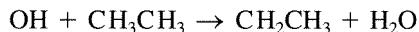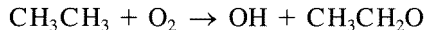# CHAPTER 2

Rate Constants of Elementary Reactions

2.1 | Elementary Reactions

Recall from the discussion of reaction networks in Chapter 1 that an elementary reaction must be written as it proceeds at the molecular level and represents an irreducible molecular event. An elementary reaction normally involves the breaking or making of a single chemical bond, although more rarely, two bonds are broken and two bonds are formed in what is denoted a four-center reaction. For example, the reaction:

$$OH + CH_3CH_3 \rightarrow CH_2CH_3 + H_2O$$

is a good candidate for possibly being an elementary reaction, while the reaction:

$$CH_3CH_3 + O_2 \rightarrow OH + CH_3CH_2O$$

is not. Whether or not a reaction is elementary must be determined by experimentation.

As stated in Chapter 1, an elementary reaction cannot be written arbitrarily and must be written the way it takes place. For example (see Table 1.4.3), the reaction:

$$2NO + O_2 \rightarrow 2NO_2 \tag{2.1.1}$$

cannot be written as:

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \tag{2.1.2}$$

since clearly there is no such entity as half a molecule of dioxygen. It is important to note the distinction between stoichiometric equations and elementary reactions (see Chapter 1) is that for the stoichiometric relation:

$$2NO + O_2 = 2NO_2 \tag{2.1.3}$$

one can write (although not preferred):

$$NO + \tfrac{1}{2}O_2 = NO_2 \tag{2.1.4}$$

The remainder of this chapter describes methods to determine the rate and temperature dependence of the rate of *elementary* reactions. This information is used to describe how reaction rates in general are appraised.

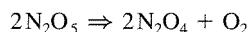## 2.2 | Arrhenius Temperature Dependence of the Rate Constant

The rate constant normally depends on the absolute temperature, and the functional form of this relationship was first proposed by Arrhenius in 1889 (see Rule III in Chapter 1) to be:

$$k = \overline{A}\exp\left[-E/(R_g T)\right] \tag{2.2.1}$$

where the activation energy, E, and the pre-exponential factor, $\overline{A}$, both do not depend on the absolute temperature. The Arrhenius form of the reaction rate constant is an empirical relationship. However, transition-state theory provides a justification for the Arrhenius formulation, as will be shown below. Note that the Arrhenius law (Equation 2.2.1) gives a linear relationship between $\ln k$ and T^{-1}.

EXAMPLE 2.2.1

The decomposition reaction:

$$2N_2O_5 \Rightarrow 2N_2O_4 + O_2$$

can proceed at temperatures below 100°C and the temperature dependence of the first-order rate constant has been measured. The data are:

T (K)	k (s^{-1})
288	1.04×10^{-5}
298	3.38×10^{-5}
313	2.47×10^{-4}
323	7.59×10^{-4}
338	4.87×10^{-3}

Suggest an experimental approach to obtain these rate constant data and calculate the activation energy and pre-exponential factor. (Adapted from C. G. Hill, *An Introduction to Chemical Engineering Kinetics & Reactor Design*, Wiley, New York, 1977.)

■ **Answer**

Note that the rate constants are for a first-order reaction. The material balance for a closed system at constant temperature is:

$$\frac{dn_{N_2O_5}}{dt} = -kn_{N_2O_5}$$

where $n_{N_2O_5}$ is the number of moles of N_2O_5. If the system is at constant volume (a closed vessel), then as the reaction proceeds the pressure will rise because there is a positive mole change with reaction. That is to say that the pressure will increase as N_2O_5 is reacted because the molar expansion factor is equal to 0.5. An expression for the total moles in the closed system can be written as:

$$n = n_0(1 + 0.5 f_{N_2O_5})$$

where n is the total number of moles in the system. The material balance on the closed system can be formulated in terms of the fractional conversion and integrated (see Example 1.5.2) to give:

