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DE CHILE

Fundamentos de Química Orgánica
Capítulo 4: “ESTRUCTURA, REACTIVIDAD Y TRANSFORMACIONES ORGÁNICAS ”

Susan Lühr

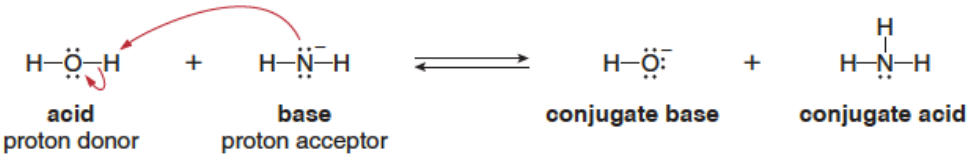
ESTRUCTURA, REACTIVIDAD Y TRANSFORMACIONES ORGÁNICAS

Resumen

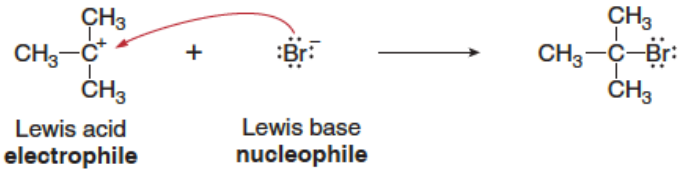
Type	Definition	Structural feature	Examples
Brønsted–Lowry acid (2.1)	proton donor	a proton	HCl, H_2SO_4, H_2O, CH_3COOH, TsOH
Brønsted–Lowry base (2.1)	proton acceptor	a lone pair *or* a π bond	^-OH, $^-OCH_3$, H^-, $^-NH_2$, NH_3, $CH_2=CH_2$
Lewis acid (2.8)	electron pair acceptor	a proton, *or* an unfilled valence shell, *or* a partial (+) charge	BF_3, $AlCl_3$, HCl, CH_3COOH, H_2O
Lewis base (2.8)	electron pair donor	a lone pair *or* a π bond	^-OH, $^-OCH_3$, H^-, $^-NH_2$, NH_3, $CH_2=CH_2$

Rx ácido-base

[1] A Brønsted–Lowry acid donates a proton to a Brønsted–Lowry base (2.2).



[2] A Lewis base donates an electron pair to a Lewis acid (2.8).



- Electron-rich species react with electron-poor ones.
- Nucleophiles react with electrophiles.

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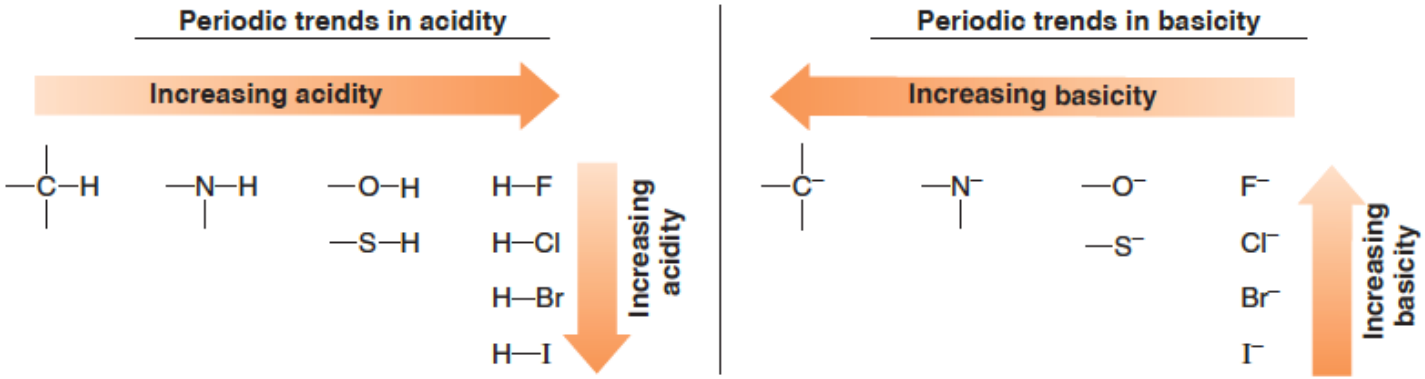
Factores importantes

- Definition: **pK_a = –log K_a. The lower the pK_a, the stronger the acid** (2.3).
- The stronger the acid, the weaker the conjugate base (2.3).
- In proton transfer reactions, equilibrium favors the weaker acid and weaker base (2.4).
- An acid can be deprotonated by the conjugate base of any acid having a higher pK_a (2.4).



[1]	**Element effects** (2.5A)	The acidity of H – A increases both left-to-right across a row and down a column of the periodic table.
[2]	**Inductive effects** (2.5B)	The acidity of H – A increases with the presence of electron-withdrawing groups in A.
[3]	**Resonance effects** (2.5C)	The acidity of H – A increases when the conjugate base A:⁻ is resonance stabilized.
[4]	**Hybridization effects** (2.5D)	The acidity of H – A increases as the percent *s*-character of the A:⁻ increases.

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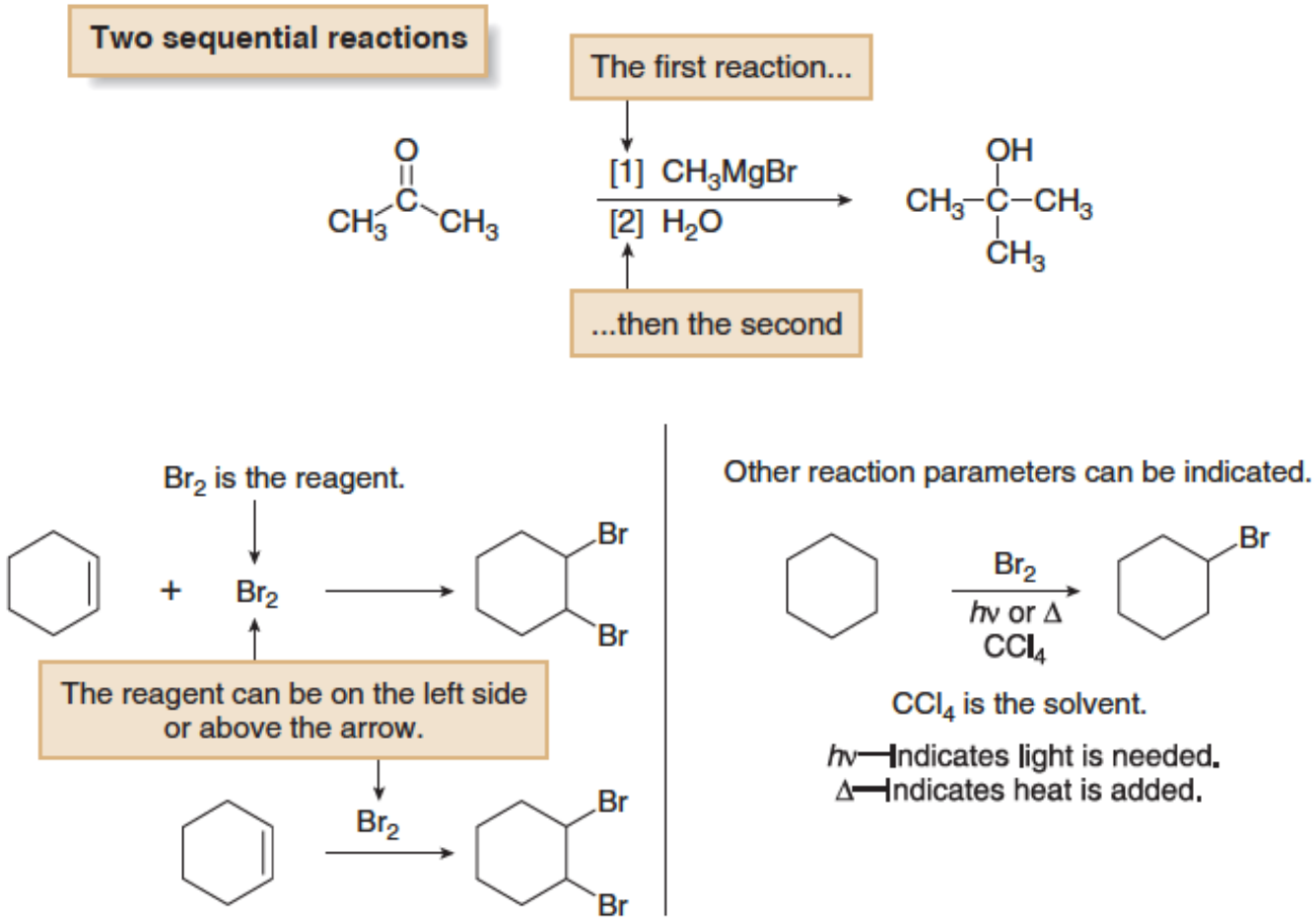
Esquemas de reacción

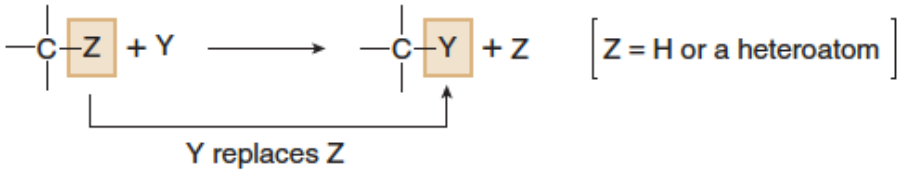


Tipos de reacciones orgánicas

Ácido-base, oxido-reducción, sustitución, eliminación, adición.

- *Substitution* is a reaction in which an atom or a group of atoms is *replaced* by another atom or group of atoms.

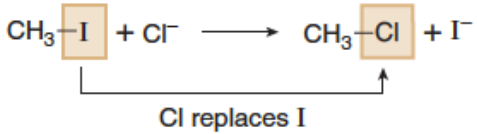
A general substitution reaction



Rxs de sustitución involucran ruptura y formación de enlaces sigma.

Examples

[1]



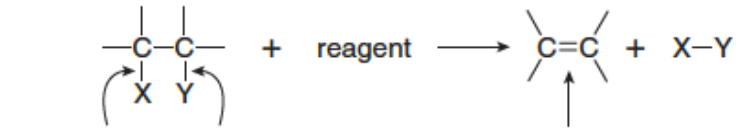
[2]

Tipos de reacciones orgánicas

Ácido-base, oxido-reducción, sustitución, eliminación, adición.

