Professional Reference Shelf

C. Molecular Dynamics

Overview

$$H + H_2 \;□□\;□\; H_2 + H$$

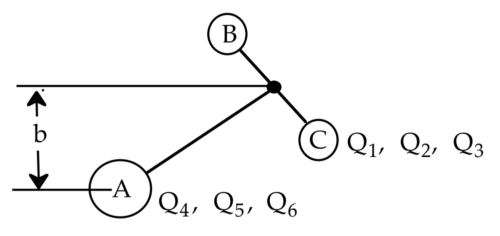
$$A + BC \;□□\;□\; AB + C$$

(1) Calculate potential energy surface, $\tilde{V}(R_{BC}, R_{AB}, R_{AC})$

(2) Carry of Trajectory Calculations
The equations of motion used to calculate the trajectories in order to obtain the internuclear distances R_{AB}, R_{AC}, and R_{BC} are

$$\frac{dQ_j}{dt} = \frac{P_j}{□}$$

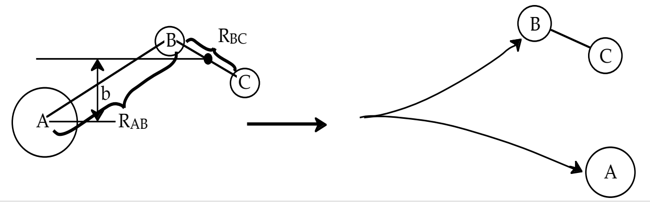
$$\frac{dP_j}{dt} = □\frac{\partial \tilde{V}(R_{BC}, R_{AB})}{\partial dQ_j}$$

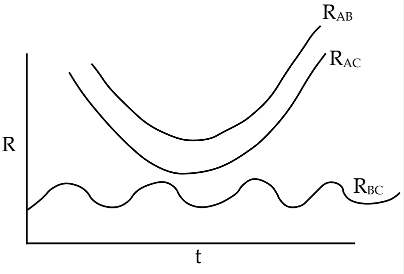


where P is the momentum and $\tilde{V}$ (R_{AB}, R_{BC}, R_{AC}) is the potential energy surface. We now answer these questions by specifying some of the variables and letting the computer randomly choose the value of the others.

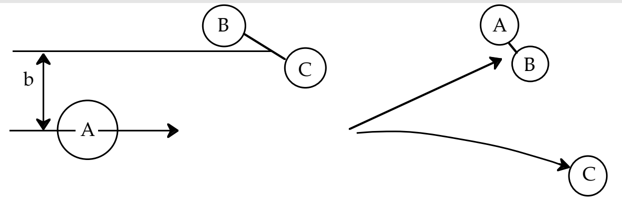
Specified Variables		Randomly Chosen Variables	
□	Vibration quantum number	R	Distance between B-C molecule
J	Rotation quantum number	□	Polar coordinate of C wrt B
V_R	Velocity	□	Polar coordinate of C wrt B
B	Impact parameters	□	Angular momentum

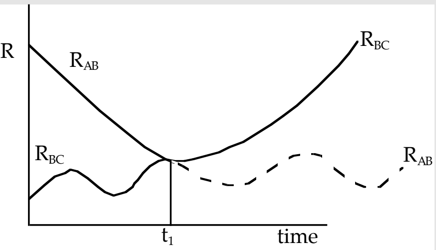
Nonreactive Trajectory





Reactive Trajectory

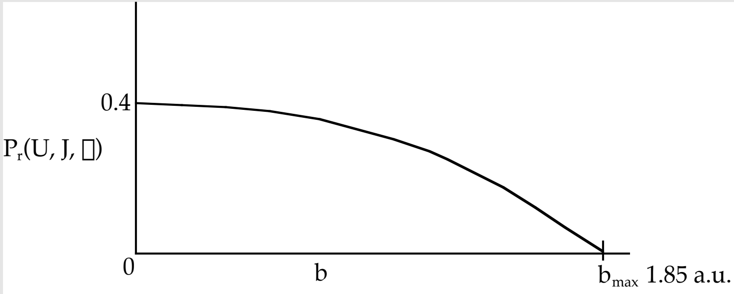




(3) We now count all the trials, N, that we carried out and all the trajectories that resulted in reaction, N_r. The probability of reaction

$$P_r = \lim_{N_{TOT}\to\infty}\left[\frac{N_r(\nu,J,U_R,b)}{N_{TOT}(\nu,J,U_R,b)}\right] = \frac{\text{number of reactive trajectories}}{\text{total number trajectories calculated}}$$