$$f_{N_2O_5} = 1 - \exp(-kt)$$

Since the closed system is at constant T and V ($PV = nR_gT$):
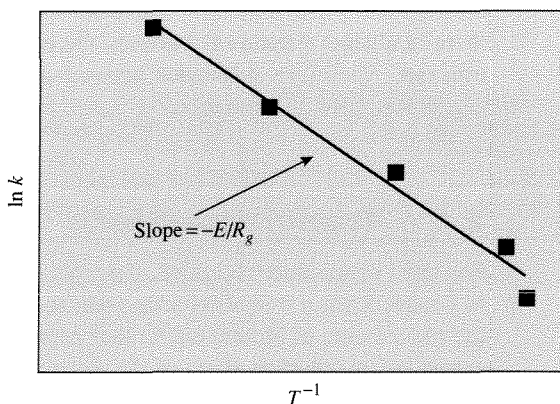
$$\frac{P}{P_0} = \frac{n}{n_0} = (1 + 0.5 f_{N_2O_5})$$

and the pressure can therefore be written as:

$$P = P_0[1.5 - 0.5 \exp(-kt)]$$

If the pressure rise in the closed system is monitored as a function of time, it is clear from the above expression how the rate constant can be obtained at each temperature.

In order to determine the pre-exponential factor and the activation energy, the $\ln k$ is plotted against T^{-1} as shown below:

From a linear regression analysis of the data, the slope and intercept can be obtained, and they are 1.21×10^4 and 30.4, respectively. Thus,

$$\text{slope} = -E/R_g \quad : \quad E = 24 \text{ kcal/mol}$$
$$\text{intercept} = \ln \overline{A} \quad : \quad \overline{A} = 1.54 \times 10^{13} \text{ s}^{-1}$$

Consider the following elementary reaction:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} S + W \tag{2.2.2}$$

At equilibrium,

$$k_1 C_A C_B = k_2 C_S C_W \tag{2.2.3}$$

and

$$K_C = \frac{k_1}{k_2} = \left(\frac{C_S C_W}{C_A C_B}\right)_{eq} \tag{2.2.4}$$

If the Arrhenius law is used for the reaction rate constants, Equation (2.2.4) can be written:

$$K_C = \frac{k_1}{k_2} = \left(\frac{\overline{A}_1}{\overline{A}_2}\right) \exp\left(\frac{E_2 - E_1}{R_g T}\right) = \left(\frac{C_S C_W}{C_A C_B}\right)_{eq} \tag{2.2.5}$$

It is easy to see from Equation (2.2.5) that if $(E_2 - E_1) > 0$ then the reaction is exothermic and likewise if $(E_2 - E_1) < 0$ it is endothermic (refer to Appendix A for temperature dependence of K_C). In a typical situation, the highest yields of products are desired. That is, the ratio $(C_S C_W / C_A C_B)_{eq}$ will be as large as possible. If the reaction is endothermic, Equation (2.2.5) suggests that in order to maximize the product yield, the reaction should be accomplished at the highest possible temperature. To do so, it is necessary to make $\exp[(E_2 - E_1)/(R_g T)]$ as large as possible by maximizing $(R_g T)$, since $(E_2 - E_1)$ is negative. Note that as the temperature increases, so do both the rates (forward and reverse). Thus, for endothermic reactions, the rate and yield must *both* increase with temperature. For exothermic reactions, there is always a trade-off between the equilibrium yield of products and the reaction rate. Therefore, a balance between rate and yield is used and the T chosen is dependent upon the situation.

2.3 | Transition-State Theory

For most elementary reactions, the rearrangement of atoms in going from reactants to products via a transition state (see, for example, Figure 1.1.1) proceeds through the movements of atomic nuclei that experience a potential energy field that is generated by the rapid motions of the electrons in the system. On this potential energy surface there will be a path of minimum energy expenditure for the reaction to proceed from reactants to products (reaction coordinate). The low energy positions of reactants and products on the potential energy surface will be separated by a higher energy region. The highest energy along the minimum energy pathway in going from reactants to products defines the transition state. As stated in Chapter 1, the transition state is not a reaction intermediate but rather a high energy configuration of a system in transit from one state to another.
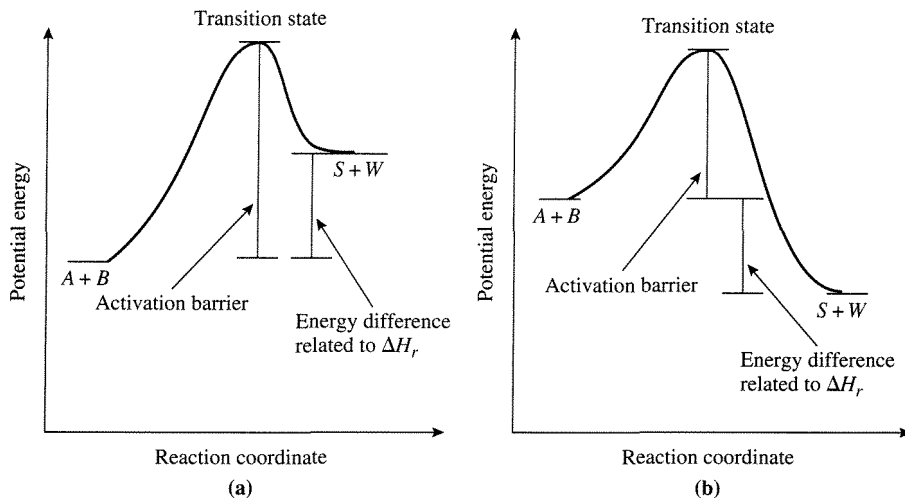
Figure 2.3.1 |
Potential energy profiles for the elementary reaction $A + B \rightarrow S + W$ for (a) an endothermic reaction and (b) an exothermic reaction.

