Reaction Thermodynamics

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Reaction thermodynamics: free energy and equilibrium, enthalpy and entropy factor, calculation of enthalpy change *via* BDE, intermolecular & intramolecular reactions.

Reaction kinetics: rate constant and free energy of activation; free energy profiles for one-step, two-step and three-step reactions; catalyzed reactions: electrophilic and nucleophilic catalysis; kinetic control and thermodynamic control of reactions; isotope effect: primary and β-secondary kinetic isotopic effect (k_H / k_D); principle of microscopic reversibility; Hammond's postulate.

Any reaction has associated with it changes in enthalpy (AH), entropy (AS), and free energy (AG). The principles of thermodynamics assure us that AH, AS, and AG are independent of the reaction path. They are interrelated by the fundamental equation

$$\Delta G = \Delta H - T\,\Delta S$$

Furthermore, the value of ΔG is related to the equilibrium constant K for the reaction

$$\Delta G = -RT \ln K$$

Example 1:

Calculate the enthalpy change associated with hydrogenation of butene.

$$CH_3CH{=}CHCH_3 + H_2 \rightarrow CH_3CH_2CH_2CH_3$$

$$-\Delta H = \Sigma \text{ bond energies}_{\text{(formed)}} - \Sigma \text{ bond energies}_{\text{(broken)}}$$

Bonds formed (kcal/mol):		Bonds broken (kcal/mol):	
2 C–H	196.4	H–H	103.2
C–C	80.5	C=C	145
	276.9		248.2

$$\Delta H = -276.9 - (-248.2) = -28.7 \text{ kcal/mol}$$

The hydrogenation is therefore calculated to be exothermic by about 29 kcal/mol.

There are extensive compilations of ΔH_f and ΔG_f for many compounds. The subscript *f* designates these as, respectively, the enthalpies and free energies of formation of the compound from its constituent elements. The superscript ° is used to designate data that refer to the substance in its standard state, i.e., the pure substance at 25° C and 1 atm. The compiled data can be used to calculate the enthalpy or free energy of a given reaction if the data are available for each reactant and product:

$$\Delta H^\circ = \Sigma \Delta H^\circ_{f_{products}} - \Sigma \Delta H^\circ_{f_{reactants}}$$

$$\Delta G^\circ = \Sigma \Delta G^\circ_{f_{products}} - \Sigma \Delta G^\circ_{f_{reactants}}$$

Estimation of the free-energy change associated with a reaction permits the calculation of the equilibrium position for a reaction and indicates the feasibility of a given chemical process.

$$\Delta G = -RT \ln K$$

A positive ΔG° imposes a limit on the extent to which a reaction can occur.

For example, a ΔG° of 1.0 kcal/mol limits conversion to product at equilibrium to 15%.

An appreciably negative ΔG° indicates that The reaction is thermodynamically favorable.

Drawbacks:

There is an even more basic limitation to the usefulness of thermodynamic data for making predictions about reactions: Thermodynamics provides no information about the energy requirements of the pathways that a potential reaction can follow; that is, thermodynamics provides no information about the rates of chemical reactions.

In the absence of a relatively low-energy pathway, two molecules that can potentially undergo a highly exothermic reaction will coexist without reacting. Thus, even if a reaction is thermodynamically favorable, it will not occur at a significant rate unless there is a low-energy mechanism by which it can occur. It is therefore extremely important to develop an understanding of reaction mechanisms and the energy requirements and rates of the various steps by which organic reactions proceed.

Reaction Kinetics

Kinetic data can provide detailed insight into reaction mechanisms. The rate given reaction can be determined by following the disappearance of a reactant appearance of product. The extent of reaction is often measured

spectroscopically,
continuous pH measurement
Conductance measurement
Polarimetry

Transition-state theory

The nature of the rate constants kr can be discussed in terms of **transition-state theory.** This is a general theory for analyzing the energetic and entropic components of a reaction process.