(4) Vary impact parameter b to obtain b_{max}



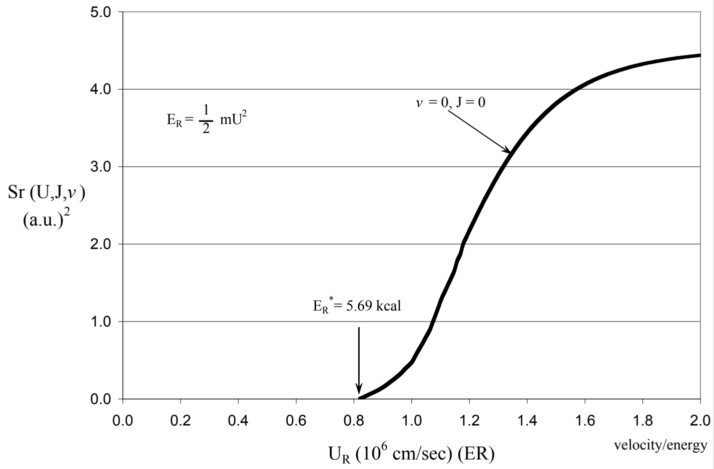
This curve can be approximated by

$$P_r = a\cos\left(\frac{\pi b}{2b_{max}}\right)$$

(5) Calculate reaction cross section as a function of kinetic energy, velocity.

$$S_r(\nu,J,U_R) = \int_0^\infty P_r(\nu,J,U_R)\,2\pi b\,db = \pi b_{max}^2 \lim_{N\to\infty}\frac{N_r(U,\nu,J)}{N(U,\nu,J)} = 1.45ab_{max}^2(\text{a.u.})^2$$

(6) Find S_r as a function of U_R for a given ν and J



(7) Calculate reaction rate and k in vibration state ν and rotation state J

$$-r_A(\nu,J) = C_A C_{BC} F_{BC}(\nu,J)\cdot\underbrace{\int_0^\infty\int_0^\infty U_R S_r(\nu,J,U_R) f_A(V_A)dV_A f_{BC}dV_{BC}}_{k_{\nu,J}}$$

$$-r_A[\nu,J] = k_{\nu,J}F_{BC}(\nu,J)C_A C_{BC}$$

In order to obtain the overall reaction, we sum over all vibrational and rotational states.

$$k = \sum_{\text{all } J\&\nu} k_{\nu,J}F_{BC}(\nu,J)$$

and obtain the overall rate of reaction

$$-r_A = kC_A C_{BC} = Ae^{-E_A/RT}C_A C_{BC}$$

The frequency factor, A, and the activation energy, E_A, calculated from molecular dynamics are in excellent agreement with the experimental values.

I. INTRODUCTION

The objective of this Reference Shelf is to use molecule dynamics to provide insight into how reactions occur. Here, we will calculate reaction probabilities, reaction cross sections, and reaction rates. We will observe the effects of vibration, rotation, and kinetic energies (velocity) on the colliding molecules. We will find that there is a minimum kinetic energy necessary to react, that the reaction cross section increases with increasing kinetic energy, and that there is a maximum value of the impact parameter related to the offset of the molecular trajectories, above which no reaction will occur.

