An elementary bimolecular reaction originates from a collision between two reactants. Whether or not a collision results in a chemical reaction is determined by the energy of the reactants and their orientation. The total energy of the two reactants must be in excess of the activation energy, $E_a$, and the reactants must be in a favorable orientation for the chemical reaction to occur. While there are many different orientations possible for the collisions, usually not all of them will result in a chemical reaction. For most reactions, if the orientation is not correct, the reactants will bounce off of each other without a chemical reaction.

**Reaction Rate**

The rate of a bimolecular reaction, between the reactants A and B is expressed as,

\[ \text{Rate} = k[A][B] \]

where $k$ is the reaction's rate constant and $[A]$ and $[B]$ are the reactants' concentrations. The reaction rate represents the "speed" of the chemical reaction and is equal to the magnitude of the change in the concentration of A or B per unit time. Thus, the reaction rate has units of concentration/time. Because one B molecule reacts for every A molecule, the loss rates of A and B are equal. The activation energy is illustrated in the following diagram. The difference in the activation energies for the forward and reverse reactions equals the change in the internal energy for the chemical reaction; i.e.,

\[ \Delta E_{\text{rxn}} = E_a^f - E_a^r \]

**Rate Constant and Arrhenius Equation**

If concentration is given in moles/liter and time in seconds, the rate constant $k$ has units of L mol$^{-1}$ sec$^{-1}$. If the concentration unit is molecules cm$^{-3}$, the rate constant has units of cm$^3$ molecule$^{-1}$ sec$^{-1}$. Every reaction has its own unique rate constant, and the larger the value of $k$ the more efficient the reaction. The rate constant may be expressed by the Arrhenius equation,

\[ k = Ae^{-\frac{E_a}{RT}} \]

where $E_a$ is the activation energy, $A$ the A-factor, $R$ the gas law constant, and $T$ the temperature. The orientation factor for a chemical reaction is incorporated in $A$ and the activation energy factor in the exponential term. The less restrictive the orientation factor for a chemical reaction, the larger the value for $A$. If the orientation is important for a chemical reaction, the constant $A$ in the Arrhenius rate law is relatively small. If $E_a$ is zero or the temperature high, so that the exponential term becomes unity, the rate constant $k$ equals $A$.

**Transition State Theory**

Transition state theory (TST) provides a theoretical model for the bimolecular rate constant. The TST expression for the rate constant is,
\[ k = \left(\frac{k_BT}{h}\right)e^{-\frac{\Delta G^\ddagger}{RT}} \]

where \(\Delta G^\ddagger\) is the free energy difference between the reaction's transition state (TS) and the A+B reactants. \(\Delta G^\ddagger\) is related to the enthalpy and entropy of activation via the following:

\[ \Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \]

such that

\[ k = \left(\frac{k_BT}{h}\right)e^{-\frac{\Delta S^\ddagger}{R}}e^{-\frac{\Delta H^\ddagger}{RT}} \]

The relationship between \(\Delta H^\ddagger\) and \(E_a\) is,

\[ \Delta H^\ddagger = E_a - 2RT \]

Inserting this relation into the above expression for \(k\) and comparing the result with the Arrhenius equation, shows that,

\[ A = \left(\frac{k_BT}{h}\right)e^{2 + \frac{\Delta S^\ddagger}{R}} \]

Collision Theory

A dynamic approach for calculating the bimolecular rate constant is to consider the A + B collisions. The rate for collisions between A and B molecules may be expressed in the unit collisions \(\text{cm}^{-3} \text{sec}^{-1}\). If every collision results in a chemical reaction, with loss of an A and B molecule, the reaction rate is then the collision rate. The rate constant for collisions, \(k_{\text{coll}}\), is written as,

\[ k_{\text{coll}} = \sigma_{\text{coll}} \langle v_{\text{vel}} \rangle \]

where \(\sigma_{\text{coll}}\) is the "collision cross-section" and \(\langle v_{\text{vel}} \rangle\) is the average A + B relative velocity. The latter equals \((8RT/\pi u)^{1/2}\), where \(u\) is the reduced mass of A and B, \([M_A M_B/(M_A + M_B)]\). The unit for \(k_{\text{coll}}\) is \((\text{area/collision}) \times \text{velocity}\); e.g. \(\text{cm}^3 \text{collision}^{-1} \text{sec}^{-1}\). If each collision leads to a chemical reaction, this rate constant can be expressed as \(\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}\).

The collision cross section represents the "area" for an A + B collision and may be understood by assuming both A and B as spheres; i.e.

