3 \text{Cl} + 1 \text{HCl}$$

uv

Initiation: $? \xrightarrow{\Delta} ?$

Overall rxn:
$$1 \text{CH}_4 + 1 \text{Cl}_2 \xrightarrow{\Delta} 1 \text{CH}_3 \text{Cl} + 1 \text{HCl}$$
uv

Initiation:
$$1 \text{ Cl}_2 \xrightarrow{\Delta} 2 \text{ Cl} \cdot$$

Overall rxn:
$$1 \text{CH}_4 + 1 \text{Cl}_2 \xrightarrow{\Delta} 1 \text{CH}_3 \text{Cl} + 1 \text{HCl}$$

uv

$$1 \text{Cl}_2 \xrightarrow{\Delta} 2 \text{Cl} \cdot$$
Initiation: $1 \text{Cl}_2 \xrightarrow{\Delta} 2 \text{Cl} \cdot$

uv

Propagation:
$$1 \text{ Cl} \cdot + 1 \text{ CH}_4 \longrightarrow ?$$

Overall rxn:
$$1 \text{CH}_4 + 1 \text{Cl}_2 \xrightarrow{\Delta} 1 \text{CH}_3 \text{Cl} + 1 \text{HCl}$$

uv

1 Cl. $\Delta > 2 \text{Cl}_4$

Initiation:
$$1 \text{ Cl}_2 \xrightarrow{\Delta} 2 \text{ Cl} \cdot$$

$$\text{uv}$$

Propagation:
$$1 \text{ Cl} \cdot + 1 \text{ CH}_4 \longrightarrow 1 \text{ HCl} + 1 \text{ CH}_3 \cdot$$

Overall rxn:
$$1 \text{CH}_4 + 1 \text{Cl}_2 \xrightarrow{\Delta} 1 \text{CH}_3 \text{Cl} + 1 \text{HCl}$$
uv

Initiation:
$$1 \text{ Cl}_2 \xrightarrow{\Delta} 2 \text{ Cl} \cdot$$

Propagation:
$$1 \text{ Cl} \cdot + 1 \text{ CH}_4 \longrightarrow 1 \text{ HCl} + 1 \text{ CH}_3 \cdot$$

Propagation:
$$1 \text{ CH}_3 \cdot + 1 \text{ Cl}_2 \longrightarrow ?$$

Overall rxn:
$$1 \text{CH}_4 + 1 \text{Cl}_2 \xrightarrow{\Delta} 1 \text{CH}_3 \text{Cl} + 1 \text{HCl}$$
uv

Initiation:
$$1 \text{ Cl}_2 \xrightarrow{\Delta} 2 \text{ Cl} \cdot$$

$$\text{uv}$$

Propagation:
$$1 \text{ Cl} \cdot + 1 \text{ CH}_4 \longrightarrow 1 \text{ HCl} + 1 \text{ CH}_3 \cdot$$

Propagation:
$$1 \text{ CH}_3 \cdot + 1 \text{ Cl}_2 \longrightarrow 1 \text{ CH}_3 \text{Cl} + 1 \text{ Cl} \cdot$$

Overall rxn:
$$1 \text{CH}_4 + 1 \text{Cl}_2 \xrightarrow{\Delta} 1 \text{CH}_3 \text{Cl} + 1 \text{HCl}$$
uv

Initiation:
$$1 \text{ Cl}_2 \xrightarrow{\Delta} 2 \text{ Cl} \cdot$$

$$\text{uv}$$

Propagation:
$$1 \text{ Cl} \cdot + 1 \text{ CH}_4 \longrightarrow 1 \text{ HCl} + 1 \text{ CH}_3 \cdot$$

Propagation:
$$1 \text{ CH}_3 \cdot + 1 \text{ Cl}_2 \longrightarrow 1 \text{ CH}_3 \text{Cl} + 1 \text{ Cl} \cdot$$

Termination: ?
$$\longrightarrow$$
 ?

Termination: ?
$$\longrightarrow$$
 ?

Overall rxn:
$$1 \text{CH}_4 + 1 \text{Cl}_2 \xrightarrow{\Delta} 1 \text{CH}_3 \text{Cl} + 1 \text{HCl}$$
uv

Initiation:
$$1 \operatorname{Cl}_2 \xrightarrow{\Delta} 2 \operatorname{Cl} \cdot$$

$$uv$$

Propagation:
$$1 \text{ Cl} \cdot + 1 \text{ CH}_4 \longrightarrow 1 \text{ HCl} + 1 \text{ CH}_3 \cdot$$

Propagation:
$$1 \text{ CH}_3 \cdot + 1 \text{ Cl}_2 \longrightarrow 1 \text{ CH}_3 \text{Cl} + 1 \text{ Cl} \cdot$$

Termination:
$$2 \text{ Cl} \cdot \longrightarrow 1 \text{ Cl}_2$$

Termination:
$$2 \text{ CH}_3 \cdot \longrightarrow 1 \text{ CH}_3 \text{CH}_3$$

Termination:
$$1 \text{ CH}_3 \cdot + 1 \text{ Cl} \cdot \longrightarrow 1 \text{ CH}_3 \text{Cl}$$