We are going to study the molecular dynamics of the reaction of the hydrogen exchange reaction

$$H + H_2 \rightarrow H_2 + H$$

written symbolically

$$A + BC \rightarrow AB + C$$

where molecule i has a velocity V_i and is in rotational state J and vibrational state ν. [e.g., BC (V_{BC}, J, ν)].

$$A\ (V_A) + BC\ (V_{BC}, J, \nu) \rightarrow AB\ (V_{AB}, J, \nu) + C\ (V_C)$$

We are going to consider the hydrogen exchange reaction discussed in an article by Karplus, Porter, and Sharma.[1]

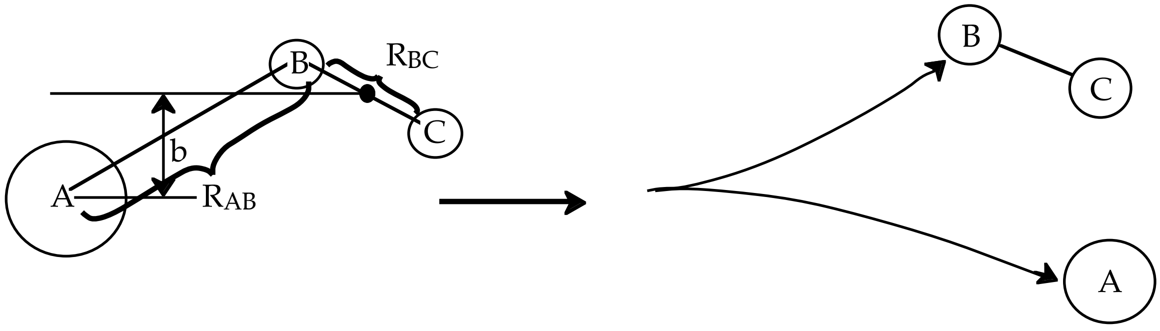
$$H + H_2 \longrightarrow H_2 + H$$

$$A + BC \longrightarrow AB + C$$

We begin with the A and BC molecules far apart and then calculate the trajectory of the A molecule as it approaches the BC molecule. The A molecule will either replace the C molecule to form AB or it will be deflected and not react.

A. No Reaction

A approaches the molecule BC and is deflected and does not react.



Let R be the distances of separation for the appropriate species. The distances of separation are shown as a function of time in Figure R3.C-1.

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[1] M. Karplus, R. N. Porter, and R. D. Sharma, *J. of Chem. Phys.*, **43**, 9 (1965) p. 3259.

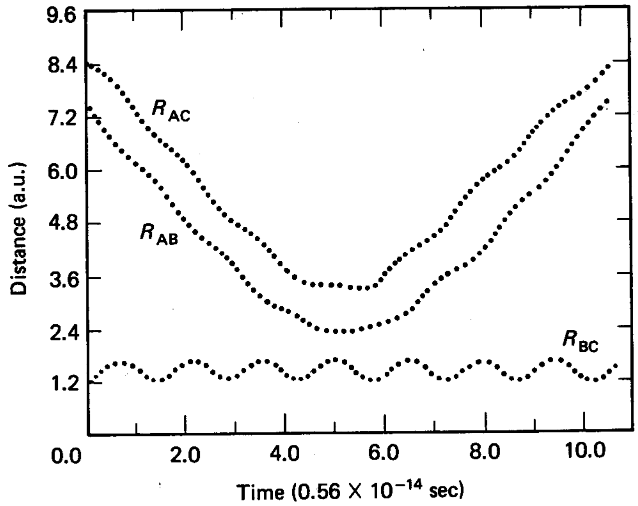
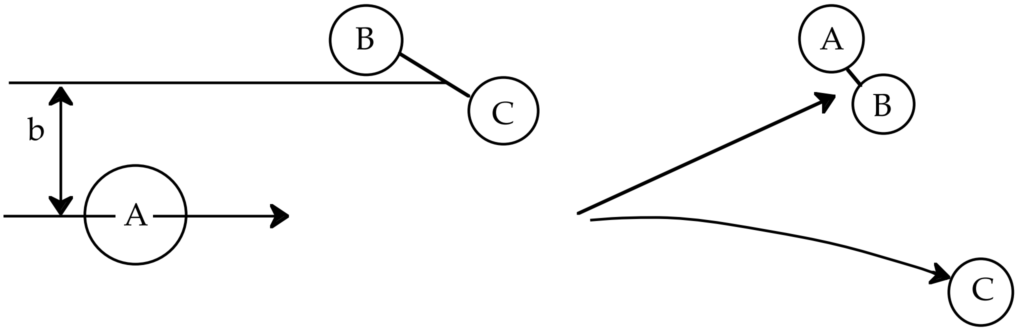


Figure R3.C-1 Trajectories when no reaction has taken place. Courtesy of M. Karplus et al., *J. of Chem. Phys.*, **43**, 1965, p. 3259.