- *Elimination* is a reaction in which elements of the starting material are "lost" and a π bond is formed.

A general elimination reaction

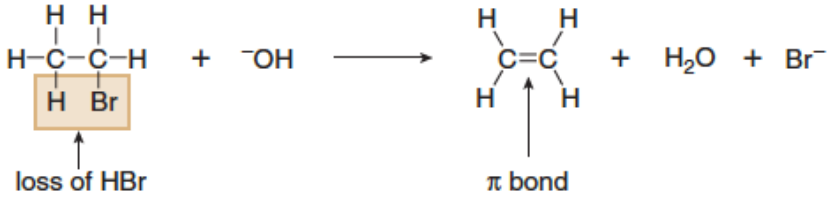


Two σ bonds are broken.

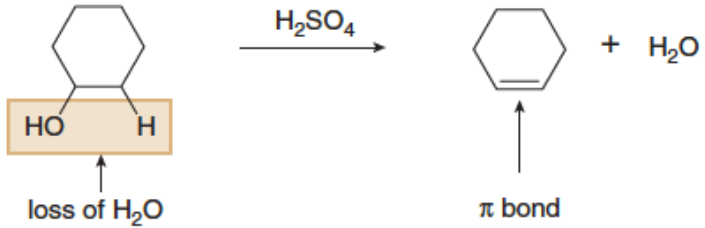
Rxs de eliminación involucran ruptura y formación de enlaces sigma.

Examples

[1]



[2]

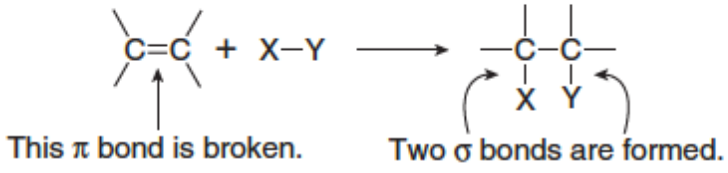


Tipos de reacciones orgánicas

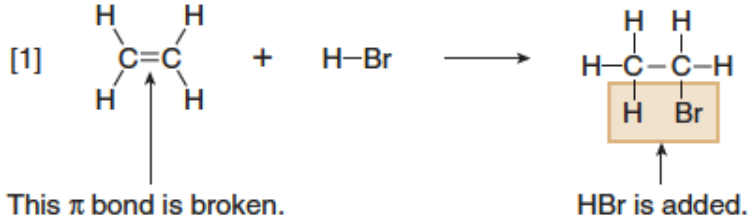
Ácido-base, oxido-reducción, sustitución, eliminación, adición.

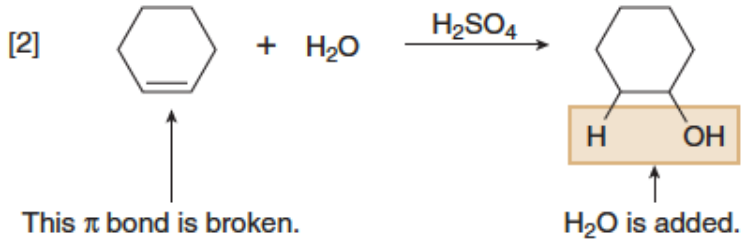
- *Addition* is a reaction in which elements are added to a starting material.

A general addition reaction



Examples





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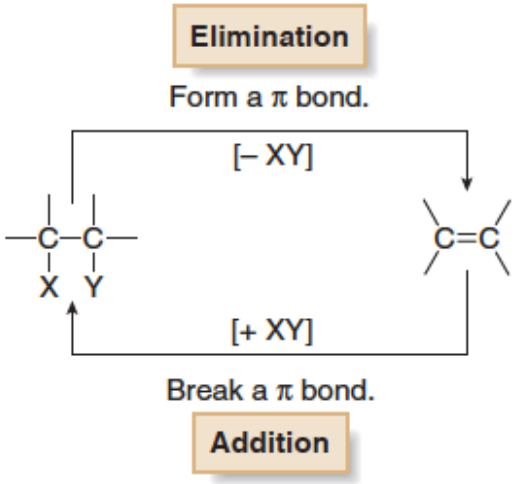
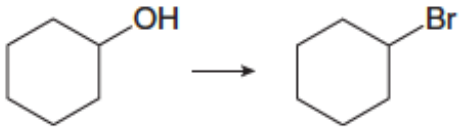
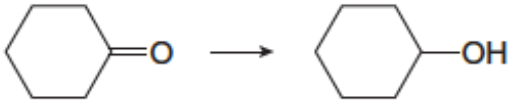
Rxs de eliminación y adición son opuestas.

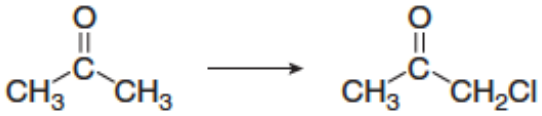


ejercicios

Classify each transformation as substitution, elimination, or addition.

a. 

b. 

c. 

d. $CH_3CH_2CH(OH)CH_3 \longrightarrow CH_3CH{=}CHCH_3$

Many classes of organic compounds undergo one or two characteristic types of reaction. For example, reaction of ethylene, $CH_2{=}CH_2$, with HCl forms CH_3CH_2Cl, and reaction with Br_2 forms $BrCH_2CH_2Br$. If these reactions are observed in all alkenes, what is the general type of reaction that alkenes undergo?

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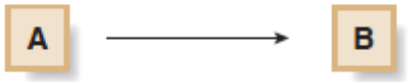
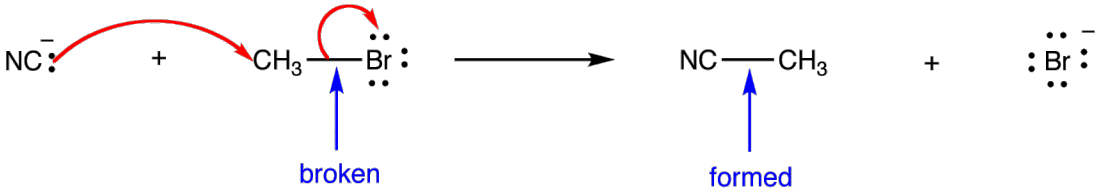
Mecanismo de reacción

A reaction can occur either in one step or in a series of steps.

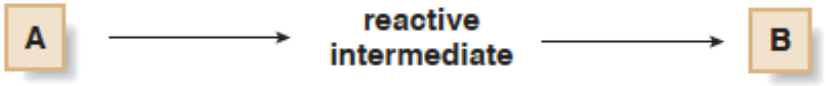
- **A one-step reaction is called a *concerted reaction*.** No matter how many bonds are broken or formed, a starting material is converted *directly* to a product.



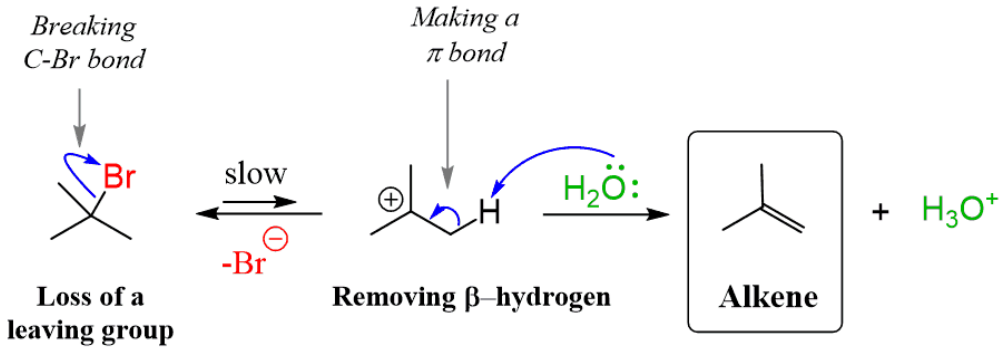


Mecanismos de reacción

- **A stepwise reaction** involves more than one step. A starting material is first converted to an unstable intermediate, called a **reactive intermediate,** which then goes on to form the product.



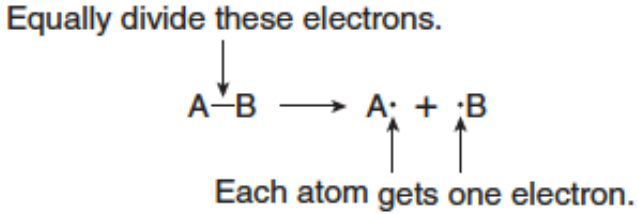
The E1 is a stepwise mechanism



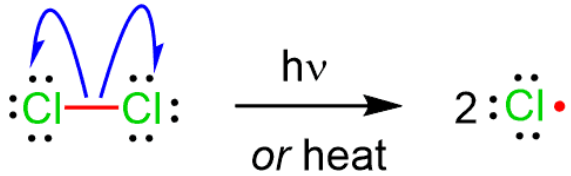
Ruptura de enlace

- Breaking a bond by **equally dividing the electrons** between the two atoms in the bond is called **homolysis** or **homolytic cleavage.**

Homolysis *or* homolytic cleavage



Each Cl takes one electron of the covalent bond



Homolytic cleavage

- Homolysis generates uncharged reactive intermediates with *unpaired* electrons.

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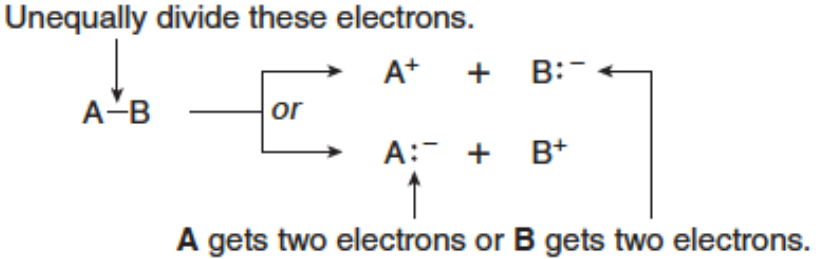
Ruptura de enlace

- Breaking a bond by **unequally dividing the electrons** between the two atoms in the bond is called **heterolysis** or **heterolytic cleavage.** Heterolysis of a bond between **A** and **B** can give either **A** or **B** the two electrons in the bond. When **A** and **B** have different electronegativities, the ***electrons normally end up on the more electronegative atom.***

Heterolysis *or* heterolytic cleavage



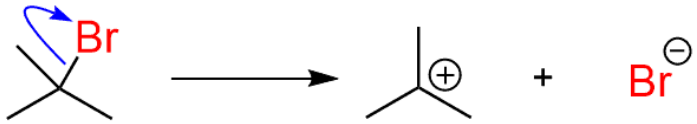
- Heterolysis generates *charged* intermediates.

