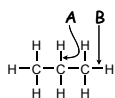
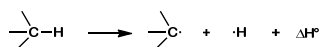


When a bond is broken two radicals are produced.



Which C-H bond of propane, A or B, is stronger?

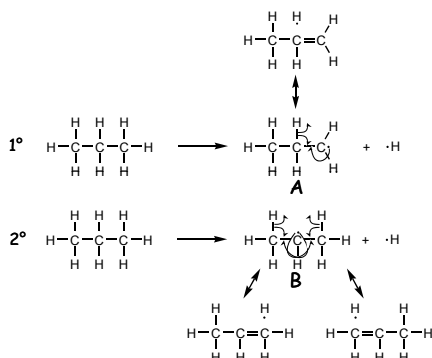
1

Which radical is more stable?



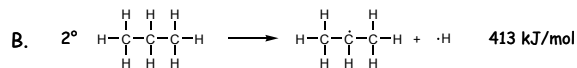
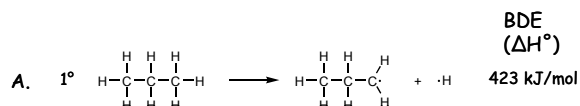
2

Which radical is more stable?



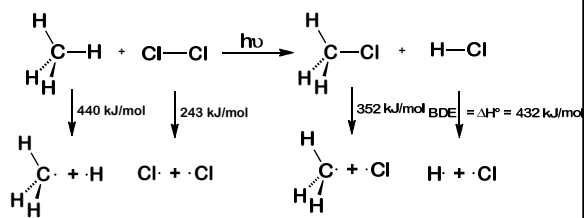
3

Which reaction has the larger BDE (ΔH°)?



4

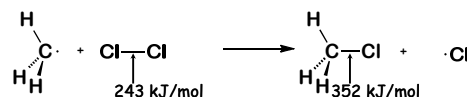
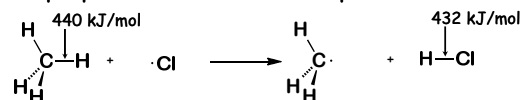
Using bond dissociation energies (BDE) estimate the ΔH° of the following reaction.



bonds of reactants	-	bonds of products	=	heat of reaction
(440 + 243)		(352 + 432)		
683	-	784	=	-101 kJ/mol

A. -784 B. +682 C. -101 D. +439 E. +32 F. 0

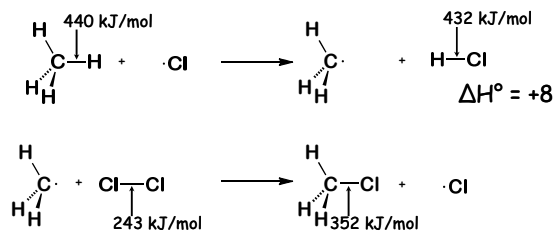
The mechanism for the chlorination of methane has been proposed to involve two steps?



What is the ΔH° of the first step in the accepted mechanism of the chlorination of methane?

A. -440 B. +109 C. -8 D. +8 E. -109 F. +440

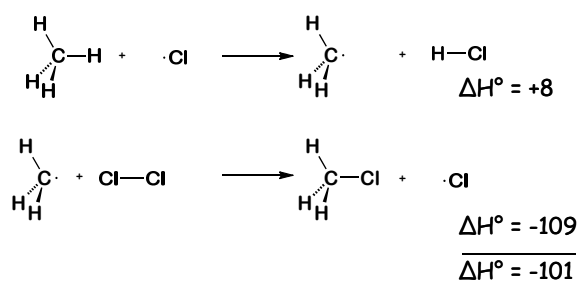
The chlorination of methane involves two steps?