B. Reaction:

The A molecule approaches the BC molecule and reacts to form AB and C.



In Figure R3.C-2 one observes that at t_1 the A molecule replaces the C molecule, the R_{BC} distance begins to increase, the R_{AB} distance undergoes oscillation, and we see that a reaction has taken place. The time it takes the reaction to occur at t_1 is about 10^{-14}s.

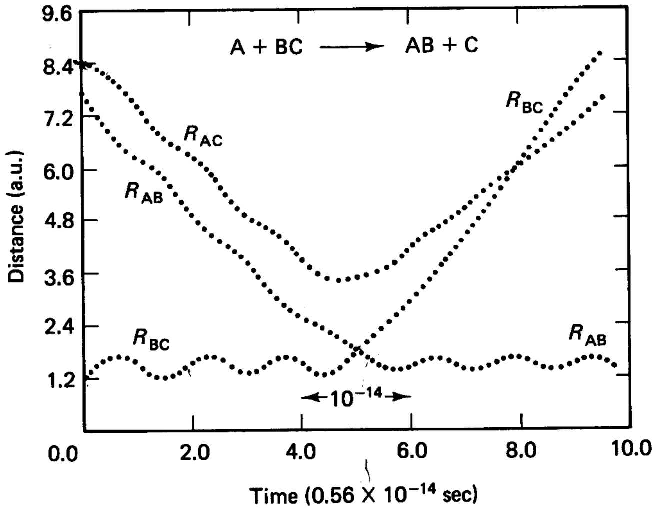


Figure R3.C-2 Trajectories when a reaction occurs. Courtesy of M. Karplus et al., *J. of Chem. Phys.*, **43**, 1965, p. 3259.

II. HOW THE TRAJECTORIES ARE CALCULATED

A. Equations of Motion

We calculate the momentum P of the molecule at a given time and position and then calculate a new position of the molecule using only the definition of force, F, and the potential energy surface, $\tilde{V}(x)$.

$$F = ma = m\frac{dv}{dt} = \frac{d(mv)}{dt} = \frac{dP}{dt} \qquad \text{(R3.C-1)}$$

$$F = -\frac{d\tilde{V}(x)}{dx} \qquad \text{(R3.C-2)}$$

$$P = mv = m\frac{dx}{dt} \qquad \text{(R3.C-3)}$$

$$\boxed{\begin{array}{l} \qquad \frac{dP}{dt} = -\frac{d\tilde{V}(x)}{dx} \\ \text{and} \\ \qquad \frac{dx}{dt} = \frac{P}{m} \end{array}} \qquad \begin{array}{l} \text{(R3.C-4)} \\ \\ \text{(R3.C-5)} \end{array}$$

Equations (R3.C-4) and (R3.C-5) can be solved simultaneously to obtain x a function of time. Also recall that the translational kinetic energy is

$$E_T = \frac{1}{2}\ mv^2 = \frac{P^2}{2m} \qquad \text{(R3.C-6)}$$

To solve this set of equations [i.e., (R3.C-4) and (R3.C-5)], we need the potential energy as a function of distance, $\tilde{V}(x)$. Similarly, for the reaction ($A + BC \rightarrow AB + C$), we need the potential energy surface, $\tilde{V}$ (R_{AB}, R_{BC}, R_{AC}).

B. Estimates of the Potential Energy Surface, $\tilde{V}$(R)

Three methods are commonly used to estimate the potential energy surface.

1) Lennard-Jones 6-12 potential

$$\tilde{V}(r) = 4\varepsilon_{LJ}\left[\left(\frac{r_o}{r}\right)^{12} - \left(\frac{r_o}{r}\right)^{6}\right] \qquad \text{(R3.C-7)}$$

2) Morse potential

$$\tilde{V}(r) = D\left[1 - e^{-\beta(r - r_o)}\right]^2$$

where ε_{LJ} is the Lennard-Jones parameter, D is the dissociation energy, r_o the equilibrium internuclear distance, and β is the Morse potential constant.

