

Organic Chemistry I

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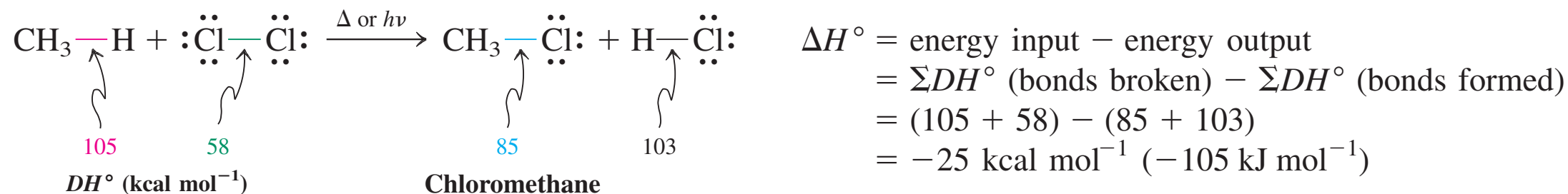
Organic Chemistry, *Structure and Function* (7th edition)

By *P. Vollhardt* and *N. Schore*, Elsevier, 2014

Halogenation of Alkane: The Radical Chain Mechanism

Alkanes undergo chemical transformations when subjected to pyrolysis, and that these processes include the formation of radical intermediates.

Chlorination reaction:



When methane and chlorine gas are mixed in the dark at room temperature, no reaction occurs.

The mixture must be heated to a temperature above 300 °C (denoted by Δ) or irradiated with ultraviolet light (denoted by $h\nu$) before a reaction takes place.

The reaction is exothermic (heat releasing).

Further substitution leads to dichloromethane (methylene chloride, CH₂Cl₂), trichloromethane (chloroform, CHCl₃), and tetrachloromethane (carbon tetrachloride, CCl₄).

The mechanism explains the experimental conditions required for reaction

A **mechanism** is a detailed, step-by-step description of all the changes in bonding that occur in a reaction.

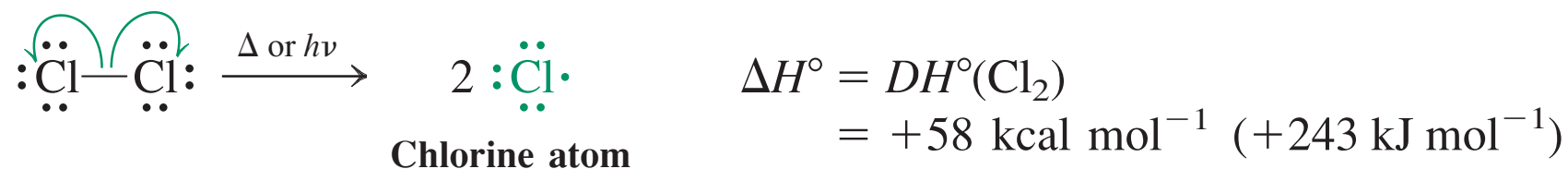
Even simple reactions may consist of several separate steps.

The mechanism shows the sequence in which bonds are broken and formed, as well as the energy changes associated with each step.

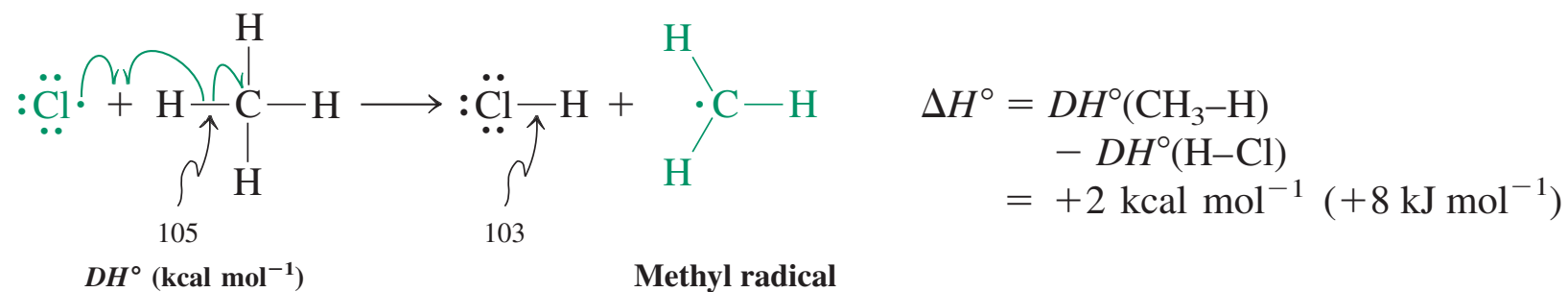
The mechanism for the chlorination of methane: **Radical reaction**

Radical reaction consists of three stages: initiation, propagation, and termination.