Ruptura de enlace

Step 1. Breaking the C-Br bond

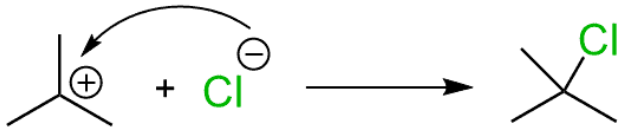
Br takes both electrons of the
vovalent bond.

Carbocation



Heterolytic cleavage Ions are formed

Step 2. Formig a C-Cl bond



- Heterolysis generates *charged* intermediates.

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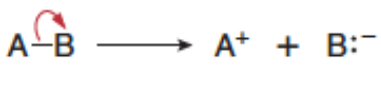
Ruptura de enlace

- To illustrate the movement of a single electron, use a half-headed curved arrow, sometimes called a *fishhook*.

Homolysis

Two **half-headed** curved arrows are needed for two **single** electrons.

Heterolysis



One **full-headed** curved arrow is needed for one electron **pair.**

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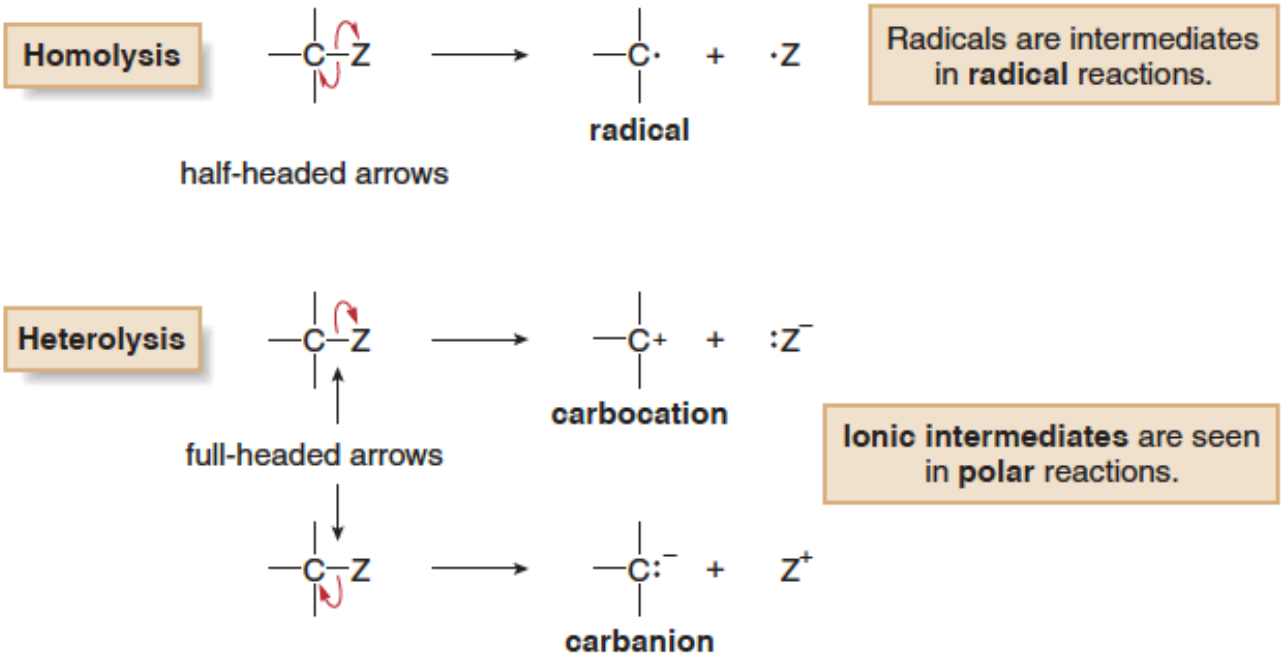
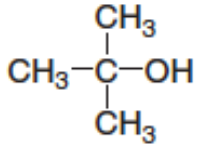
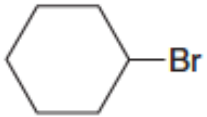
Productos de ruptura de nlaces



Ejercicios

By taking into account electronegativity differences, draw the products formed by heterolysis of the carbon–heteroatom bond in each molecule. Classify the organic reactive intermediate as a carbocation or a carbanion.

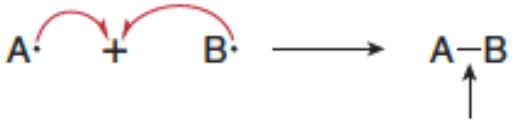
a. 

b. 

c. CH_3CH_2-Li

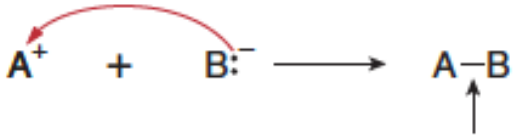
Formación de enlace

Forming a bond from two radicals



One electron comes from each atom.

Forming a bond from two ions



Both electrons come from one atom.

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Flechas

Arrow	Name	Use
	Reaction arrow	Drawn between the starting materials and products in an equation
	Double reaction arrows (equilibrium arrows)	Drawn between the starting materials and products in an equilibrium equation
	Double-headed arrow	Drawn between resonance structures
	Full-headed curved arrow	Shows movement of an electron pair
	Half-headed curved arrow (fishhook)	Shows movement of a single electron

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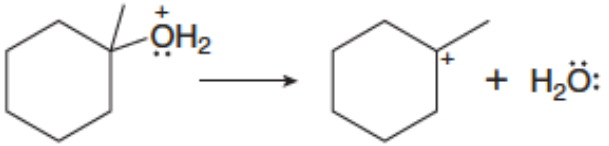
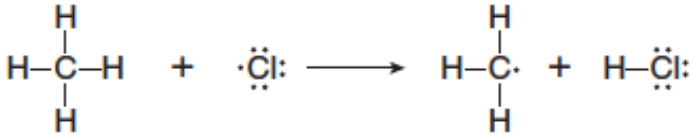
Ejercicios

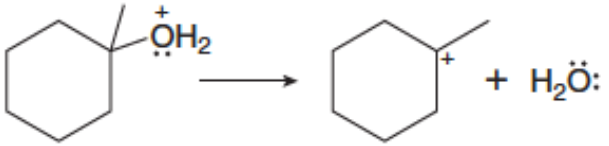
Use full-headed or half-headed curved arrows to show the movement of electrons in each equation.

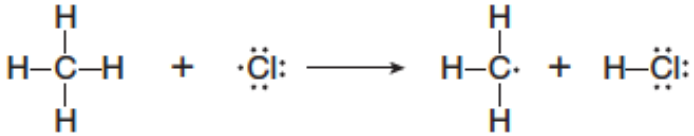
a. 

b. 

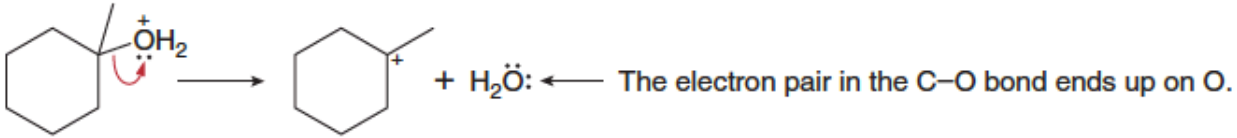
Ejercicios

Use full-headed or half-headed curved arrows to show the movement of electrons in each equation.

a. 

b. 

a. In this reaction, the C – O bond is broken heterolytically. Because only one electron pair is involved, **one full-headed curved arrow** is needed.



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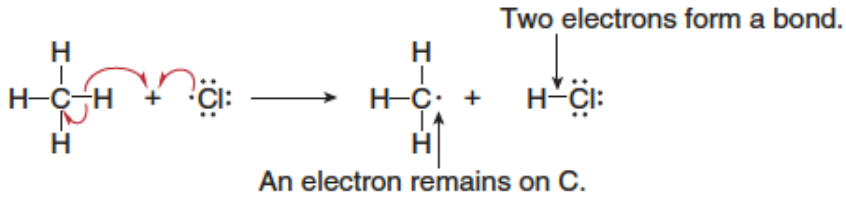
b. This reaction involves radicals, so half-headed curved arrows are needed to show the movement of single electrons. One new two-electron bond is formed between H and Cl, and an unpaired electron is left on C. Because a total of three electrons are involved, **three half-headed curved arrows are needed.**

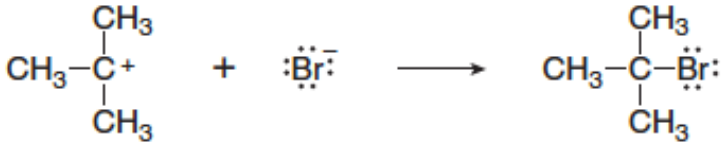


Ejercicios

Use curved arrows to show the movement of electrons in each equation.

a. $(CH_3)_3C-\overset{+}{N}\equiv N: \longrightarrow (CH_3)_3C^+ + :N\equiv N:$

b. $\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3-CH_3$

c. 

d. 

Diagramas de energía

Un diagrama de energía es una representación esquemática de los cambios energéticos que Ocurren cuando los reactantes son convertidos en productos.
Un diagrama de energía representa:

- Qué tan rápida es la reacción.
- Cuántos pasos están involucrados.
- Comparación de las energías de reactantes, productos e intermediarios.