For a 3-body system ABC[2]

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[2] J. I. Steinfeld, J. S. Francisco, and W. L. Hase, *Chemical Kinetics and Dynamics* (Englewood Cliffs, NJ: Prentice Hall, 1989).

$$\tilde{V}(r_{AB},\ r_{BC}) = D_{AB}\left[1 - e^{-\beta_{AB}(r_{AB}-r_o)}\right]^2 + D_{BC}\left[1 - e^{-\beta_{BC}(r_{BC}-r_o)}\right]^2$$
$$+ D_{BC}\left[1 - \tanh(ar_{AB} + c)\right]\exp\left[-\beta_{BC}\left(r_{BC} - r_{BC}^0\right)\right]$$
$$+ D_{AC}\exp\left[-\beta_{AC}\left(r_{AC} - r_{AC}^0\right)\right]^{\dagger} \qquad \text{(R3.C-8)}$$

where D_{ij} is the dissociation energy for molecules i and j.

3) The Potential Energy Surface can also be calculated by
   a) Ab Initio [Cerius^2] methods
   b) Semiempirical methods, such as the London-Eyring-Polanyi-Sato Surface (LEPS surface)

A schematic of the potential energy surface is shown in Figure R3.C-3.

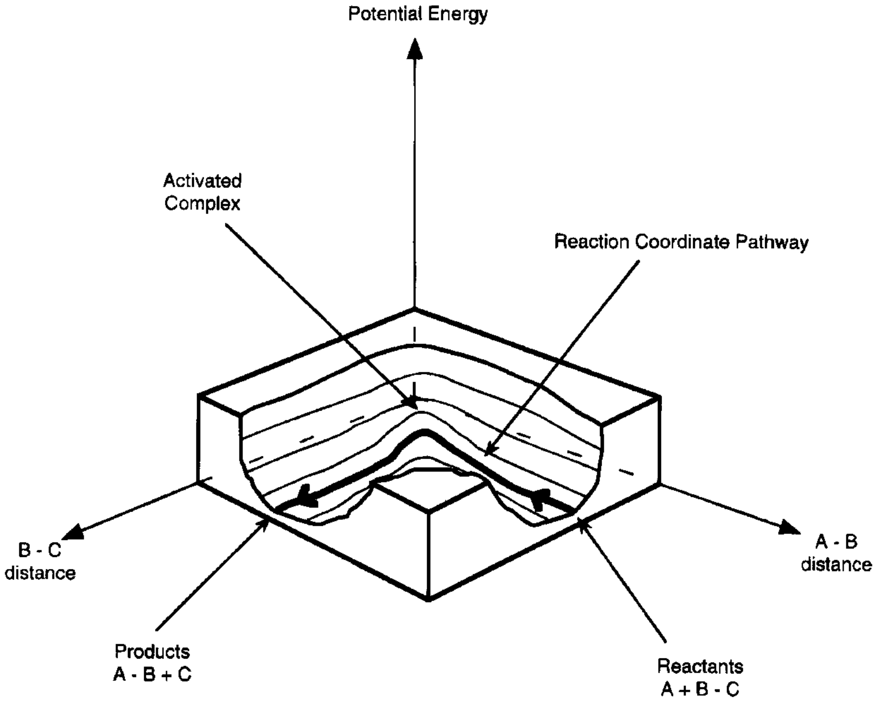


Figure R3.C-3 Potential energy surface.

C. Method of Solution to Map Out Trajectories

C.1 Momentum as a function of time and position.

Consider the motion of molecule A. The x component of momentum for species A is related to the potential energy by

$$\frac{dP_x}{dt} = -\frac{\partial \tilde{V}(x,y,z)}{\partial x} \qquad \text{(R3.C-9)}$$

Integrating we can find the x component of momentum as a function of time and position

$$\boxed{P_x = P_{xo} + \int_0^t \left[-\frac{\partial \tilde{V}(x,y,z)}{\partial x}\right]dt} \qquad \text{(R3.C-10)}$$

Similar expressions exist for y and z, e.g.,

$$P_y = P_{yo} + \int_0^t \left(-\frac{\partial \tilde{V}(x,y,z)}{\partial y}\right) dt \qquad \text{(R3.C-11)}$$

To illustrate the concept, we use the Euler method of integration

$$\left[P_y = P_{yo} + \left(-\frac{\partial \tilde{V}(x,y,z)}{\partial y}\right)\Delta t\right] \qquad \text{(R3.C-12)}$$

C.2 Location of molecules (e.g. A) as a function of time.