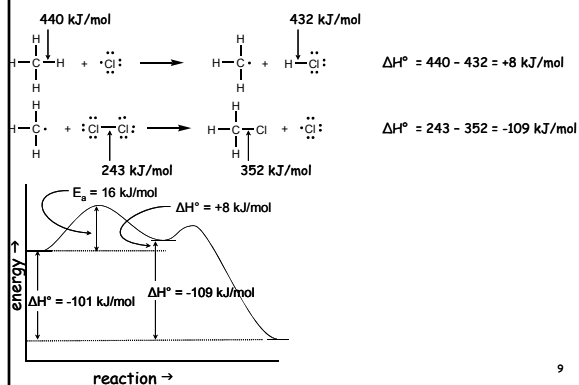
What is the ΔH° of the second step in the accepted mechanism of the chlorination of methane?

- A. -440 B. +109 C. -8 D. +8 E. -109 F. +440

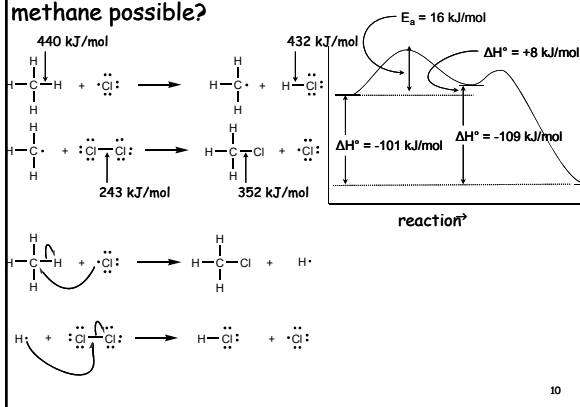
What is the overall ΔH° for the chlorination of methane?



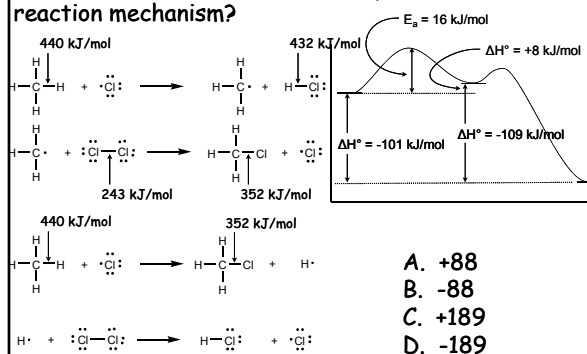
What is the slow or rate determining step for the reaction?



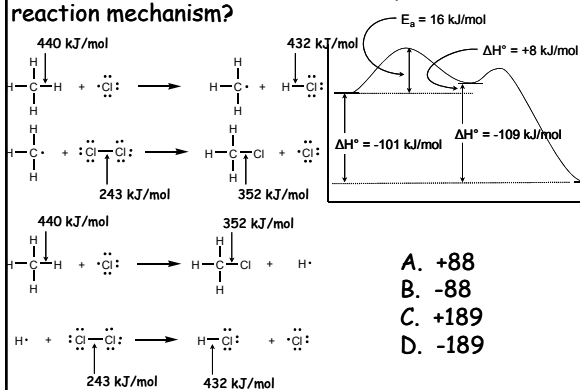
Are other mechanisms for the chlorination of methane possible?



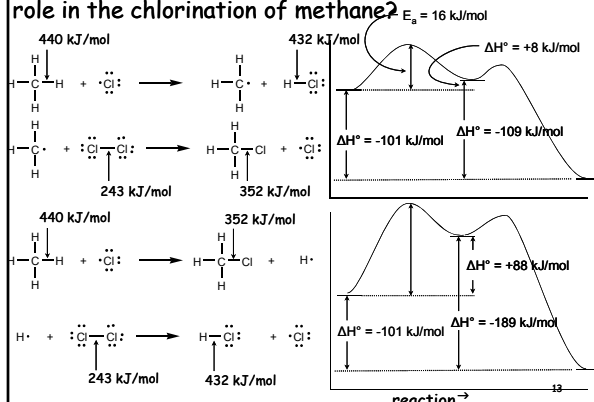
What is the ΔH° for the *first* step of the second reaction mechanism?