Overall rxn:
$$1 \text{CH}_4 + 1 \text{Cl}_2 \xrightarrow{\Delta} 1 \text{CH}_3 \text{Cl} + 1 \text{HCl}$$
uv

Initiation:
$$1 \operatorname{Cl}_2 \xrightarrow{\Delta} 2 \operatorname{Cl} \cdot$$

Propagation:
$$1 \text{ Cl} \cdot + 1 \text{ CH}_4 \longrightarrow 1 \text{ HCl} + 1 \text{ CH}_3 \cdot$$

Propagation:
$$1 \text{ CH}_3 \cdot + 1 \text{ Cl}_2 \longrightarrow 1 \text{ CH}_3 \text{Cl} + 1 \text{ Cl} \cdot$$

Termination:
$$2 \text{ Cl} \cdot \longrightarrow 1 \text{ Cl}_2$$

Termination:
$$2 \text{ CH}_3 \cdot \longrightarrow 1 \text{ CH}_3 \text{CH}_3$$

Termination:
$$1 \text{ CH}_3 \cdot + 1 \text{ Cl} \cdot \longrightarrow 1 \text{ CH}_3 \text{Cl}$$

Inhibition:
$$1 \text{ CH}_3 \cdot + 1 \text{ HCl} \longrightarrow 1 \text{ CH}_4 + 1 \text{ Cl} \cdot$$

Inhibition:
$$1 \text{ CH}_3 \cdot + 1 \text{ CH}_3 \text{Cl} \longrightarrow 1 \text{ CH}_4 + 1 \text{ CH}_2 \text{Cl}$$

Inhibition:
$$1 \text{ Cl} \cdot + 1 \text{ CH}_3 \text{ Cl} \longrightarrow 1 \text{ HCl} + 1 \text{ CH}_2 \text{ Cl}$$

A Chain Reaction - Problem #1

Consider the <u>jumbled</u> sequence of steps shown below for the formation of hydrogen bromide from its elements:

Overall rxn:
$$1 ext{ H}_2 + 1 ext{ Br}_2 \longrightarrow 2 ext{ HBr}$$

Equation #1: $1 ext{ Br}_2 + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ Br} \cdot \longrightarrow 1 ext{ HBr}$

Equation #2: $1 ext{ H} \cdot + 1 ext{ Br} \cdot \longrightarrow 1 ext{ HBr}$

Equation #3: $1 ext{ Br}_2 \longrightarrow 2 ext{ Br} \cdot \longrightarrow 1 ext{ H}_2 + 1 ext{ Br} \cdot \longrightarrow 1 ext{ Br}_2$

Equation #5: $2 ext{ Br} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ H} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ HBr} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ HBr} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ HBr} \cdot \longrightarrow 1 ext{ HBr} + 1 ext{ HBr} \cdot \longrightarrow 1 ext{ HBr} \cdot$

Designate each of the above steps as <u>initiating</u>, <u>propagating</u>, <u>inhibiting</u>, or <u>terminating</u>.

A Chain Reaction - Problem #2

Consider the <u>jumbled sequence</u> of steps shown below for the formation of ethyl chloride and tert-butyl alcohol from ethane and tert-butyl hypochlorite:

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Overall rxn: 1 CH<sub>3</sub>CH<sub>3</sub> + 1 (CH<sub>3</sub>)<sub>3</sub>COCl \longrightarrow 1 CH<sub>3</sub>CH<sub>2</sub>Cl + 1 (CH<sub>3</sub>)<sub>3</sub>COH

Equation #1: 1CH<sub>3</sub>CH<sub>2</sub>· + 1 (CH<sub>3</sub>)<sub>3</sub>COCl \longrightarrow 1 CH<sub>3</sub>CH<sub>2</sub>Cl + 1 (CH<sub>3</sub>)<sub>3</sub>CO·

Equation #2: 1 (CH<sub>3</sub>)<sub>3</sub>CO· + 1 CH<sub>3</sub>CH<sub>2</sub>· \longrightarrow 1 (CH<sub>3</sub>)<sub>3</sub>C-O-CH<sub>2</sub>CH<sub>3</sub>

Equation #3: 1CH<sub>3</sub>CH<sub>2</sub>· + 1 (CH<sub>3</sub>)<sub>3</sub>COH \longrightarrow 1 CH<sub>3</sub>CH<sub>3</sub> + 1 (CH<sub>3</sub>)<sub>3</sub>CO·

Equation #4: 1 CH<sub>3</sub>CH<sub>3</sub> + 1 (CH<sub>3</sub>)<sub>3</sub>CO· \longrightarrow 1 CH<sub>3</sub>CH<sub>2</sub>· + 1 (CH<sub>3</sub>)<sub>3</sub>COH

Equation #5: 1 (CH<sub>3</sub>)<sub>3</sub>COCl \longrightarrow 1 (CH<sub>3</sub>)<sub>3</sub>CO· + 1 Cl·
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Designate each of the above steps as <u>initiating</u>, <u>propagating</u>, <u>inhibiting</u>, or <u>terminating</u>.