If the centers of masses of A and B are separated by less than \(d = r_A + r_B\) as they approach, A and B undergo a collision. The "dashed circle" in the above diagram depicts the cross-sectional area, \(\pi d^2\), for an A + B collision. All relative A + B orientations are considered in determining this "collision area".

Because of the orientation requirement and activation energy for a bimolecular reaction, very few of these reactions have a rate constant equal to \(k_{\text{coll}}\). The orientation requirement for reaction may be incorporated by multiplying \(k_{\text{coll}}\) by the parameter \(\rho\leq1\), often called the steric factor. The reactant molecules at a temperature T have a Maxwell-Boltzmann distribution of energies. Some molecules have high energies, whereas others have low energies. The energy of the
reactants must be greater than the activation energy of the chemical reaction for the chemical reaction to occur. If the Maxwell-Boltzmann distribution of A + B relative translational energies is considered and if it is assumed that the collision must have a relative translational energy in excess of the activation energy $E_a$, the fraction of molecules that have enough energy to overcome the activation energy is proportional to $e^{-E_a/RT}$. Including this factor and the steric factor, one obtains a modified $k_{coll}$ for reaction:

$$k_{coll} = \rho \pi d^2 \left( \frac{8k_BT}{\pi u} \right)^{1/2} e^{-E_a/RT}$$

A molecule has three types of motions: translational, vibrational, and rotational. The extent of each of these motions is determined by their energies. Thus, the molecule's total energy is a sum of its translation ($t$), rotational ($r$), and vibrational ($v$) energies:

$$E = E_t + E_v + E_r$$

Each of these energies may be used to overcome the activation energy $E_a$. The relative importance of these different types of energy for a promoting reaction differs for different chemical reactions. To have an understanding of how these different types of energies may affect the reaction rate constant, it is necessary to use a more sophisticated approach than the above collision model which only treats the relative translational energy. A chemical dynamics simulation, as described below, is a way to study how $E_t$, $E_v$, and $E_r$ affect the probability of a chemical reaction when A and B collide.

### S$_N$2 Reactions

A bimolecular reaction found in organic chemistry is bimolecular nucleophilic substitution, also known as the S$_N$2 mechanism. In nucleophilic substitution, a nucleophile attaches to the central carbon of an organic halide, causing the departure of the leaving group:

$$\text{OH}^- + \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{OH} + \text{Br}^-$$

As it has a concerted mechanism, substitution occurs in only one step. However, at the microscopic, atomic-level there are many complex details in the mechanism for S$_N$2 reactions.

A nucleophile can be classified as a Lewis base, meaning it has a pair of electrons to donate to the molecule to which it bonds. Although any molecule that has a pair of electrons to be used for a bond is a nucleophile, ions are more effective than neutral compounds. For the most effective reaction, the molecule attacked by the nucleophile should be either a primary halide or a tosylate. Because halides are compounds of halogen ions bound to carbon, and carbon is much less electronegative than any halogen, polar bonds are formed and the carbon gains a slightly positive charge, which attracts the nucleophile. When the nucleophile attaches to the central carbon, it attaches from the side opposite the leaving group. Because of the direction of the attachment, the new structure is the inverse of the previous one; i.e. a mirror image if the attacking anion and leaving anion are the same.

$$\text{Cl}^- + \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 + \text{Cl}^-$$

Although secondary halides undergo S$_N$2 nucleophilic substitution, tertiary halides are very inefficient. Examples of primary, secondary, and tertiary halides are CH$_3$Cl, CH(CH$_3$)$_2$Cl, and C(CH$_3$)$_3$Cl, respectively. If the alkyl group to which
the leaving group is attached is larger than CH₃, elimination (E) may also accompany nucleophilic substitution:

\[
\begin{eqnarray}
\text{OH}^- + C_2H_5Cl &\rightarrow& C_2H_5OH + Cl^- \quad (S_N2) \\
\text{OH}^- + C_2H_5Cl &\rightarrow& C_2H_4 + H_2O + Cl^- \quad (E)
\end{eqnarray}
\]

\[\text{SN2 Potential Energy Curve}\]

Consider the following \(S_N2\) reaction:

\[
[\text{Cl}^- + CH_3Br \rightarrow ClCH_3 + Br^-]
\]

As a result of the attractive interactions between the Cl\(^-\) and Br\(^-\) ions and the dipoles of the CH\(_3\)Br and CH\(_3\)Cl molecules, the potential energy curve for this reaction has potential energy minima in addition to a central barrier separating reactants and products. The potential energy curve for this reaction is shown below:

CR, the reactants’ Cl\(^-\)--CH\(_3\)Br complex.
CP, the products’ ClCH\textsubscript{3}---Br\textsuperscript{-} complex.

TS, the transition state separating the complexes.