Initiation: Homolytic cleavage of the Cl–Cl bond

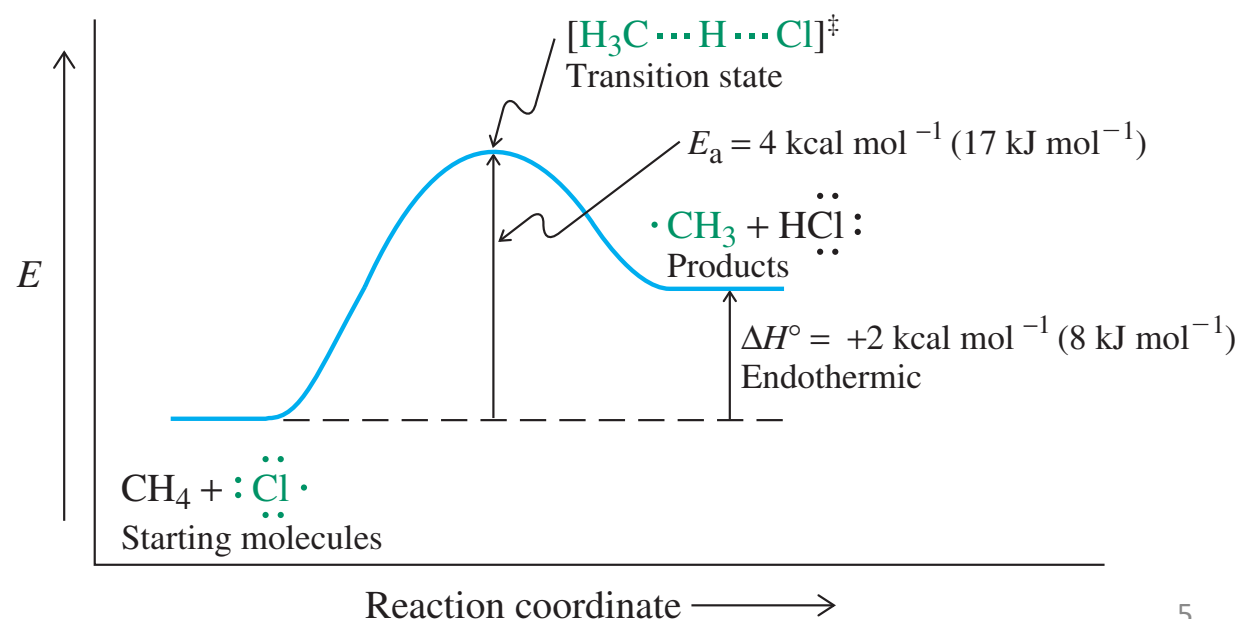
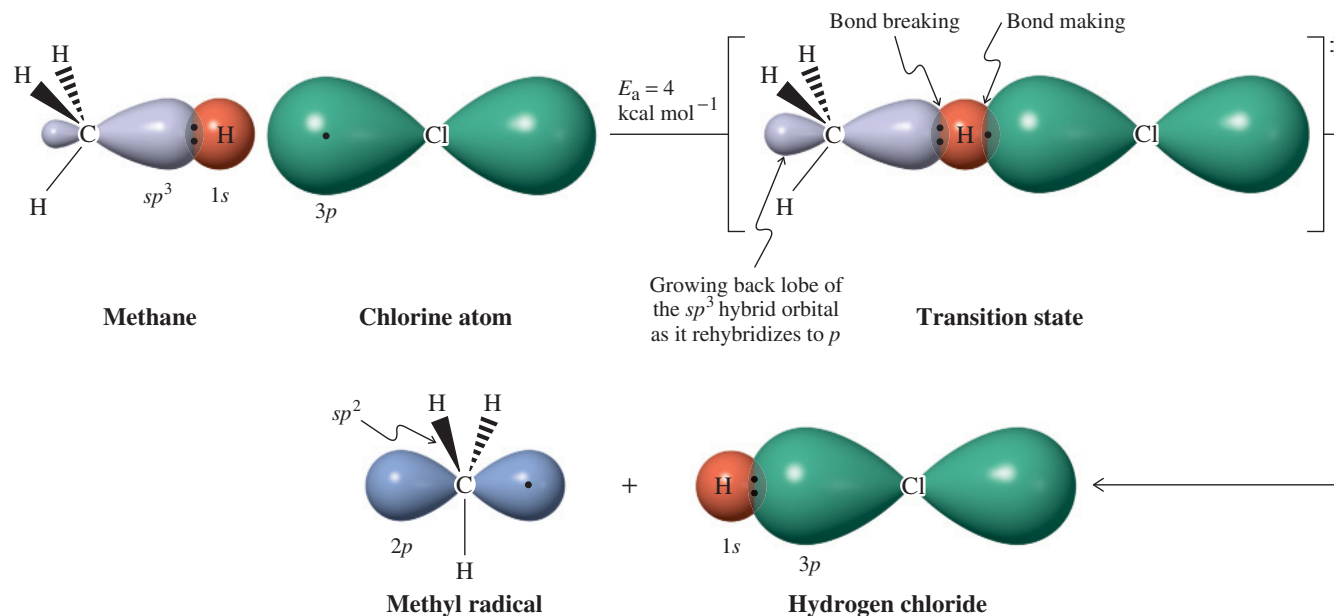