In transition-state theory, a reaction is assumed to involve the formation of an activated complex that goes on to product at an extremely rapid rate. The rate of decomposition of the activated complex has been calculated from the assumptions of the theory to be $6 \times 10^{-12}\ s^{-1}$ at room temperature and is given by the expression

$$\text{rate of activated complex decomposition} = \frac{\kappa k T}{h}$$

in which κ is the transmission coefficient, which is usually taken to be 1, κ is Boltzmann's constant, h is Planck's constant, and T is absolute temperature. The rate of reaction is thus given by the following expression:

$$\text{rate of reaction} = \frac{\kappa k T}{h}[\text{activated complex}]$$

If the activated complex is considered to be in equilibrium with its component molecules, the attainment of the transition state (T.S.) can be treated as being analogous to a bimolecular reaction:

$$A + B \rightarrow C$$

$$A + B \rightleftharpoons T.S. \rightarrow C$$

$$K^{\ddagger} = \frac{[T.S.]}{[A][B]}$$

The position of this equilibrium is related to the free energy required for attainment of the transition state. The double-dagger superscript (*) is used to specify that the process under consideration involves a transition state or activated complex:

$$\Delta G^{\ddagger} = -RT \ln K^{\ddagger}$$

This free energy is referred to as the free energy of activation. The rate of the reaction is then given by

$$\text{rate} = \frac{\kappa k T}{h}[\text{T.S.}]$$

$$[\text{T.S.}] = K^{\ddagger}[\text{A}][\text{B}]$$

Since

$$K^{\ddagger} = e^{-\Delta G^{\ddagger}/RT}$$

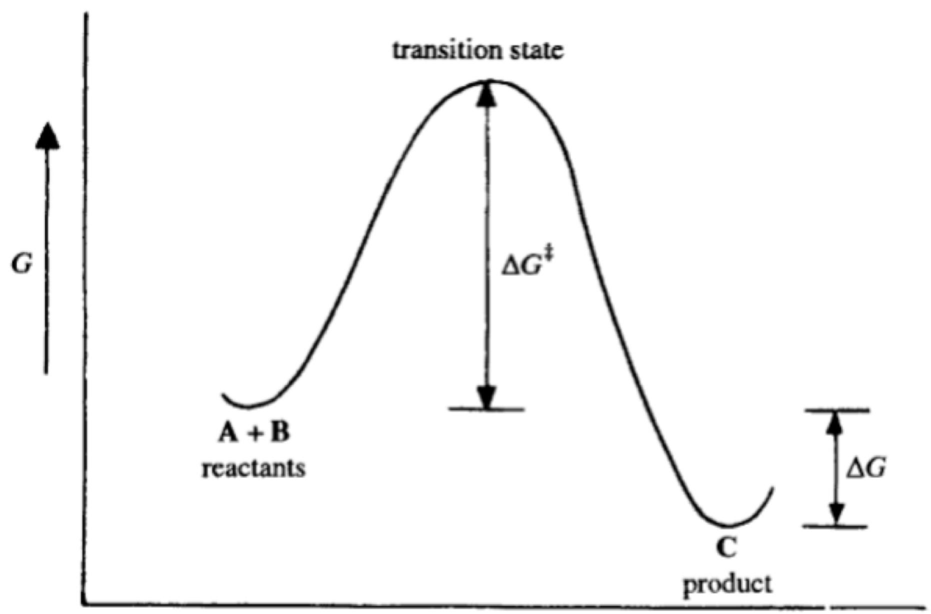
$$\text{rate} = \frac{\kappa k T}{h} e^{-\Delta G^{\ddagger}/RT}[\text{A}][\text{B}]$$

Comparison with the form of the expression for the rate of any single reaction step

$$\text{rate} = k_r[\text{A}][\text{B}]$$

reveals that the magnitude of ΔG^* will be the factor that determines the magnitude of kr at any given temperature.