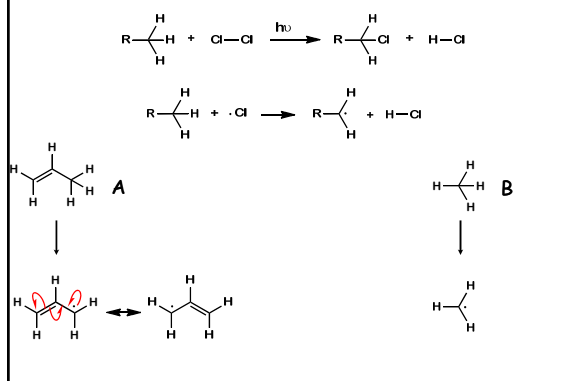
What is the ΔH° for the *second* step of the second reaction mechanism?



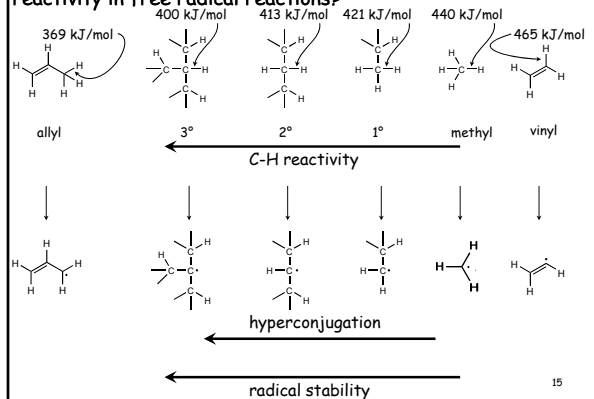
Why is the second mechanism unlikely to play a major role in the chlorination of methane?



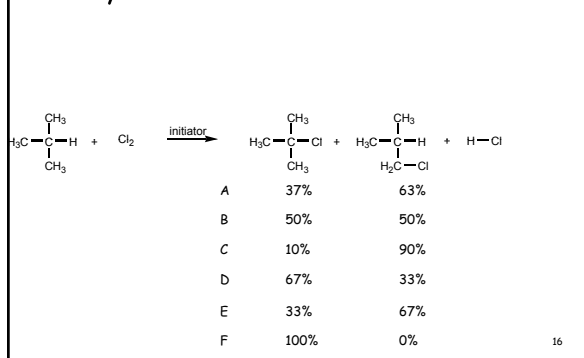
Which compound would be predicted to react faster in a free radical chlorination reaction?



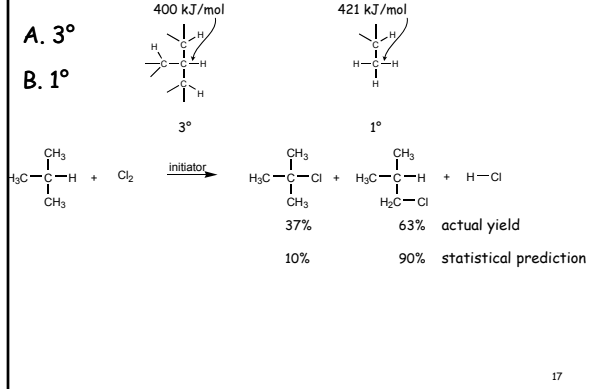
Do other different C-H bonds show different rates of reactivity in free radical reactions?



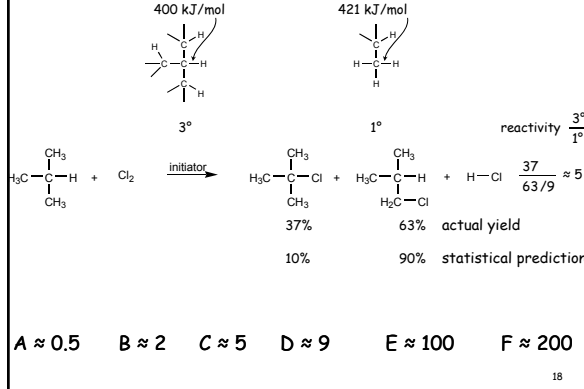
What would be predicted to be the product yields of the following compound if all C-H bonds had the same reactivity?