The position of A, x, is related to the momentum, P_x, by the equation

$$m_A v = P_x = m_A \frac{dx}{dt} \qquad \text{(R3.C-13)}$$

Integrating, we find the location of A as a function of time

$$x = x_o + \frac{1}{m_A}\int_0^t P_x dt \cong x_o + \frac{P_x}{m_A}\Delta t \qquad \text{(R3.C-14)}$$

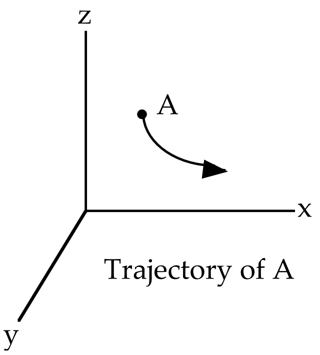
Because V(x) depends upon x, in practice we need to use a more sophisticated method than the Euler method (R3.C-14) to solve these equations for P_x and x and, simultaneously, to obtain the trajectory of molecule A as a function of time as shown in Table PRS.C-1.

Table R3.C-1 3-D Solution Technique to Calculate Trajectory of A

$$P_x = P_{xo} + \int_0^t \left(-\frac{dV(x,y,z)}{dx}\right) dt \qquad x = x_o + \frac{1}{m_A}\int_0^t P_x dt \qquad P_x = m_A v_x$$

$$P_y = P_{yo} + \int_0^t \left(-\frac{dV(x,y,z)}{dy}\right) dt \qquad y = y_o + \frac{1}{m_A}\int_0^t P_y dt \qquad P_y = m_A v_y$$

$$P_z = P_{zo} + \int_0^t \left(-\frac{dV(x,y,z)}{dz}\right) dt \qquad z = z_o + \frac{1}{m_A}\int_0^t P_z dt \qquad P_z = m_A v_z$$



Of course, the time interval for each interaction must be small as we carry out each integration.

C.3 Calculating the trajectories of all the molecules using the Hamiltonian.

Because the Hamiltonian is used in classical mechanics to describe the motion of particles, let's see how it gives the same equation as those given in Table R3.C-1. The Hamiltonian is the sum of the kinetic and potential energies

$$H_A = \frac{1}{2m_A}\left[P_x^2 + P_y^2 + P_z^2\right] + \tilde{V}(x,y,z) \qquad \text{(R3.C-15)}$$

Differentiating the Hamiltonian wrt momentum, P_x, we find

$$\frac{\partial H_A}{\partial P_x} = \frac{2P_x}{2m_A} = \frac{m_A v_x}{m_A} = v_x = \frac{dx}{dt} \qquad \text{(R3.C-16)}$$

$$\boxed{\frac{\partial H_A}{\partial P_x} = \frac{2P_x}{2m_A} = \frac{dx}{dt}}$$

Similarly,

$$\boxed{\frac{\partial H_A}{\partial x} = -\frac{\partial \tilde{V}}{\partial x} = P_x}$$

We see that by using the Hamiltonian and coupling these same six equations we can trace out a trajectory for molecule A as shown in Table R3.C-1.

Change in Coordinate System

Now let's return to the hydrogen exchange reactor

$$A + BC \rightarrow AB + C$$

We are going to redesign our coordinate system because we are only interested in the relative positions of the molecules to one another, not where they are in a 3-D space. This redesign is called *mass weighted coordinate system* or *affine transformation*.