This curve shows how the potential energy of the chemical reaction changes from reactants to products. The intermediate complexes, CR and CP, are in potential energy wells separated by a transition state (TS). The CR and CP complexes are formed by the attractive interaction between the anion and the dipole moment of the molecule; the CH\textsubscript{3} moiety of the CH\textsubscript{3}Br molecule has a positive charge, while the Br atom has a negative charge of the same magnitude. If the CR and CP complexes do not have any excess energy, their structures are given by their potential energy minima (distances are in angstroms):

Similarly, if the TS has no excess energy, its structure is given by the saddlepoint;

In the TS, both the C-Cl and C-Br bonds are elongated from their values in CH\textsubscript{3}Cl and CH\textsubscript{3}Br, and the CH\textsubscript{3} moiety is nearly planar. In addition, the negative charge is delocalized over all the atoms.

**Statistical Model**

For a S\textsubscript{N}2 reaction in the gas-phase, energy is not removed from the reacting species and the reactants, products, complexes, and TS retain their excess energies. In the statistical model for the S\textsubscript{N}2 reaction it is assumed that this excess energy is randomly distributed across the vibrational modes of the CR and CP complexes, the TS, and the products. This proposed energy redistribution produces CR and CP complexes with finite lifetimes and which undergo unimolecular decomposition; e.g. CR can decompose to products or cross the TS to form CP:
\[ \text{Cl}^- + \text{CH}_3\text{Br} \rightarrow \text{Cl}^-\text{--CH}_3\text{Br} \text{ (CR),} \]

\[ \text{CR} \rightarrow \text{Cl}^- + \text{CH}_3\text{Br}, \]

\[ \text{CR} \rightarrow \text{ClCH}_3\text{--Br}^- \text{ (CP),} \]

\[ \text{CP} \rightarrow \text{CR}, \]

\[ \text{CP} \rightarrow \text{ClCH}_3 + \text{Br}^-; \]

Because the activation energy for \( k_2 \) is much larger than that for \( k_3 \), the statistical model assumes that CP preferentially dissociates to products. Therefore, crossing the transition state (i.e., CR → CP) leads to products with a near unit efficiency. As a result, the rate constant for the \( \text{Cl}^- + \text{CH}_3\text{Br} \rightarrow \text{ClCH}_3 + \text{Br}^- \text{ } \text{S}N_2 \) reaction is,

\[ k_{\text{S}N_2} = \frac{k_1 k_2}{k_{-1} + k_2} \]

The Rice-Ramsperger-Kassel-Marcus (RRKM) statistical unimolecular rate theory is used to calculate the rate constants \( k_{-1} \) and \( k_2 \).

**Atomic-level Dynamics of S\(_N\)2 reactions**

The above statistical theory is a model for the S\(_N\)2 reaction. The actual manner in which the reaction occurs may not conform to this model. For example, the formation of a complex during the reaction depends upon energy transfer processes. Consider the possible formation of CR, the \( \text{Cl}^-\text{--CH}_3\text{Br} \) complex. To form this complex, all of the initial \( \text{Cl}^- + \text{CH}_3\text{Br} \) relative translational energy must be transferred to \( \text{CH}_3\text{Br} \) vibrational and/or rotational energy so that this energy is not available to return to reactants. If all of the initial \( \text{Cl}^- + \text{CH}_3\text{Br} \) relative translational energy is not transferred in this manner, \( \text{Cl}^- \) will hit \( \text{CH}_3\text{Br} \), reverse its velocity, and return to products. In a similar way, formation of the CP complex, \( \text{ClCH}_3\text{--Br}^- \), occurs if, after passing the TS, there is insufficient energy in \( \text{ClCH}_3 + \text{Br}^- \) relative translation to proceed to products; i.e. the excess energy is in \( \text{ClCH}_3 \) vibration and rotation. If vibrational energy is not distributed randomly in CP, it may recross the TS instead of forming products as predicted by RRKM theory.

The \( \text{Cl}^- + \text{CH}_3\text{Br} \rightarrow \text{ClCH}_3 + \text{Br}^- \text{ } \text{S}N_2 \) reaction may occur directly without forming either the CR or CP complex. This happens if energy is transferred to the C-Br bond as \( \text{Cl}^- \) collides so that the reactants move directly past the TS. If energy is then released to \( \text{ClCH}_3 + \text{Br}^- \) relative translation, CP is not formed and the products are formed directly.