The difference in energies of the reactants and products is related to the heat of reaction—a thermodynamic quantity. Figure 2.3.1 shows potential energy profiles for endothermic and exothermic elementary reactions.

Transition-state theory is used to calculate an elementary reaction that conforms to the energetic picture illustrated in Figure 2.3.1. How this is done is described next.

VIGNETTE 2.3.1 |

Since transition states exist for only picoseconds or less, the ability to observe them in real time requires femtosecond (10^{-15} s) time resolution. Femtochemistry, or chemistry on the femtosecond time scale, has been defined as the field of chemical dynamics concerned with the act of chemical transformation (i.e., the process of bond breaking and making). Femtochemistry requires ultrafast lasers to initiate and observe chemical reactions with femtosecond time resolution. Ahmed Zewail and his coworkers have carried out those types of experiments beginning in the late 1980s (*The Chemical Bond Structure and Dynamics*, ed. A. Zewail, Academic Press, San Diego, 1992). Figure 2.3.2 illustrates the femtochemistry experiment of "watching" excited ICN dissociate. The reaction is initiated by addition of light energy from a laser to bring ICN from the ground state to an excited state (upper to lower energy curves) where the I-CN is now completely in a repulsive state. As the I and CN depart from one another, the intermediates are observed. For example, at 100 femtoseconds, the distance between I and CN (I $\cdots$ CN) has increased 1 Å. These studies provide insights and help confirm theories of how reactions proceed at the molecular level.
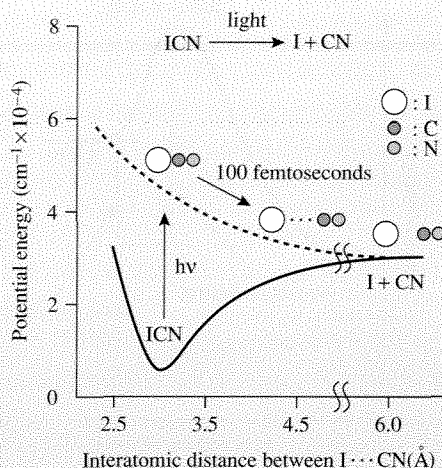
Figure 2.3.2 | Schematic diagram of the femtochemistry experiment of A. Zewail and coworkers.

Consider again the reaction given by Equation (2.2.2). At thermodynamic equilibrium, Equation (2.2.3) is satisfied. In the equilibrated system, there must also exist an equilibrium concentration of transition states: C_{TS}. The rates of the forward and the reverse reactions are equal, implying that there is an equivalent number of species traversing the activation barrier from either the reactant side or the product side. Thus,

$$k_1(C_A C_B)_{eq} = k_2(C_S C_W)_{eq} = \lambda C_{TS} \tag{2.3.1}$$

where λ is a frequency. Since C_{TS} is a thermodynamic quantity, it can be calculated from statistical thermodynamics. A fundamental assumption of transition-state theory is that if the system is perturbed from equilibrium by product removal, the rate of the forward reaction remains:

$$k_1 C_A C_B = \lambda C_{TS} \tag{2.3.2}$$

where C_{TS} is the concentration of transition-states in equilibrium with reactants A and B. The fictitious equilibrium:

$$A + B \rightleftharpoons TS \tag{2.3.3}$$

allows for the formulation of an equilibrium constant as shown below:

$$K^{\ddagger} = \frac{C_{TS}}{C_A C_B} \tag{2.3.4}$$

where

$$R_g T \ln K^{\ddagger} = -\Delta G_0^{\ddagger} = -\Delta H_0^{\ddagger} + T \Delta S_0^{\ddagger} \tag{2.3.5}$$