Let

Q_1, Q_2, Q_3 = Location of C with B as the origin

Q_4, Q_5, Q_6 = Location of A wrt center of mass of BC

Q_7, Q_8, Q_9 = Location of center of mass of the 3-particle system

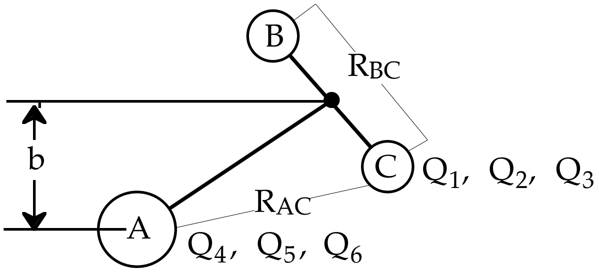


Figure R3.C-4 New coordinate system.

For example, Q_1, Q_2, and Q_3 could represent x_1, y_1, and z_1 components of C, with either B as the origin or the radial components r, θ, and φ with $r = 0$ as the origin. Similarly Q_4, Q_5, and Q_6 could represent the x, y, z coordinates of A with the center mass of BC as the origin or the radial coordinates r, θ, and φ. Knowing the location of C and A with regard to their respective origins, the distances between

A and B is R_{AB}

B and C is R_{BC}

A and C is R_{AC}

can easily be found. See Figure R3.C-6).

III. THE MONTE CARLO SIMULATION

In classical and statistical mechanics, the Hamiltonian (H) is used to express the total energy. The Hamiltonian is the sum of the kinetic energy (KE)- $\frac{1}{2}mv^2$- and the potential energy (PE), $\tilde{V}(R_{AB},R_{AC},R_{BC})$.

$$H = KE + PE = KE + \tilde{V}(R_{AB},R_{AC},R_{BC})$$

$$(KE\ \text{of}\ A) = \frac{1}{2}m_A v_x^2 + \frac{1}{2}m_A v_y^2 + \frac{1}{2}m_A v_z^2 = \frac{1}{2}m_A\left(P_x^2 + P_y^2 + P_z^2\right)$$

In our new coordinate systems, the KE of A is written as

$$(KE\ \text{of}\ A) = \frac{1}{2\ m_A}P_x^2 + \frac{1}{2\ m_A}P_y^2 + \frac{1}{2\ m_A}P_z^2 \qquad \text{(R3.C-17)}$$

with

$$\frac{dP}{dt} = -\frac{\partial \tilde{V}(R_{AB},\ R_{BC},\ R_{AC})}{\partial Q_j}$$

and

$$\frac{dQ_j}{dt} = \frac{1}{\mu_{BC}}P_j \text{ for } i = 1,\ 2,\ \text{or}\ \ 3$$

For our two-body 3-molecule system, A + BC, we must use the reduced masses

$$H = \frac{1}{2\mu_{BC}}\sum_1^3 P_j^2 + \frac{1}{2\mu_{A,BC}}\sum_4^6 P_j^2 + \tilde{V}(R_{AB},R_{AC},R_{BC}) \qquad \text{(R3.C-18)}$$

$\tilde{V}(R_{AB},R_{AC},R_{BC})$ is the potential energy surface. We only need to specify two distances (R_{AB} and R_{BC}) because the other is then a fixed quantity.

The distances R_{AB} and R_{BC} are shown in the potential energy surface $\tilde{V}$ (R_{AB}, R_{BC}), along with the trajectory of the reaction (Figure R3.C-5).