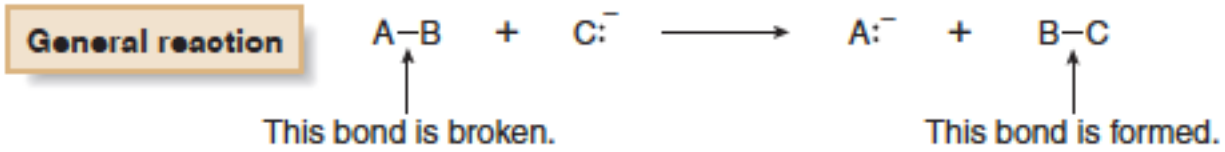


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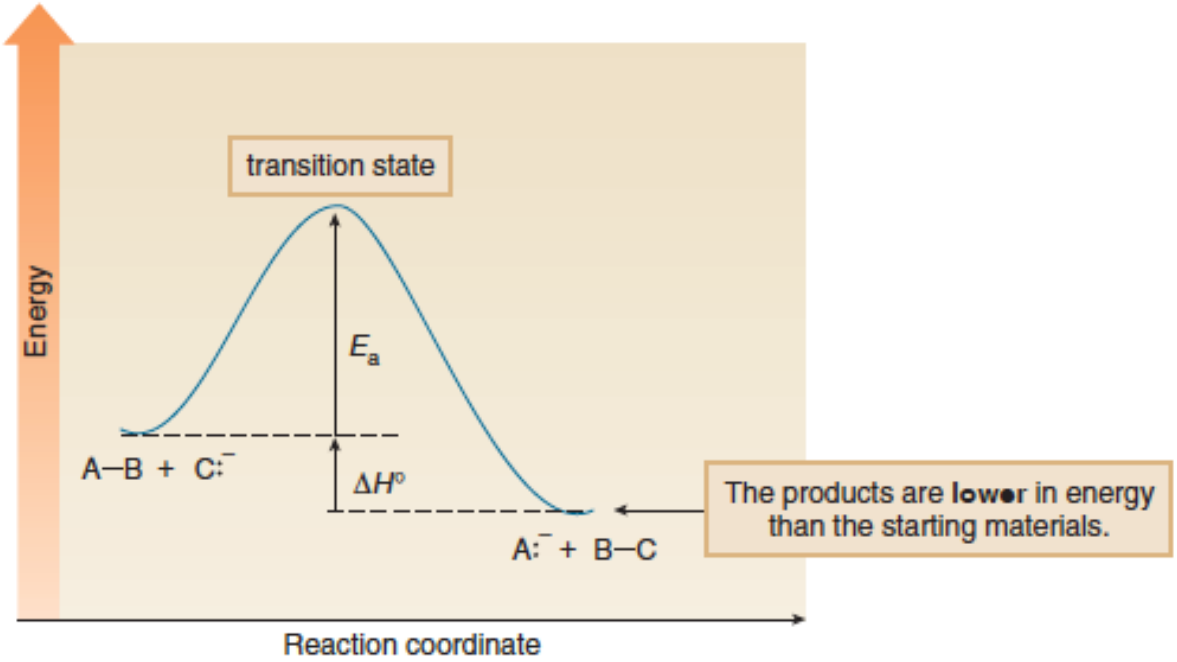
Diagrama de energía – Rx concertada

Rx concertada: ocurre en un solo paso. La ruptura del enlace A-B ocurre a medida que se forma el nuevo enlace B-C.

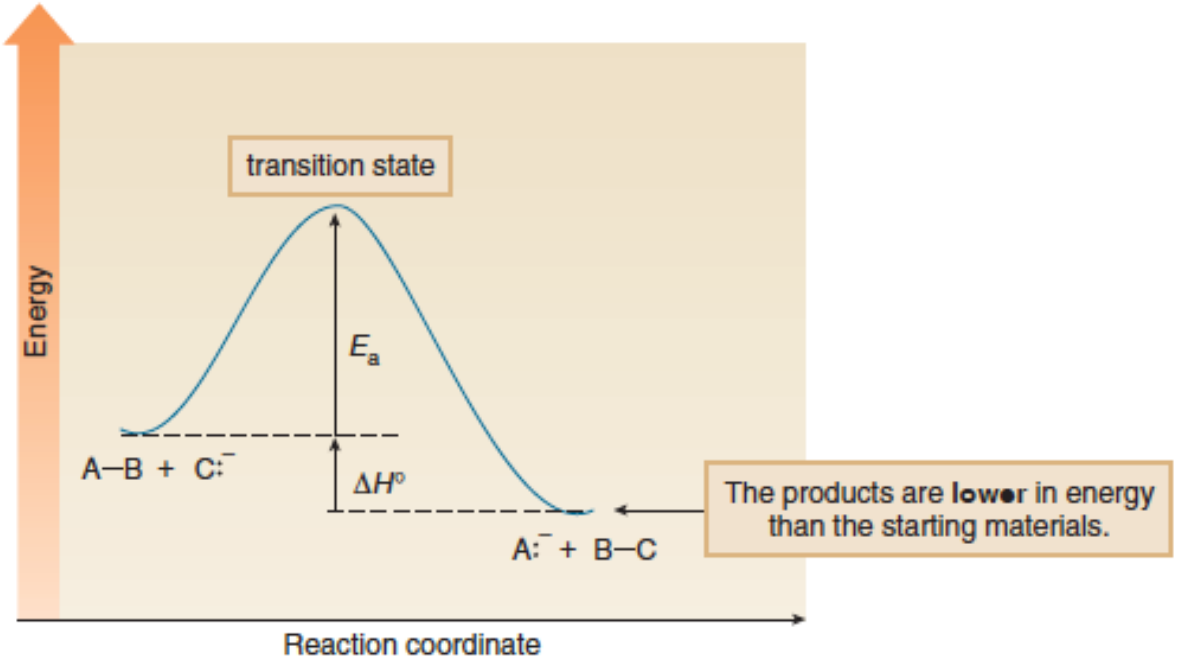


(Progreso de la reacción)

- When ΔH° is positive (+), energy is absorbed and the reaction is *endothermic.*
- When ΔH° is negative (–), energy is released and the reaction is *exothermic.*

Diagrama de energía – Rx concertada

Rx concertada: ocurre en un solo paso. La ruptura del enlace A-B ocurre a medida que se forma el nuevo enlace B-C.



Al inicio de la Rx ocurre una repulsión entre la nube electrónica, causando un aumento en la energía hasta que un máximo valor es alcanzado. Este máximo de energía inestable es llamado estado de transición (ET), en donde la ruptura del enlace A-B es parcial y el enlace B-C está parcialmente formado. El ET nunca puede ser aislado.

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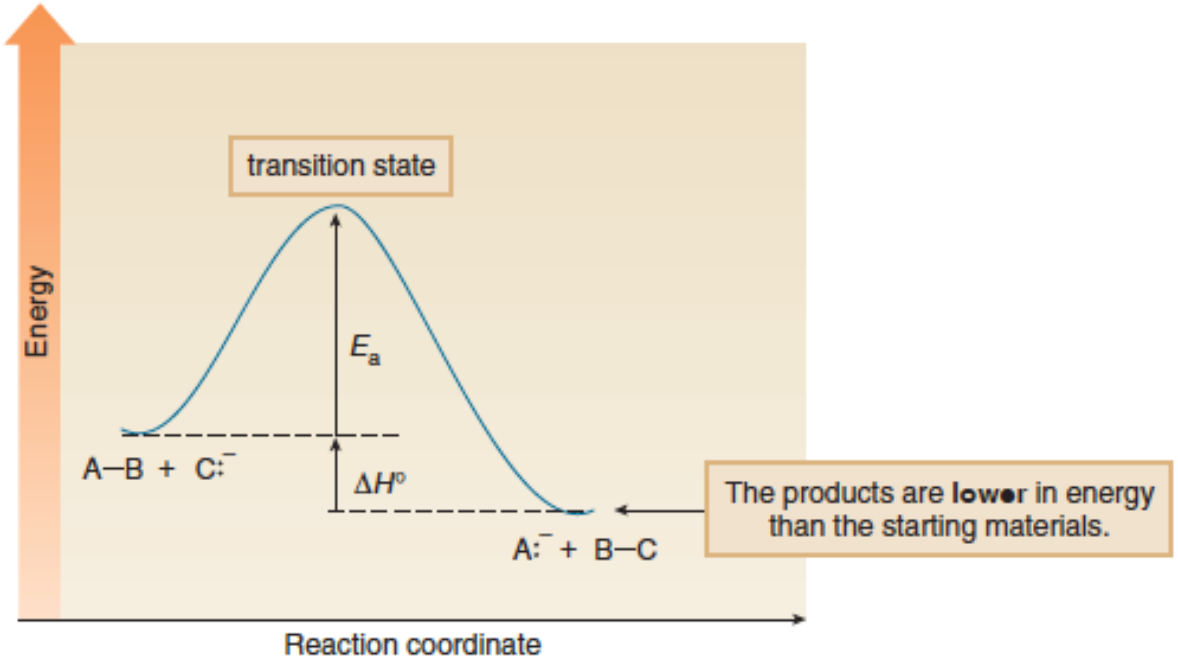
Diagrama de energía – Rx concertada



En el ET, el enlace A-B puede ser restaurado para generar nuevamente los reactantes o el enlace B-C puede completarse para generar los productos, disminuyendo la energía.
Cambio Entalpía: diferencia de energía entre R y P. Rx exotérmica (libera energía), ya que los productos tienen menor energía que los reactantes.
Energía de activación (Ea): Diferencia de energía entre los reactantes y el ET. Es la energía mínima para producir la ruptura de enlace en los reactantes. Representa una barrera energética para que la reacción ocurra. A mayor Ea, mayor energía es necesaria para que la reacción se lleva a cabo, por lo que la velocidad de reacción es lenta.