Propagation step 1: Abstraction of an H atom by $\cdot\text{Cl}$

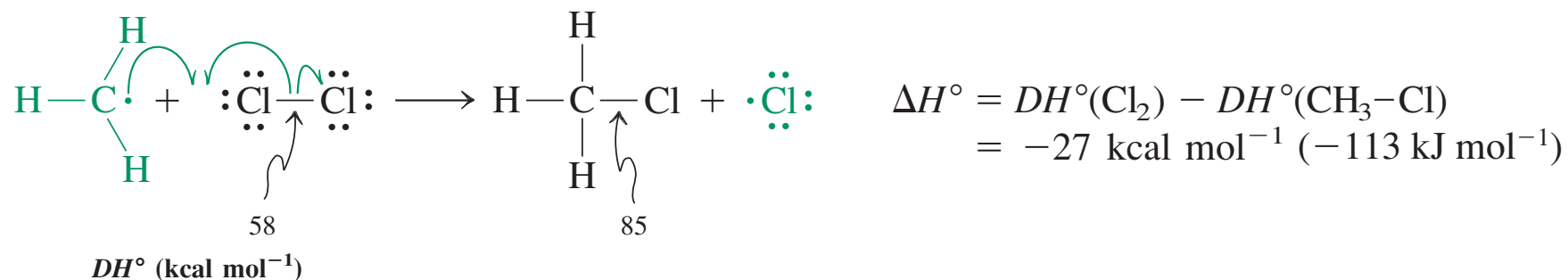


The ΔH° for this transformation (propagation step 1) is positive; the process is **endothermic** (heat absorbing), and its equilibrium is slightly **unfavorable**.

The transition state, which is labeled by the symbol \ddagger , is located only about 4 kcal mol⁻¹ above the starting materials.



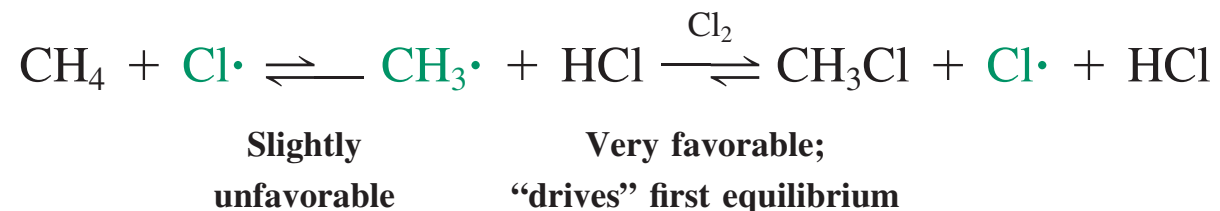
Propagation step 2: Abstraction of a Cl atom by $\cdot\text{CH}_3$



A new chlorine atom formed and re-enters propagation step 1 to react with a new molecule of methane. Thus, one propagation cycle is closed, and a new one begins, *without the need for another initiation step to take place.*