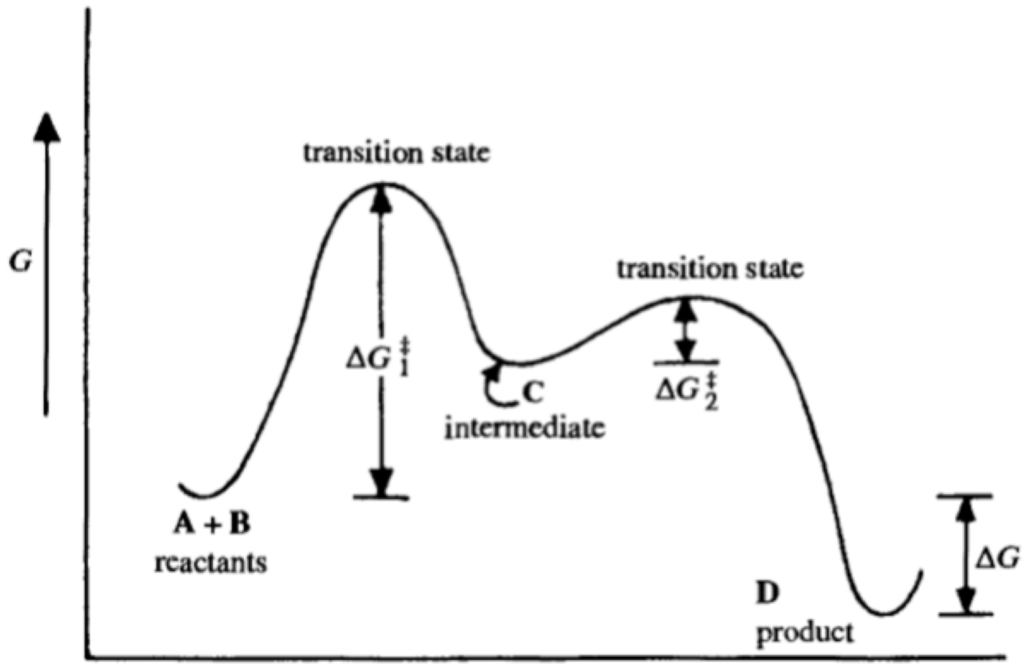
Qualitative features of reaction mechanisms are often described in the context of transition-state theory and illustrated with potential energy diagrams.



Reaction coordinate for a single-step reaction

Reaction coordinate for a single-step reaction

Reaction coordinate for a Two-step reaction



Reaction coordinate for a two-step reaction

The principle of microscopic reversibility

The principle of microscopic reversibility arises directly from transition-state theory.

The same pathway that is traveled in the forward direction of a reaction will be traveled in the reverse direction, since it affords the lowest energy barrier for either process.

The temperature dependence of reaction rates permits evaluation of the enthalpy and entropy components of the free energy of activation. The terms corresponding to kr can be expressed as

--

$$k_r = \frac{\kappa kT}{h}(e^{-\Delta H^{\ddagger}/RT})(e^{\Delta S^{\ddagger}/R})$$

The term $(\kappa kT/h)e^{\Delta S^{\ddagger}/R}$ varies only slightly with T compared to $e^{-\Delta H^{\ddagger}/RT}$ because of the exponential nature of the latter. To a good approximation, then

--

$$\frac{k_r}{T} = Ce^{-\Delta H^{\ddagger}/RT}$$

$$\ln\frac{k_r}{T} = \frac{-\Delta H^{\ddagger}}{RT} + C'$$

A plot of $\ln(k_r/T)$ versus $1/T$ is then a straight line, and its slope is $-\Delta H^\ddagger/R$. Once $\Delta H^\ddagger$ is determined in this manner, $\Delta S^\ddagger$ is available from the relationship

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger}{T} + R \ln \frac{hk_r}{\kappa k T} \tag{4.8}$$

The temperature dependence of reactions can also be expressed in terms of the Arrhenius equation:

$$k_r = Ae^{-E_a/RT}$$

$$\ln k_r = -E_a/RT + \ln A$$

Comparing the form of Eq. (4.9) with Eq. (4.5) indicates that A in the Arrhenius equation corresponds to $(\kappa kT/h)e^{\Delta S^{\ddagger}/R}$. The Arrhenius equation shows that a plot of $\ln k_r$ versus $1/T$ will have the slope $-E_a/R$. For reactions in solution at a constant pressure, $\Delta H^{\ddagger}$ and

$$E_a = \Delta H^{\ddagger} + RT$$

The magnitudes of ΔH^* and ΔS^* reflect transition-state structure. Atomic positions in the transition state do not correspond to their positions in the ground state. In particular, the reacting bonds will be partially formed and partially broken. The energy required for bond reorganization is reflected in the higher potential energy of the activated complex and corresponds to the enthalpy of activation ΔH^*. The entropy of activation is a measure of the degree of order produced in the formation of the activated complex. If translational, vibrational, or rotational degrees of freedom are lost in going to the transition state, there will be a decrease in the total entropy of the system. Conversely, an increase of translational, vibrational, or rotational degrees of freedom will result in a positive entropy of activation.