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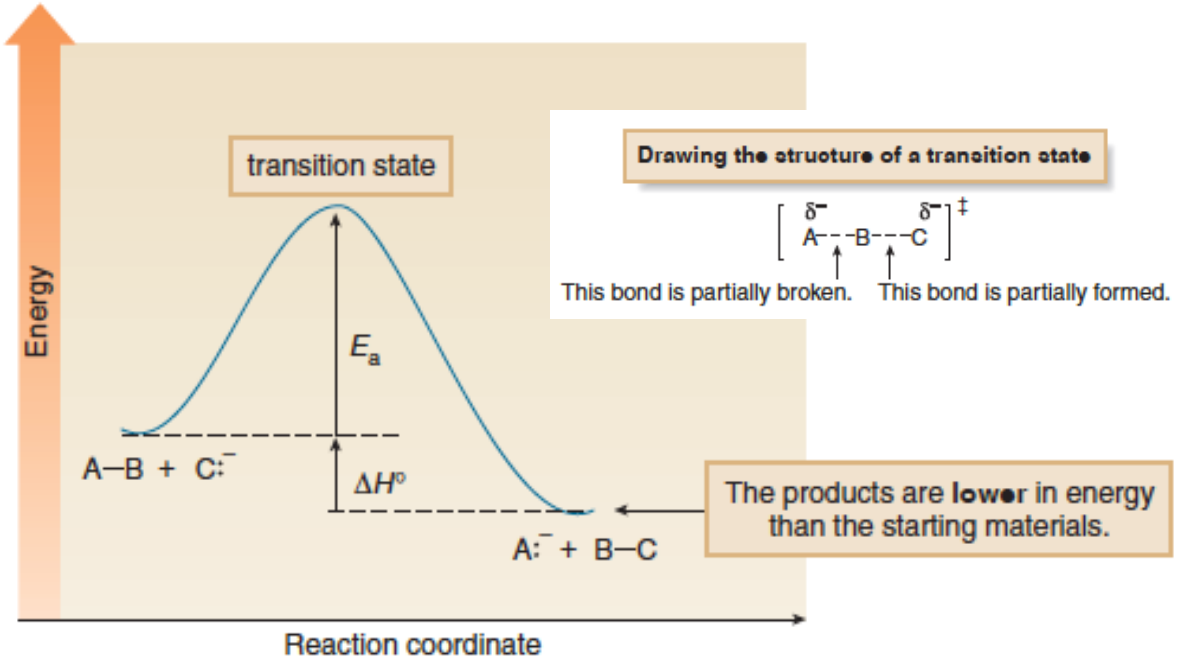

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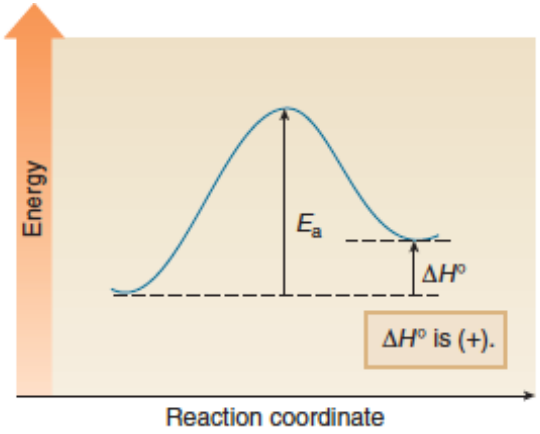
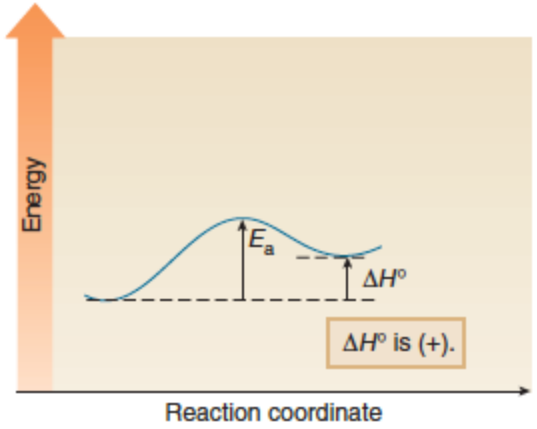
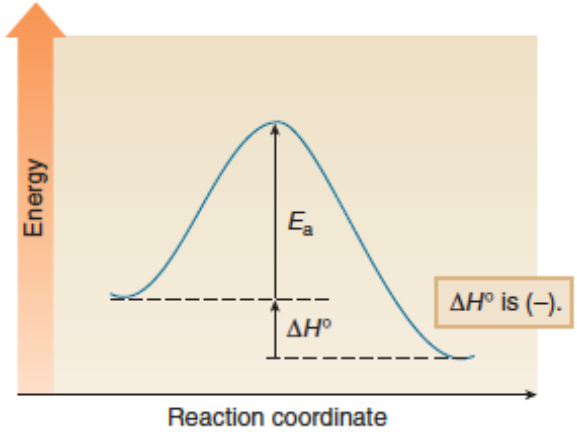
Diagrama de energía

- E_a determines the height of the energy barrier.
- $\Delta H°$ determines the relative position of the reactants and products.







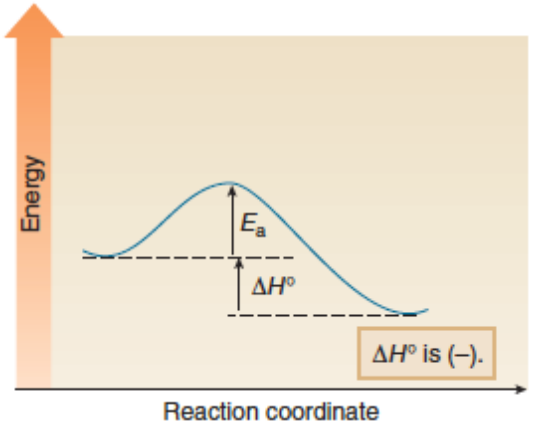


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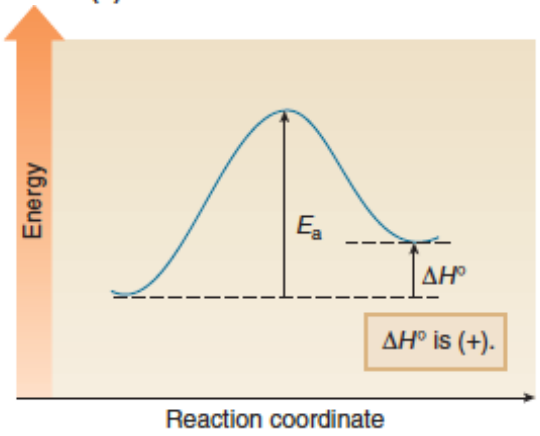
Diagrama de energía

- Large E_a ⟶ slow reaction
- (+) ΔH° ⟶ endothermic reaction



- Low E_a ⟶ fast reaction
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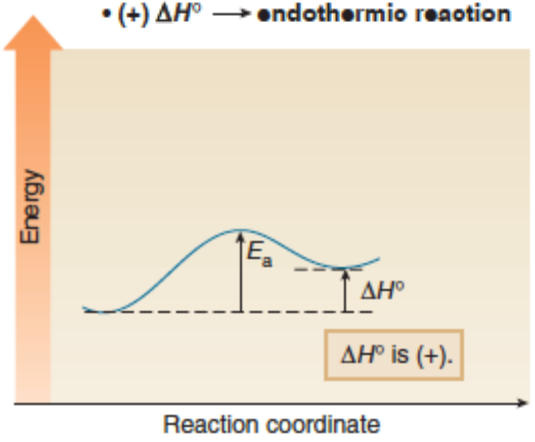

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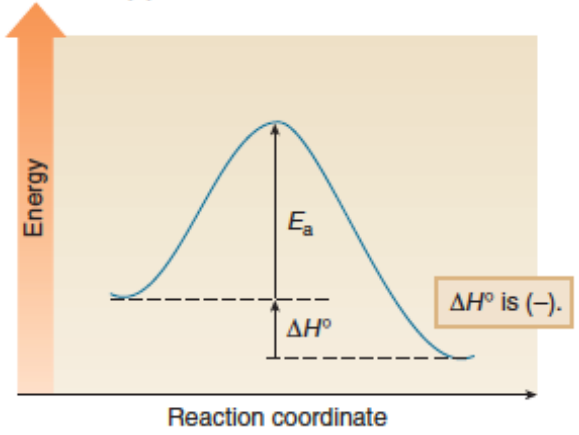

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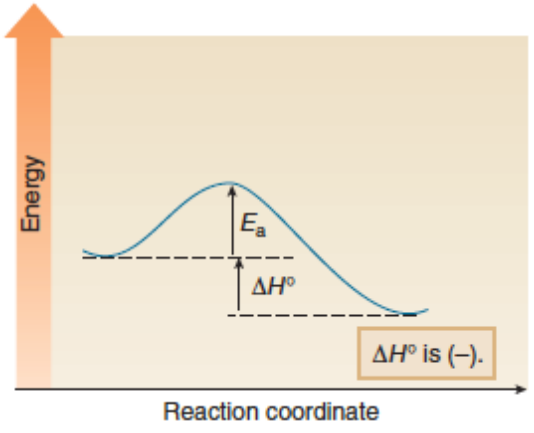

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Ejercicios

Draw an energy diagram for a reaction in which the products are higher in energy than the starting materials and E_a is large. Clearly label all of the following on the diagram: the axes, the starting materials, the products, the transition state, $\Delta H°$, and E_a.

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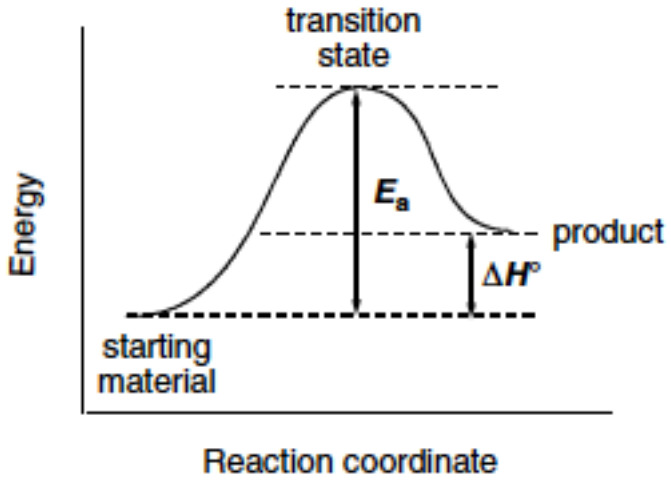

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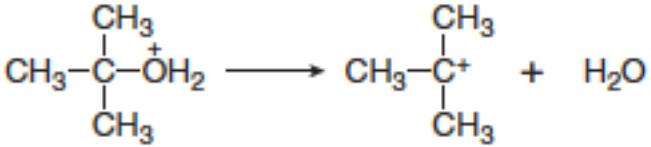
Ejercicios

Draw the structure for the transition state in each reaction.

a. 

b. 