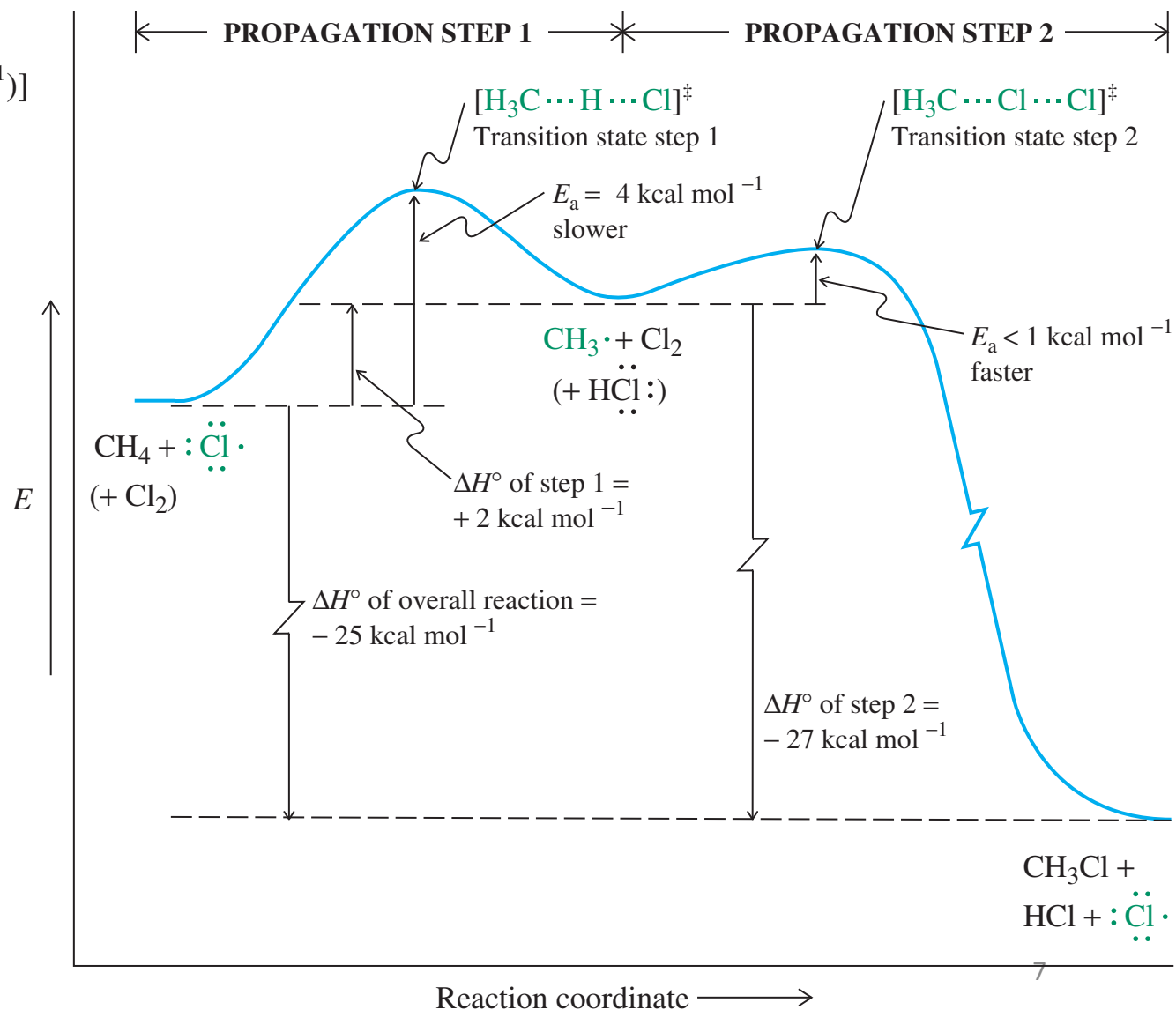
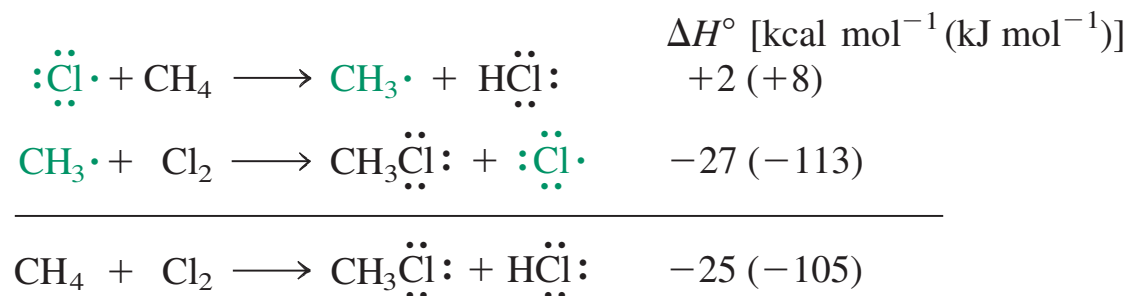
The propagation step 2 is exothermic, $-27 \text{ kcal mol}^{-1}$.