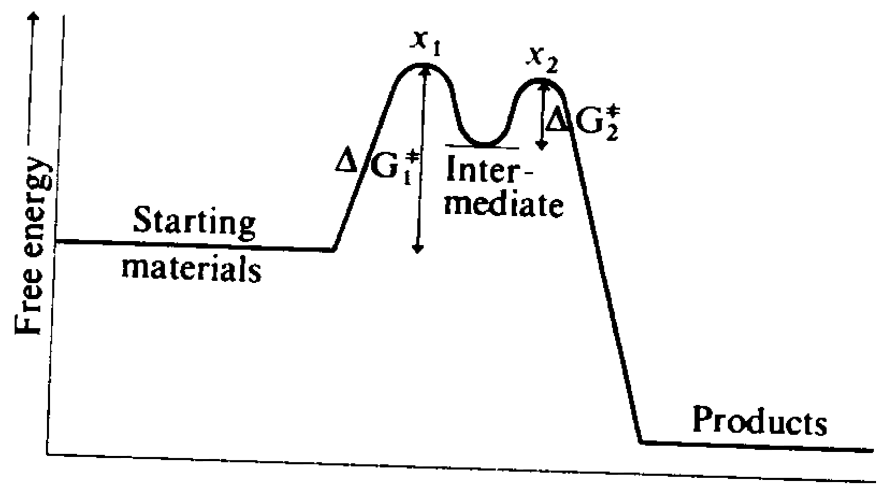
To be Continued....

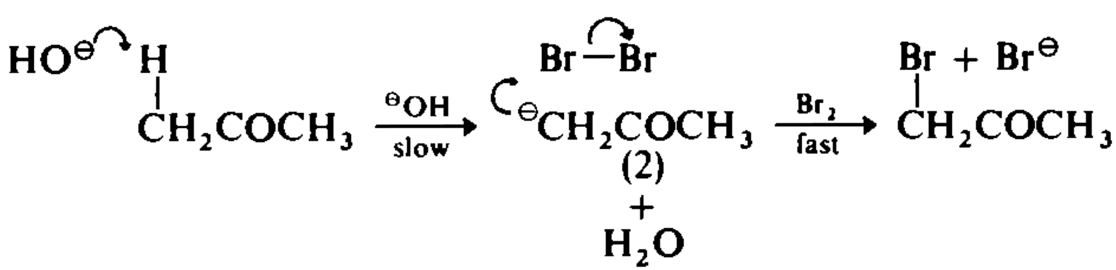
Reference:

Carey and Sundberg-Advance Organic Chemistry-Part-A

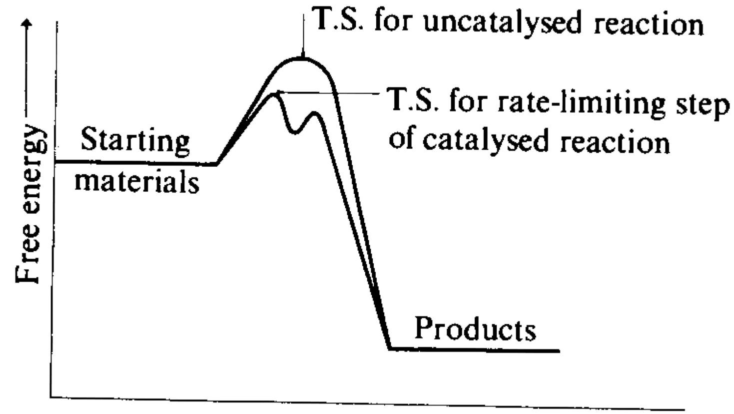
$$CH_3COCH_3 + Br_2 \xrightarrow{^{\ominus}OH} CH_3COCH_2Br + HBr$$

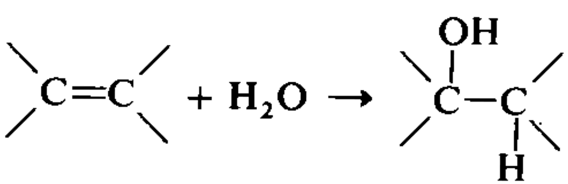
$$\text{Rate} = k[CH_3COCH_3][^{\ominus}OH]$$

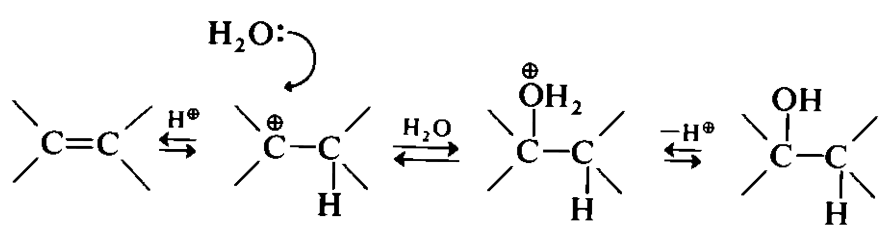




The effect of a catalyst is to increase the rate at which a reaction will take place; this is done by making available an alternative path of less energetic demand, often through the formation of a new, and more