and $\Delta G_0^{\ddagger}$ is the change in the standard Gibbs function for the reaction given in Equation (2.3.3) and $\Delta H_0^{\ddagger}$ and $\Delta S_0^{\ddagger}$ are the corresponding changes in standard enthalpy and entropy, respectively. The subscript 0 is used to denote the standard state while the superscript $\ddagger$ denotes quantities pertaining to the transition state. By combining Equations (2.3.5) and (2.3.4), C_{TS} can be written as:

$$C_{TS} = \exp\left[\frac{\Delta S_0^{\ddagger}}{R_g}\right]\exp\left[\frac{-\Delta H_0^{\ddagger}}{R_g T}\right]C_A C_B \qquad (2.3.6)$$

Using this formulation for C_{TS} in Equation (2.3.2) allows the reaction rate to be of the form:

$$r = k_1 C_A C_B = \lambda \exp\left[\frac{\Delta S_0^{\ddagger}}{R_g}\right]\exp\left[\frac{-\Delta H_0^{\ddagger}}{R_g T}\right]C_A C_B \qquad (2.3.7)$$

A fundamental assumption of transition-state theory is that λ is a *universal frequency* and does not depend upon the nature of the reaction being considered. It can be proven that (see, for example, M. Boudart, *Kinetics of Chemical Processes*, Butterworth-Heinemann, 1991, pp. 41–45):
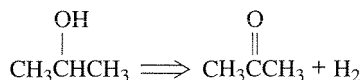
$$\lambda = \frac{\bar{k}T}{h} \qquad (2.3.8)$$

where h is Planck's constant and $\bar{k}$ is Boltzmann's constant. Using Equation (2.3.8) in Equation (2.3.7) gives:

$$r = \left(\frac{\bar{k}T}{h}\right)\exp\left[\frac{\Delta S_0^{\ddagger}}{R_g}\right]\exp\left[\frac{-\Delta H_0^{\ddagger}}{R_g T}\right]C_A C_B \qquad (2.3.9)$$

This is the general equation of transition-state theory in its thermodynamic form.

    Equation (2.3.9) helps in the comprehension of how reactions proceed. In order for a reaction to occur, it is necessary to overcome not just an energy barrier but a free energy barrier. That is to say, a reaction involves not only energy but also requires reaching a favorable configuration associated with a change in entropy. These two effects can often compensate each other. For example, McKenzie et al. [*J. Catal.*, **138** (1992) 547] investigated the reaction:

$$\underset{\text{CH}_3\overset{\overset{\displaystyle\text{OH}}{|}}{\text{CH}}\text{CH}_3}{} \Longrightarrow \underset{\text{CH}_3\overset{\overset{\displaystyle\text{O}}{||}}{\text{C}}\text{CH}_3 + \text{H}_2}{}$$

over a series of solid catalysts called hydrotalcites, and obtained the following data:

Catalyst	$\bar{A}$ (s^{-1})	E $(kJ(mol)^{-1})$
1	4.3×10^{12}	172
2	2.3×10^{11}	159
3	2.2×10^{10}	146
4	1.6×10^{9}	134

If Equation (2.3.9) is compared to Equation (2.2.1), then:

$$\overline{A} = \left(\frac{\overline{k}T}{h}\right)\exp\left[\frac{\Delta S_0^{\ddagger}}{R_g}\right] \tag{2.3.10}$$

$$E = \Delta H_0^{\ddagger} \tag{2.3.11}$$

The data of McKenzie et al. clearly show that as the energy barrier increases (higher E), the entropy of activation becomes more positive (larger $\Delta S_0^{\ddagger}$ implies more favorable configurational driving force for the reaction, since entropy will always attempt to be maximized). Thus, energy and entropy compensate in this example.

The Arrhenius form of the rate constant specifies that both $\overline{A}$ and E are independent of T. Note that when the formulation derived from transition-state theory is compared to the Arrhenius formulation [Equations (2.3.10) and (2.3.11)], both $\overline{A}$ and E do have some dependence on T. However, $\Delta H_0^{\ddagger}$ is very weakly dependent on T and the temperature dependence of:

$$\left(\frac{\overline{k}T}{h}\right)\exp\left[\frac{\Delta S_0^{\ddagger}}{R_g}\right] \tag{2.3.12}$$

can normally be neglected as compared to the strong exponential dependence of:

$$\exp\left[\frac{-\Delta H_0^{\ddagger}}{R_g T}\right] \tag{2.3.13}$$

Thus, the Arrhenius form is an excellent approximation to that obtained from transition-state theory, provided the temperature range does not become too large.