Ejercicios

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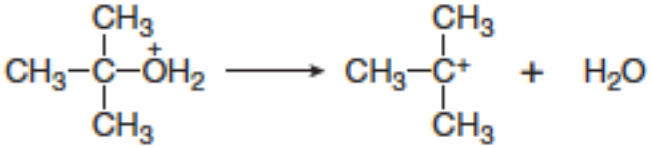
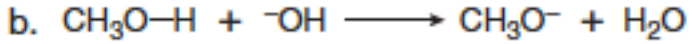
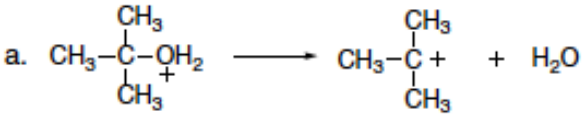
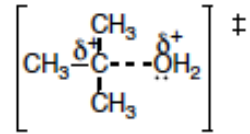
a. 

b. 

A transition state is drawn with dashed lines to indicate the partially broken and partially formed bonds. Any atom that gains or loses a charge contains a partial charge in the transition state.

a. 

transition state: 

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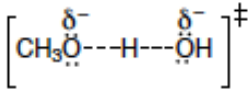
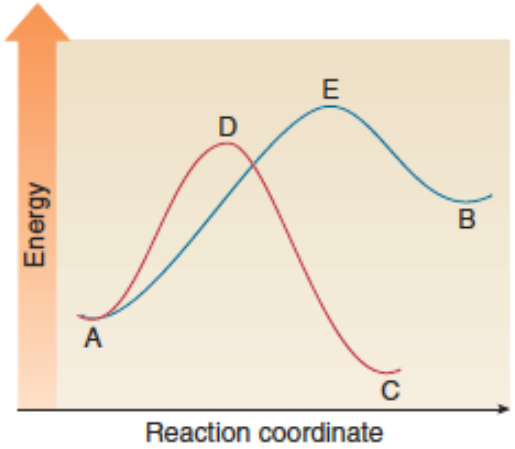
transition state: 

Ejercicios

Compound **A** can be converted to either **B** or **C**. The energy diagrams for both processes are drawn on the graph below.



a. Label each reaction as endothermic or exothermic.
b. Which reaction is faster?
c. Which reaction generates the product lower in energy?
d. Which points on the graphs correspond to transition states?
e. Label the energy of activation for each reaction.
f. Label the $\Delta H°$ for each reaction.

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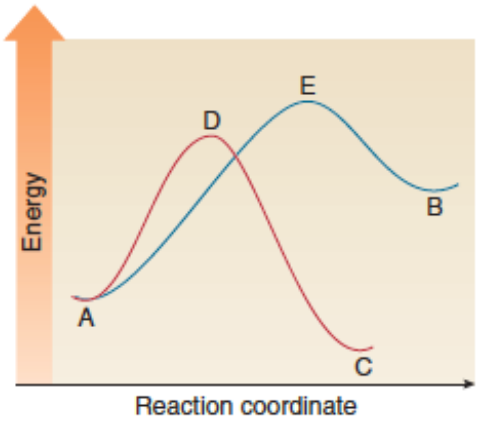

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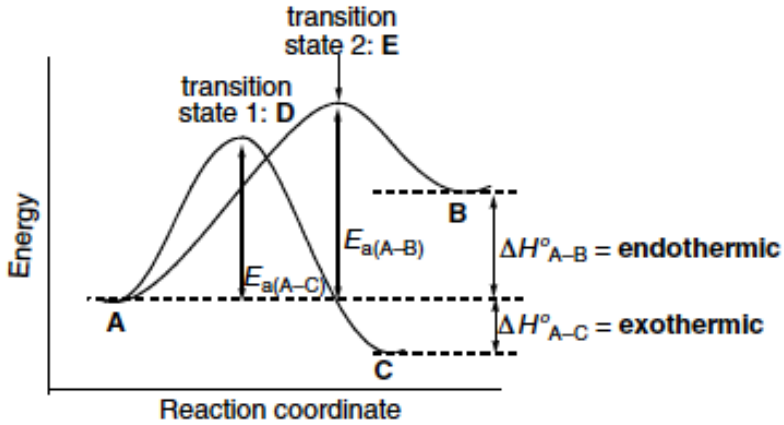

a. Reaction A–C is exothermic. Reaction A–B is endothermic.
b. Reaction A–C is faster.
c. Reaction A–C generates a lower-energy product.
d. See labels.
e. See labels.
f. See labels.

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Diagrama energético – Rx 2 pasos

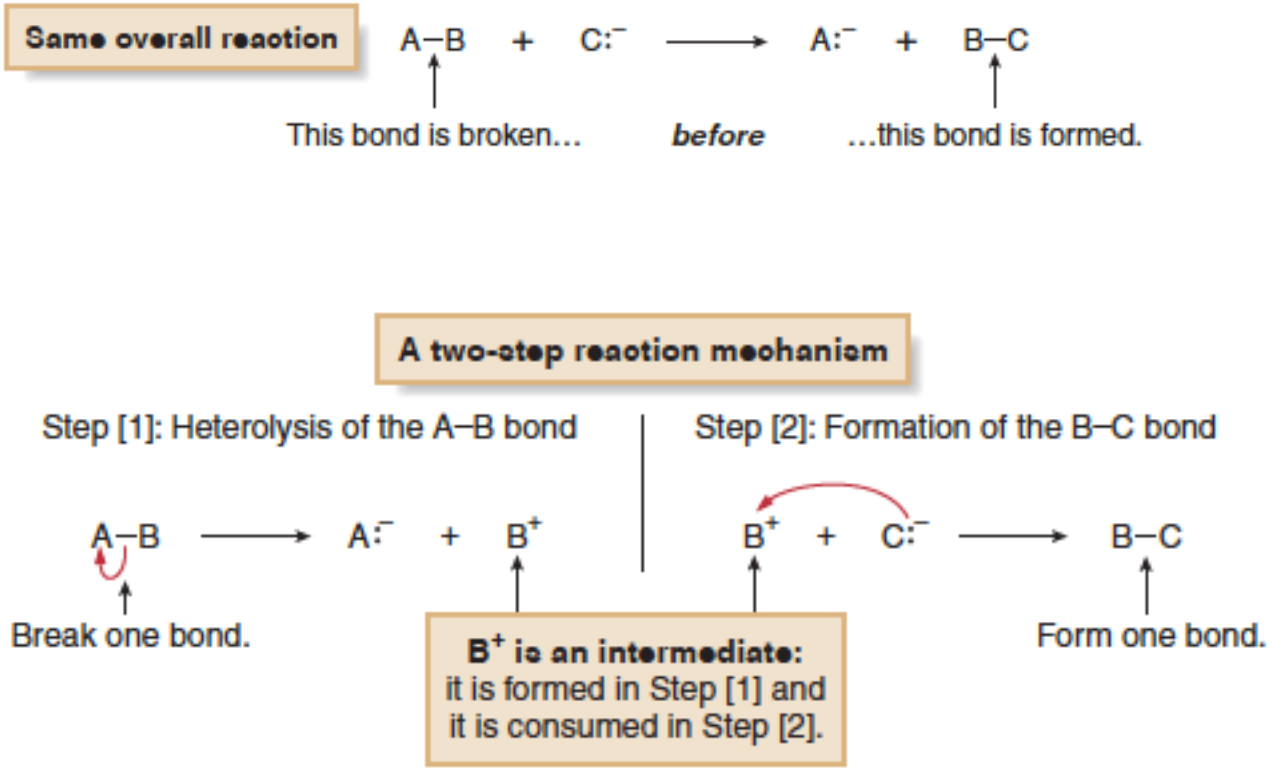
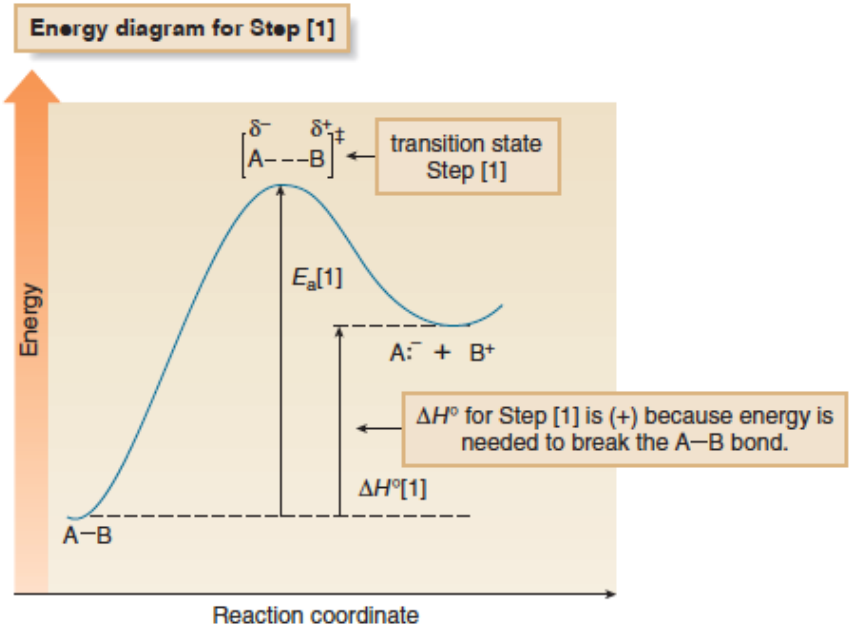
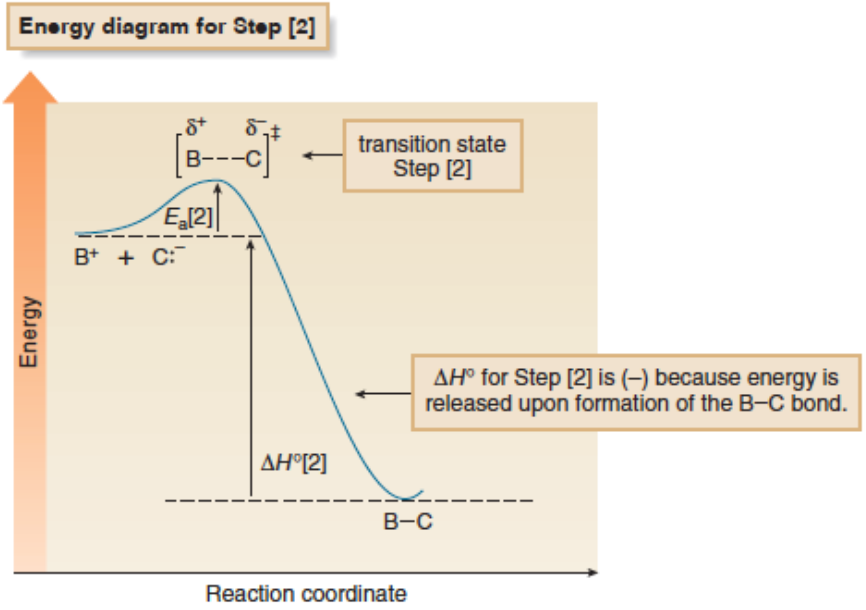