From the product yields which hydrogen, 3° or 1°, is most reactive?



How many times more reactive is 3° compared to a 1° C-H bond?



What is the selectivity of bromination in this reaction?

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \text{Cl}_2 \xrightarrow{\text{initiator}} \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{Cl} + \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{Cl} + \text{H}-\text{Cl}$$

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \text{Br}_2 \xrightarrow{\text{initiator}} \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{Br} + \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{Br} + \text{H}-\text{Br}$$

400 kJ/mol (3°) 421 kJ/mol (1°) reactivity $\frac{3^\circ}{1^\circ} \approx 5$
 243 kJ/mol 349 kJ/mol $\frac{37}{63/9} \approx 5$
 99.4% 0.6% $\frac{99.4}{0.6/9} \approx 1600$

19

What is the mechanism of this reaction?

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\cdot + \text{H}-\text{Cl} \quad \Delta H^\circ = 400 - 432 = -32 \text{ kJ/mol}$$

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\cdot + \text{Cl}-\text{Cl} \rightarrow \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{Cl} + \cdot\text{Cl} \quad \Delta H^\circ = 243 - 349 = -106 \text{ kJ/mol}$$

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \text{Cl}_2 \xrightarrow{\text{initiator}} \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{Cl} + \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{Cl} + \text{H}-\text{Cl}$$

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \text{Br}_2 \xrightarrow{\text{initiator}} \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{Br} + \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{Br} + \text{H}-\text{Br}$$

Is the first step exothermic? A. yes B. no
 What is the ΔH° for the overall reaction?

20

Why isn't chlorination more selective?

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\cdot + \text{H}-\text{Cl} \quad \Delta H^\circ = 400 - 432 = -32 \text{ kJ/mol}$$

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\cdot + \text{Cl}-\text{Cl} \rightarrow \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{Cl} + \cdot\text{Cl} \quad \Delta H^\circ = 243 - 349 = -106 \text{ kJ/mol}$$

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \text{Cl}_2 \xrightarrow{\text{initiator}} \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{Cl} + \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{Cl} + \text{H}-\text{Cl}$$

21

What is the difference in ΔH° of the first two steps?

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\cdot + \text{H}-\text{Cl} \quad \Delta H^\circ = 400 - 432 = -32 \text{ kJ/mol}$$

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\cdot + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \text{H}-\text{Cl} \quad \Delta H^\circ = 421 - 432 = -11 \text{ kJ/mol}$$

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \text{Cl}_2 \xrightarrow{\text{initiator}} \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{Cl} + \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{Cl} + \text{H}-\text{Cl}$$

22

What is the reactivity of 3° to 1° if $\Delta\Delta H^\ddagger = 21 \text{ kJ/mol}$?

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\cdot + \text{H}-\text{Cl} \quad \Delta H^\circ = 400 - 432 = -32 \text{ kJ/mol}$$

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\cdot + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \text{H}-\text{Cl} \quad \Delta H^\circ = 421 - 432 = -11 \text{ kJ/mol}$$

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \text{Cl}_2 \xrightarrow{\text{initiator}} \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{Cl} + \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{Cl} + \text{H}-\text{Cl}$$

A = 1
 B = 5
 C = 50
 D = 500
 E = 5000

transition state theory (Ch 6)
 $K_{eq} = 10^{21/5.7} = 10^{3.7} \approx 5000$

23

Why isn't chlorination more selective?

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\cdot + \text{H}-\text{Cl} \quad \Delta H^\circ = 400 - 432 = -32 \text{ kJ/mol}$$

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\cdot + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \text{H}-\text{Cl} \quad \Delta H^\circ = 421 - 432 = -11 \text{ kJ/mol}$$

$$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{H} + \text{Cl}_2 \xrightarrow{\text{initiator}} \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{Cl} + \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{Cl} + \text{H}-\text{Cl}$$

A = 1
 B = 5
 C = 50
 D = 500
 E = 5000

24