Previously, the concentration C_{TS} was expressed in simple terms assuming ideal conditions. However, for nonideal systems, $K^{\ddagger}$ must be written as:

$$K^{\ddagger} = \frac{a_{TS}}{a_A a_B} \tag{2.3.14}$$

where a_i is the activity of species i. If activity coefficients, $\overline{\gamma}_i$, are used such that $a_i = \overline{\gamma}_i C_i$, then Equation (2.3.14) can be formulated as:

$$K^{\ddagger} = \left[\frac{\overline{\gamma}_{TS}}{\overline{\gamma}_A \overline{\gamma}_B}\right]\left[\frac{C_{TS}}{C_A C_B}\right] \tag{2.3.15}$$

Following the substitutions and equation rearrangements used for ideal conditions, the nonideal system yields:

$$k = \left(\frac{\overline{k}T}{h}\right)\frac{\overline{\gamma}_A \overline{\gamma}_B}{\overline{\gamma}_{TS}}K^{\ddagger} \tag{2.3.16}$$

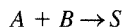At infinite dilution where the activity coefficients are one (ideal conditions), k_0 can be written as:

$$k_0 = \left(\frac{\overline{k}T}{h}\right)K^{\ddagger} \tag{2.3.17}$$

Thus, the rate constant at nonideal conditions relative to the ideal system is:

$$\frac{k}{k_0} = \frac{\overline{\gamma}_A \overline{\gamma}_B}{\overline{\gamma}_{TS}} \qquad (2.3.18)$$

EXAMPLE 2.3.1

Predict how the rate constant of the reaction:

$$A + B \rightarrow S$$

would vary as a function of ionic strength, $\overline{I}$, if A and B are both ions in aqueous solutions at 25°C. The Debye-Hückel theory predicts that:

$$-\log(\overline{\gamma}_i) = 0.5 \overline{Z}_i^2 \sqrt{\overline{I}}$$

where $\overline{Z}_i$ is the charge of species i and

$$\overline{I} = \frac{1}{2} \sum_i \overline{Z}_i^2 c_i \qquad (i = A, B, S)$$

where c_i is the concentration of species i in units of molality.

■ Answer

Although the structure of the transition state is not given, it must have a charge of $\overline{Z}_A + \overline{Z}_B$. Using the Debye-Hückel equation in Equation (2.3.18) gives:

$$\log\left(\frac{k}{k_0}\right) = \log\left(\frac{\overline{\gamma}_A \overline{\gamma}_B}{\overline{\gamma}_{TS}}\right)$$

or

$$\log\left(\frac{k}{k_0}\right) = 0.5[\overline{Z}_A + \overline{Z}_B]^2 \sqrt{\overline{I}} - 0.5 \overline{Z}_A^2 \sqrt{\overline{I}} - 0.5 \overline{Z}_B^2 \sqrt{\overline{I}}$$

After simplification, the above equation reduces to:

$$\log\left(\frac{k}{k_0}\right) = [\overline{Z}_A \overline{Z}_B] \sqrt{\overline{I}}$$

This relationship has been experimentally verified. Note that if one of the reactants is uncharged, for example, B, then $\overline{Z}_B = 0$ and $k = k_0$. If the rate is mistakenly written:

$$r = k_0 a_A a_B = k_0 \overline{\gamma}_A \overline{\gamma}_B c_A c_B$$

application of the Debye-Hückel equation gives:

$$\log\left(\frac{k}{k_0}\right) = \log\left(\frac{k_0 \overline{\gamma}_A \overline{\gamma}_B}{k_0}\right) = -0.5[\overline{Z}_A^2 + \overline{Z}_B^2] \sqrt{\overline{I}}$$

Note that this relationship gives the wrong slope of $\log\left(\dfrac{k}{k_0}\right)$ versus $\sqrt{\overline{I}}$, and if $\overline{Z}_B = 0$, it does not reduce to $k = k_0$.

It is expected that the transition state for a unimolecular reaction may have a structure similar to that of the reactant except for bond elongation prior to breakage. If this is the case, then $\Delta S_0^{\ddagger} \cong 0$ and

$$\overline{A} \cong \frac{\overline{k}T}{h} \cong 10^{13} \text{ s}^{-1} \tag{2.3.19}$$

It has been experimentally verified that numerous unimolecular reactions have rate constants with pre-exponential factors on the order of 10^{13} s^{-1}. However, the pre-exponential factor can be either larger or smaller than 10^{13} s^{-1} depending on the details of the transition state.