Diagrama energético – Rx 2 pasos

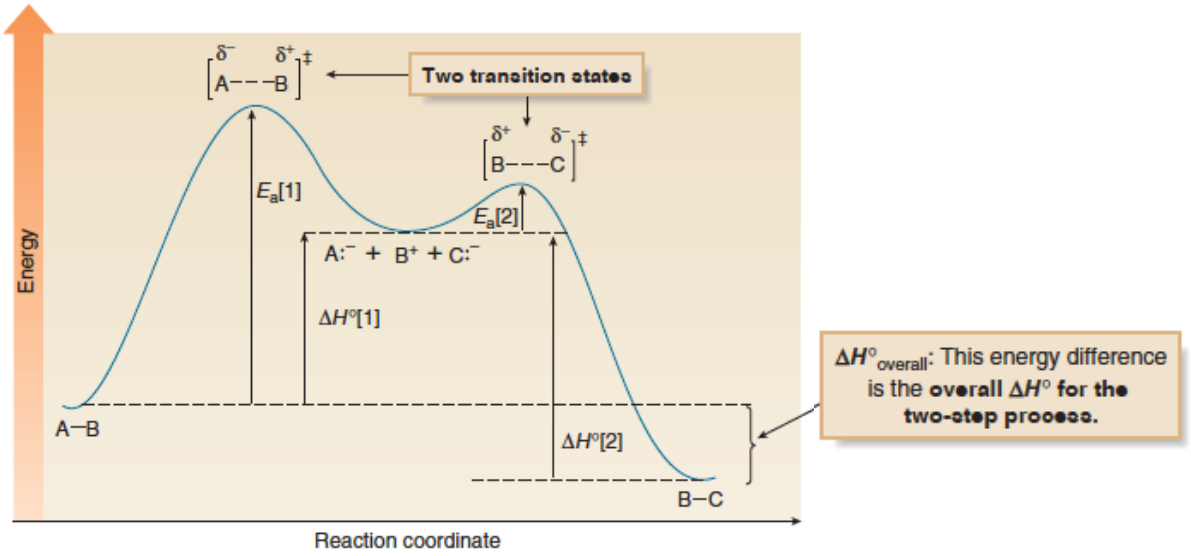
Paso 1: es endotérmic, ya que se necesita energía para romper el enlace A-B, haciendo ΔHº positivo. Por lo tanto los P tienen mayor energía que los reactivos. En el ET el enlace A-B está parcialmente roto.





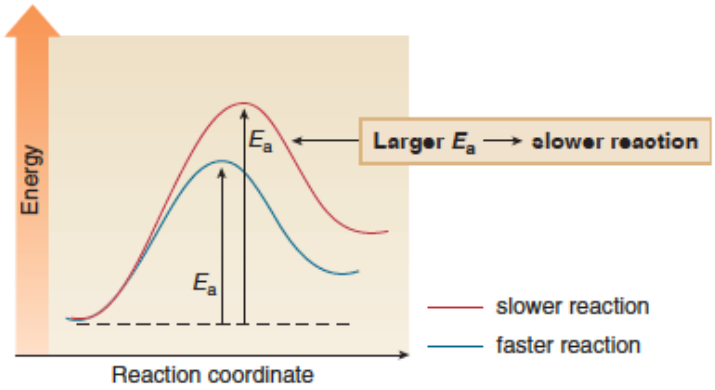
Paso 2: es enxotérmico, ya que se libera energía al formar el enlace B-C, haciendo ΔHº negativo. Por lo tanto los P tienen menor energía que los reactivos del paso 2. En el ET el enlace B-C está parcialmente formado.

Diagrama energético – Rx 2 pasos



El proceso completo se representa por un solo diagrama de energía que combina ambos pasos. Ya que existen 2 pasos, hay dos ET, cado uno con una barrera energética correspondiente. Estos ETs está separados por un mínimo de energía, donde se coloca el intermediario reactivo B+. Como se asumió que el proceso completo de 2 etapas es exotérmico, la diferencia de energía final de reactantes y P tiene un valor negativo, por lo que los P tiene menor energía que los reactantes.
La barrera energética del paso 1 es de mayor energía que la del paso 2- esto es porque la ruptura de enlace del paso 1 requiere mayor energía que la formación del enlace en el paso 2. El ET de mayor energía, paso 1, es el paso más lento del mecanismo y es llamado el **paso determinante de velocidad**.

Cinética



- The *larger* the E_a, the *slower* the reaction.

Factores que influyen en la velocidad de reacción:

- The *higher* the concentration, the *faster* the rate. Increasing concentration increases the number of collisions between reacting molecules, which in turn increases the rate.

- The *higher* the temperature, the *faster* the rate. Increasing temperature increases the average kinetic energy of the reacting molecules. Because the kinetic energy of colliding molecules is used for bond cleavage, increasing the average kinetic energy increases the rate.

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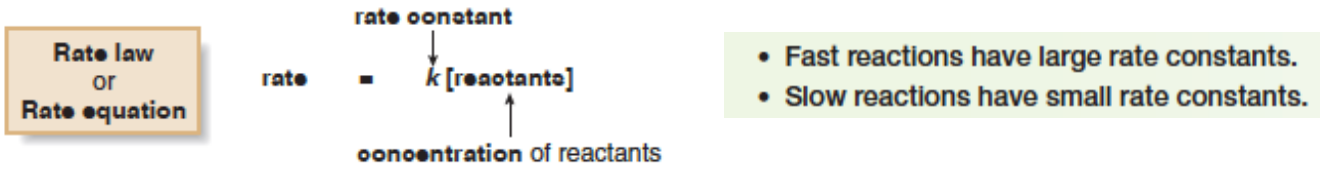
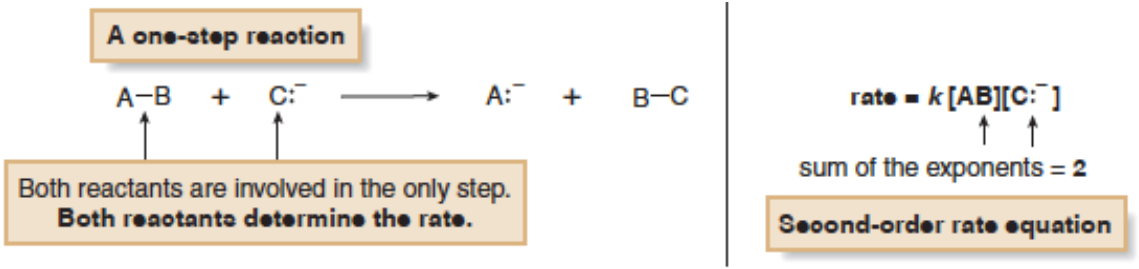
Cinética – Ley de velocidad

La velocidad de una reacción química está determinada al medir la disminución de la concentración de los reactantes en el tiempo o el aumento de la concentración de los P en el tiempo.

La ley de velocidad es una ecuación que muestra la relación entre la velocidad de Rx y la concentración de reactantes. Se determina experimentalmente y depende del mecanismo de reacción.



Bimolecular



Cinética – Ley de velocidad

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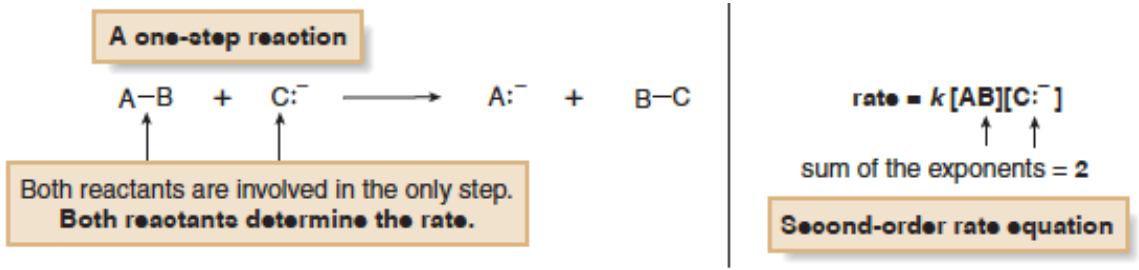
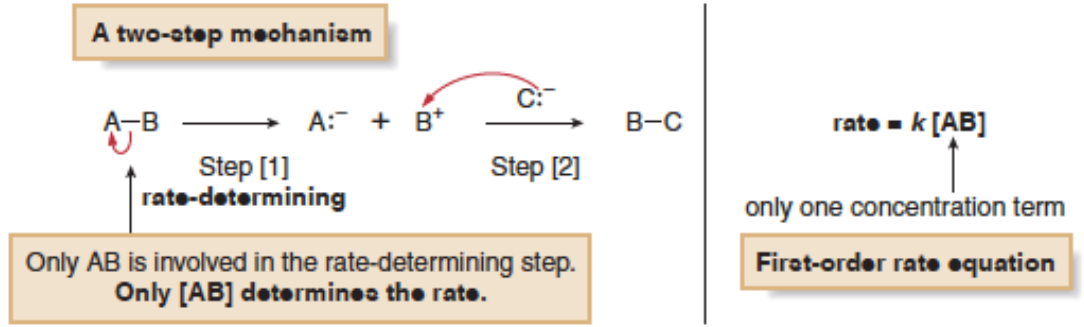