Kinetic versus thermodynamic control

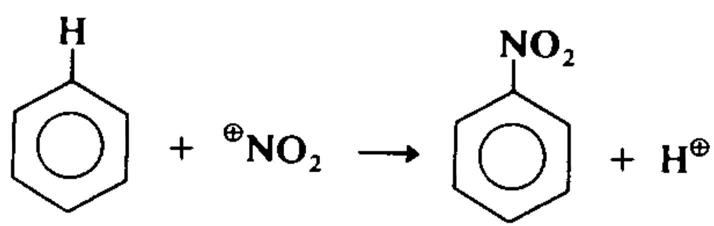
dynamic or *equilibrium control*. Thus the nitration of methylbenzene is found to be kinetically controlled, whereas the Friedel–Crafts alkylation of the same species is often thermodynamically controlled (p. 163). The form of control that operates may also be influenced by the reaction condition, thus the sulphonation of naphthalene with concentrated H_2SO_4 at 80° is essentially kinetically controlled, whereas at 160° it is thermodynamically controlled (p. 164).

The use of isotopes

Thus in the oxidation

$$Ph_2C\begin{smallmatrix}OH\\ H\end{smallmatrix} \xrightarrow[{}^{\ominus}OH]{MnO_4^{\ominus}} Ph_2C{=}O$$

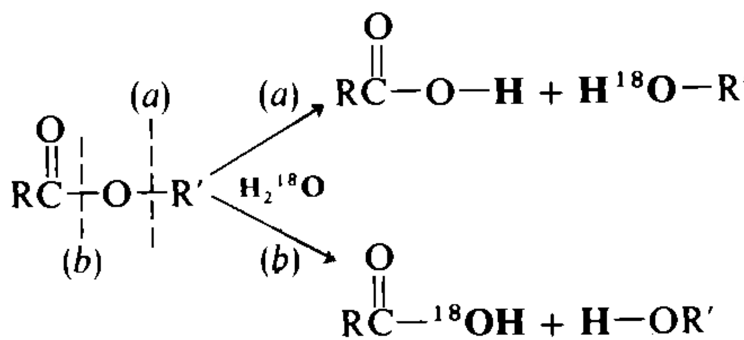
it is found that Ph_2CHOH is oxidised 6·7 times as rapidly as Ph_2CDOH; the reaction is said to exhibit a *primary kinetic isotope effect*, and breaking of the C—H bond must clearly be involved in the rate-limiting step of the reaction. By contrast benzene, C_6H_6, and hexadeuterobenzene, C_6D_6, are found to undergo nitration at essentially the same rate, and C—H bond-breaking, that must occur at some stage in the overall process,

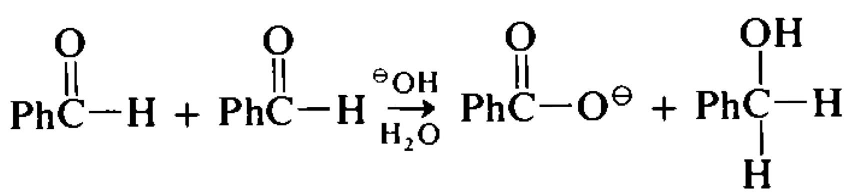


thus cannot be involved in the rate-limiting step (*cf.* p. 136).

$$HO^{\ominus} + {}^{12(14)}CH_3{-}I \longrightarrow HO{-}{}^{12(14)}CH_3 + I^{\ominus} \qquad \frac{k_{^{12}C}}{k_{^{14}C}} = 1{\cdot}09\ (25^{\circ})$$

$$PhCH_2{-}{}^{35(37)}Cl + H_2O \longrightarrow PhCH_2{-}OH + H^{\oplus}\,{}^{35(37)}Cl^{\ominus} \qquad \frac{k_{^{35}Cl}}{k_{^{37}Cl}} = 1{\cdot}0076\ (25^{\circ})$$


(a)
(b)
H₂¹⁸O
RC—O—H + H¹⁸O—R′
RC—¹⁸OH + H—OR′


PhC—H + PhC—H
⊖OH
H₂O
PhC—O⊖ + PhC—H