The manner in which this S\(_N\)2 reaction occurs at the atomic-level may be studied by a chemical dynamics computer simulation. The atomic-level mechanisms for the reaction may be visualized by animating the results of these simulations.
Six animations of computer simulations of the Cl\(^-\) + CH\(_3\)Br SN2 nucleophilic substitution reaction are presented here. The animations were prepared from trajectories calculated as part of a chemical dynamics computer simulation published in the *Journal of Chemical Physics* 118, 2688 (2003). A trajectory determines the positions of all the atoms as a function of time and one can study atomic-level mechanisms for chemical reactions and molecular collisions. To compare with an experiment, a large number of trajectories must be calculated to properly average all the different possibilities for the initial positions, velocities, orientations, etc. of the reactant molecules. The animations are for representative trajectories among the large number which were calculated. The following are brief descriptions of the animations:

- **Animation 1** - reaction by a direct mechanism without forming CR or CP. Note the high collision energy.
- **Animation 2** - reaction by an indirect mechanism, involving CR.
- **Animation 3** - reaction by an indirect mechanism, involving CR and CP.
- **Animation 4** - non-reactive collision without forming CR or CP.
- **Animation 5** - non-reactive collision which forms CR.
- **Animation 6** - reaction by a complex mechanism, involving the formation of both CR and CP and recrossing of the TS.

### Problems

**Bimolecular Kinetics and Dynamics**

1. What is the basic requirement of a reaction to be classified as a bimolecular reaction?
2. What are the two factors which affect the rate constant of a bimolecular reaction?
3. What does the rate constant and variables A and E\(_a\) in the Arrhenius rate law tell us about the chemical reaction?
4. Do all of the reactant particles have the same amount of energy at a given temperature? Why or why not?
5. If the temperature for a chemical reaction is increased, what effect would you predict this has on the rate constant?
6. Why would the rate of a reaction increase if the molecules began moving faster, and it was assumed the fraction of collisions which had an effective orientation remained constant?
7. Explain why the reactant molecules need to be oriented correctly for a reaction to occur.
8. Show how to determine the enthalpy of activation, \(\Delta H^\ddagger\), and entropy of activation, \(\Delta S^\ddagger\), from the Arrhenius parameters.
9. What does the \(\rho\)-factor account for in the collision theory of bimolecular reactions.

**SN2 Reaction Dynamics**

1. What significance does electronegativity have pertaining to a nucleophilic substitution?
2. Explain why the structure of the molecule is inverted in a nucleophilic substitution.
3. Alkyl groups are leaving groups that do not work well for nucleophilic substitution. Why do you think this is?
4. What is a tertiary halide?
5. Give four examples of nucleophiles.
Potential Energy Curves and Energetics

1. How much potential energy is released when the complex CP is formed for the Cl⁻ + CH₃Br SN₂ reaction?
2. What is the exothermicity of this reaction?
3. If the Cl⁻ + CH₃Br reactants have an excess energy of 10 kcal/mol, what is the excess energy of the products?
4. Would you expect CP to preferentially cross the TS or form products? Why?
5. Where is the negative charge localized for the CR and CP complexes?
6. Describe the distribution of the negative charge for the TS.

Cl⁻ + CH₃Br --> ClCH₃ + Br⁻ Dynamics and Animations:

1. Give a reason why the reaction in animation 1 occurs by a direct mechanism, while those in animations 2, 3, and 6 occur by indirect, complex forming mechanisms.
2. In animation 4, why does Cl⁻ bounce off CH₃Br without forming a Cl⁻---CH₃Br complex?
3. In animation 5, why does the Cl⁻---CH₃Br⁻ complex dissociate back to reactants instead of crossing the TS and forming the CICH₃ + Br⁻ products?
4. Why is the CP complex formed in animation 3, but not in animation 2?
5. The following questions pertain to the translational, vibrational, and rotational motions during the animations.
6. Describe how the atoms of CH₃Br would move if the molecule had only translational energy.
7. Describe the motion of either the CR or CP complex, if it only had rotational energy.
8. Describe the motion of either the CR of CP complex, if it only had vibrational energy.
9. For animations 1, 2, 3, and 6 for which reaction occurs, study the vibrational and rotational motions of the CH₃Br reactant and CH₃Cl product. Try to determine whether the product has more or less vibrational energy than the reactant. Do the same for the rotational energy. Try to explain your findings.
10. The following questions pertain to the dynamics of complex formation and decomposition as illustrated by the animations.
11. Assume complex CR is formed and energy is removed by some means so that its excess energy is less than that of the TS. Can CR decompose back to reactants or form products?
12. Assume CR is formed by a Cl⁻ + CH₃Br collision and no energy is removed, as is the case for the animations. Why do Cl⁻ and CH₃Br persist as a complex and not return immediately to reactants or cross the TS? What has to happen for CR to cross the TS?
13. Compare animations 4 and 5. Describe what is needed to form the complex CR.

Answers

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