Because propagation step 2 is exothermic, the unfavorable equilibrium in the propagation step 1 is pushed toward the product by the rapid depletion of the methyl radical.

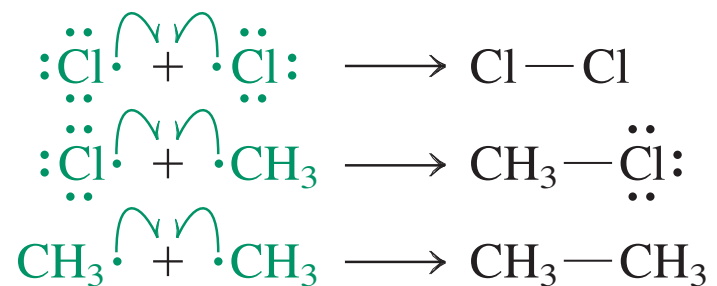


Propagation step 1 has the higher activation energy and is therefore slower than step 2.

The energy diagram also shows that the overall ΔH° of the reaction is $-25 \text{ kcal mol}^{-1}$.



Chain termination: Radical–radical combination

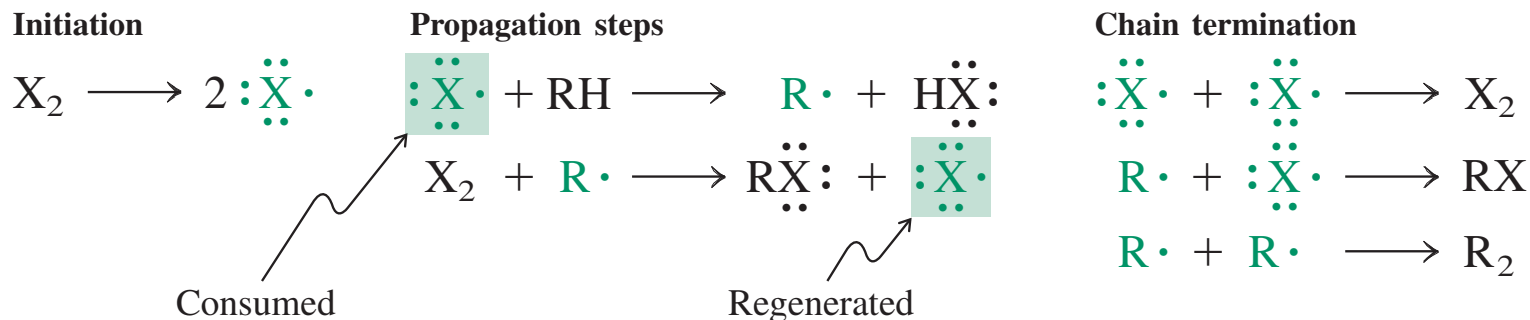


Radicals and free atoms are capable of undergoing direct covalent bonding with one another.

The concentrations of radicals and free atoms in the reaction mixture are very low, however, the chance of one radical or free atom finding another is small.

Small amounts of *ethane* are identified among the products of chlorination of methane.

A Radical Chain Mechanism



One of the practical problems in chlorinating methane is the control of product **selectivity**. The reaction does not stop at the formation of chloromethane but continues to form di-, tri-, and tetrachloromethane by further substitution.

A practical solution to this problem is the use of a large excess of methane in the reaction.

Under such conditions, the reactive intermediate chlorine atom is at any given moment surrounded by many more methane molecules than product CH_3Cl . Thus, the chance of $\cdot\text{Cl}$ finding CH_3Cl to eventually make CH_2Cl_2 is greatly diminished, and product selectivity is achieved.