Although it is clear that transition-state theory provides a molecular perspective on the reaction and how to calculate the rate, it is difficult to apply since $\Delta S_0^{\ddagger}$, $\Delta H_0^{\ddagger}$, and $\overline{\gamma}_{TS}$ are usually not known *a priori*. Therefore, it is not surprising that the Arrhenius rate equation has been used to systemize the vast majority of experimental data.

Exercises for Chapter 2

1. For a series of similar reactions, there is often a trend in the equilibrium constants that can be predicted from the rate constants. For example, the reaction coordinate diagrams of two similar reactions are given below. If the difference in free energy of formation of the transition state is proportional to the difference in the free energy change upon reaction, that is, $\Delta G_1^{\ddagger} - \Delta G_2^{\ddagger} = \alpha(\Delta G_1 - \Delta G_2)$, derive the relationship between the rate constants k_1 and k_2 and the equilibrium constants (K_1 and K_2).
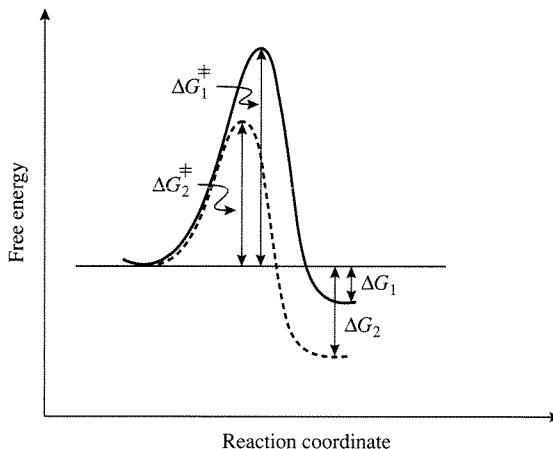
Schematic diagram of two similar reactions.

2. The decomposition of gaseous 2-propanol over a mixed oxide catalyst of magnesia and alumina produces both acetone and propene according to the following equations:

2-propanol   acetone

2-propanol   propene
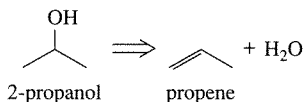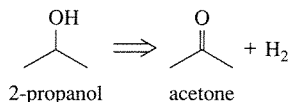
From the data presented below, calculate the activation energy for each reaction (A. L. McKenzie, M.S. Thesis, Univ. of Virginia, 1992). Assume the concentration of 2-propanol is constant for each experiment. Selectivity to acetone is defined with respect to the products acetone and propene.

Temperature (K)	573	583	594	603	612
Rate of acetone formation (mol gcat^{-1} s^{-1})	4.1×10^{-7}	7.0×10^{-7}	1.4×10^{-6}	2.2×10^{-6}	3.6×10^{-6}
Selectivity to acetone (%)	92	86	81	81	81

3. Use the data in Exercise 7 at the end of Chapter 1 to determine the activation energy and pre-exponential factor of the rate constant for the Diels-Alder reaction of 2,3-dimethyl-1,3-butadiene (DMB) and acrolein to produce 3,4-dimethyl-Δ^3-tetrahydro-benzaldehyde.

DMB   Acrolein   3,4-Dimethyl-Δ^3-
                                 tetrahydro-benzaldehyde
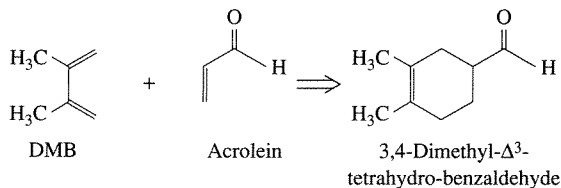
4. Explain how the pre-exponential factor of a unimolecular reaction can be greater than 10^{13} s^{-1}.

5. Discuss the strengths and weaknesses of transition-state theory.

6. Irradiation of water solutions with gamma rays can produce a very active intermediate known as a hydrated electron. This species can react with many different neutral and ionic species in solution. Devise an experiment to check the electrical charge of the hydrated electron. (Problem adapted from M. Boudart, *Kinetics of Chemical Processes,* Prentice Hall, Englewood Cliffs, NJ, 1968, p. 55.)