Unimolecular



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Ejercicios

Write a rate equation for each reaction, given the indicated mechanism.

a. $CH_3CH_2{-}Br + {}^{-}OH \longrightarrow CH_2{=}CH_2 + H_2O + Br^-$

b. $(CH_3)_3C{-}Br \xrightarrow[\text{slow}]{} (CH_3)_3C^+ + Br^- \xrightarrow[\text{fast}]{{}^{-}OH} (CH_3)_2C{=}CH_2 + H_2O$

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a. $CH_3CH_2{-}Br + {}^{-}OH \longrightarrow CH_2{=}CH_2 + H_2O + Br^{-}$ one step

rate = $k[CH_3CH_2Br][{}^{-}OH]$

b. $(CH_3)_3C{-}Br \xrightarrow[\text{slow}]{} (CH_3)_3C^{+} + Br^{-} \xrightarrow[\text{fast}]{{}^{-}OH} (CH_3)_2C{=}CH_2 + H_2O$ two steps

The slow step determines the rate equation.

rate = $k[(CH_3)_3CBr]$

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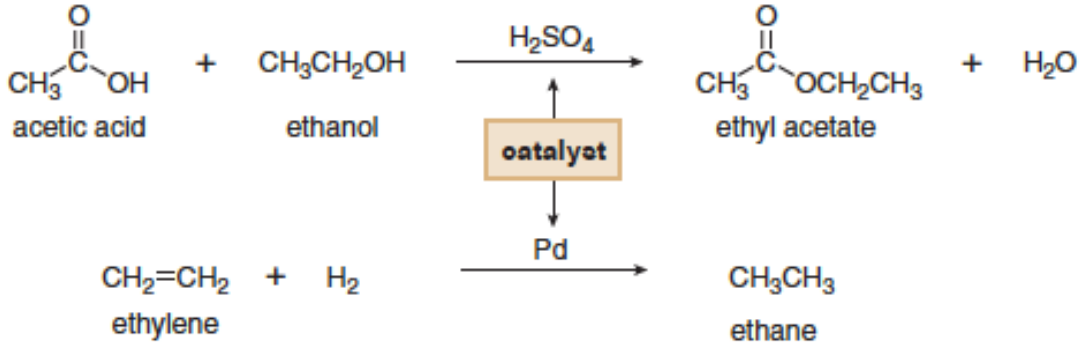
Catálisis

- A *catalyst* is a substance that speeds up the rate of a reaction. A catalyst is recovered unchanged in a reaction, and it does not appear in the product.



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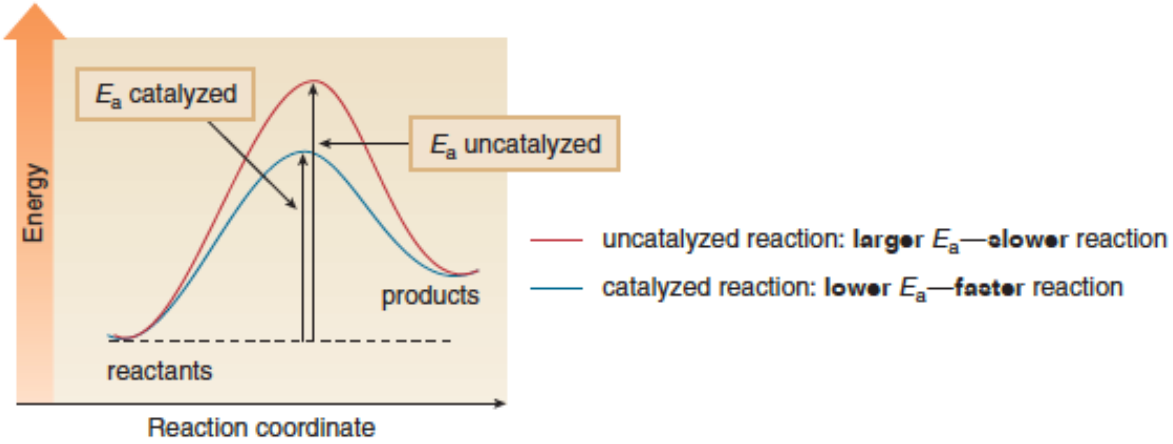

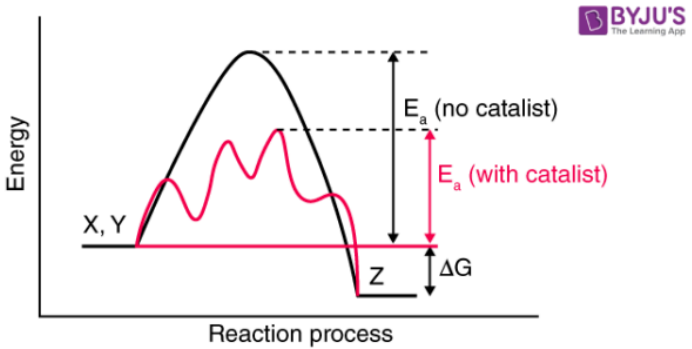

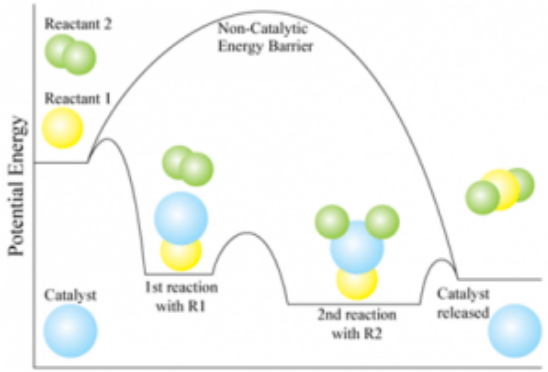

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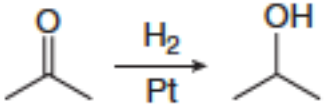
Ejercicios

Identify the catalyst in each equation.

a. $CH_2{=}CH_2 \xrightarrow[H_2SO_4]{H_2O} CH_3CH_2OH$

b. $CH_3Cl \xrightarrow[^-OH]{I^-} CH_3OH + Cl^-$

c. 

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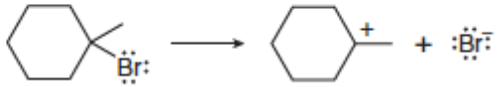
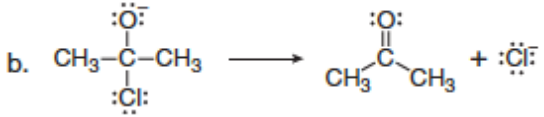
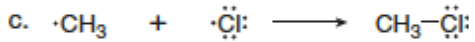
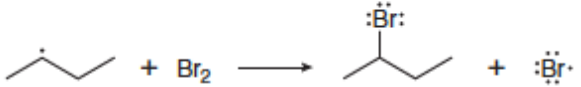
Ejercicios

Use full-headed or half-headed curved arrows to show the movement of electrons in each reaction.

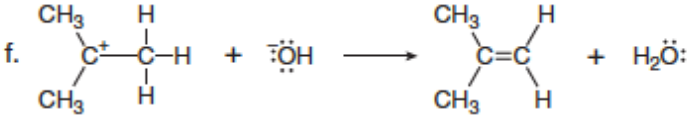
a. 

b. 

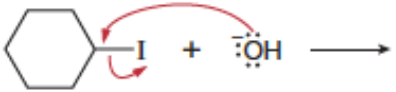
c. 

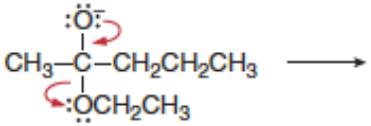
d. 

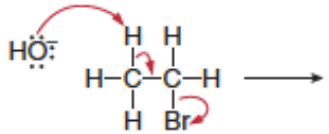
e. 

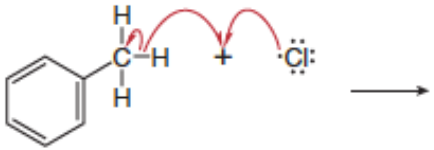
f. 

Draw the products of each reaction by following the curved arrows.

a. 

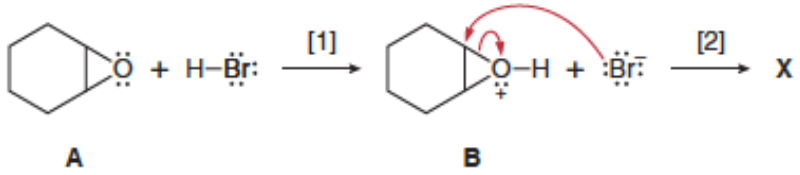
b. 

c. 

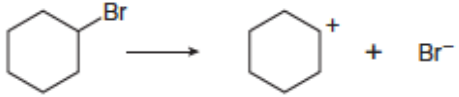
d. 

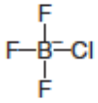
Ejercicios

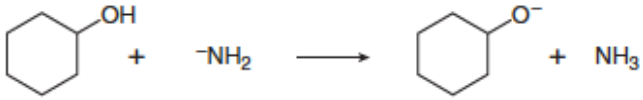
(a) Draw in the curved arrows to show how **A** is converted to **B** in Step [1]. (b) Identify **X**, using the curved arrows drawn for Step [2].

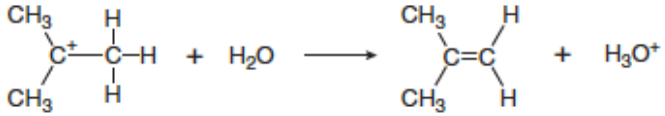


Draw the transition state for each reaction.

a. 

b. $BF_3 + Cl^- \longrightarrow$ 

c. 

d. 

Ejercicios

Draw an energy diagram for each reaction. Label the axes, the starting material, product, transition state, $\Delta H°$, and E_a.

a. A concerted, exothermic reaction with a low energy of activation.
b. A one-step endothermic reaction with a high energy of activation.
c. A two-step reaction, **A → B → C,** in which the relative energy of the compounds is **A < C < B,** and the step **A → B** is rate-determining.
d. A concerted reaction with $\Delta H° = -80$ kJ/mol and $E_a = 16$ kJ/mol.

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