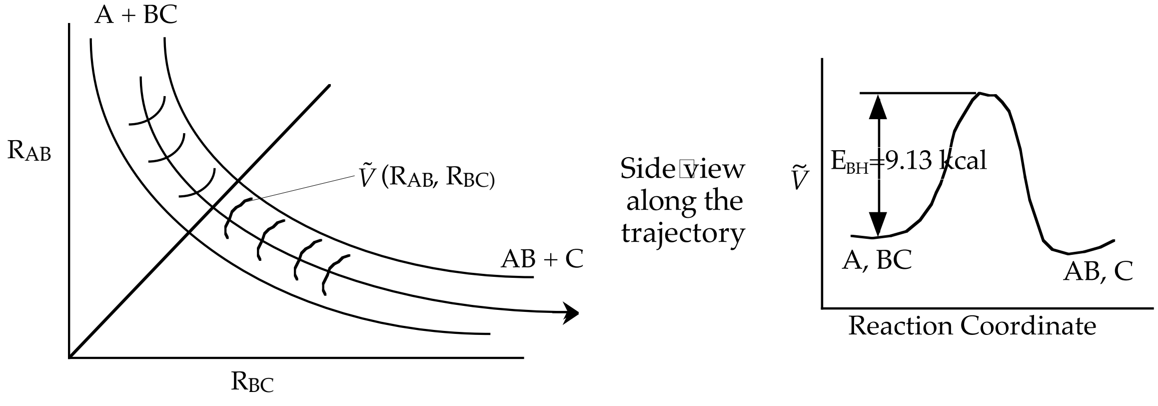


Figure R3.C-5 Reactant coordinates and the potential energy surface.

A summary of the equations above used to solve for the molecular trajectories is shown in Table R3.C-3.

Table R3.C-2—Equations to Be Solved to Predict the Trajectories

$$\frac{dQ_j}{dt} = \frac{\partial H}{\partial P_j}$$

[To get an idea where this equation comes from, recall for the A molecule $\frac{dH}{dP} = \frac{P}{m} = \frac{dx}{dt}$]

For j = 1, 2, 3

(A) $$\frac{dQ_j}{dt} = \frac{1}{\mu_{BC}} P_j$$

For j = 4, 5, 6

(B) $$\frac{dQ_j}{dt} = \frac{1}{\mu_{A,BC}} P_j \ , \qquad Q_j(t) = Q_{jo} + \frac{1}{\mu_{A,BC}} \int_0^t P_j dt$$

(C) $$\frac{dP_j}{dt} = -\frac{\partial \tilde{V}(R_{AB}, R_{BC})}{\partial Q_j} \ , \qquad P_j(t) = P_{jo} + \int_0^t \left(-\frac{\partial \tilde{V}}{\partial Q_j} \right) dt$$

(D) $$\tilde{V}(R_{AB}, R_{BC}, R_{AC}) = D_{AB}\left[1 - e^{-\beta_{AB}(r_{AB} - r_o)}\right]^2 + D_{BC}\left[1 - e^{-\beta_{BC}(r_{BC} - r_o)}\right]^2$$
$$+ D_{BC}\left[1 - \tanh(ar_{AB} + c)\right]\exp\left[-\beta_{BC}\left(R_{BC} - R^0_{BC}\right)\right]$$
$$+ D_{AC}\exp\left[-\beta_{AC}\left(R_{AC} - R^0_{AC}\right)\right]$$[3]

These equations are analogous to the P_x and x,y,z equations shown on pages 3 and 4.

The equations in Table R3.C-2 can be solved simultaneously (using a software package) to predict the location Q_i, from which one can determine the molecular distances, R_{BC}, R_{AB}. However, before we begin to do this we need to specify the parameter values and the initial conditions.

To map out the molecular trajectories to determine if a reaction has occurred, we needs

1. The governing equations: These equations are given in Table R3.C-2.
2. The specified values of the variables: These values fall in two categories and are shown in Table R3.C-3.
   (a) Those variables to be studied to learn their effect on the reaction rate. These are the specified variables.
   (b) Those variables whose numerical values are specified by the Monte Carlo Simulation.
3. The initial values to calculate the molecular trajectories. The initial parameter values are given in Table R3.C-4 and corresponds to the orientation of the A and BC molecules shown in Figure R3.C-6.

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[3] Steinfeld, loc. cit. for $\tilde{V}$ see p. 264.

Table R3.C-3 Categories of Variable Parameter Values

(1) Specified and Given a Numerical Value
- (a) Initial Relative Velocity, U_R
- (b) Impact Parameter, b
- (c) Vibrational Quantum Number, □
- (d) Rotational Quantum Number, J

(2) Chosen by the Monte Carlo Simulation
- (a) Distance between the B and the C molecule, R_{BC} ($R_- < R_{BC} < R_+$)
- (b) Orientation of BC relative to A specified by angles □ (0<□<□) and □ (0<□<2□) See Figure R3.C-6.
- (c) Internal angular momentum of H_2 molecule specified by an angle □ (i.e., which direction it is rotating).

We are going to choose our coordinate system such that molecule A and the center of mass of B–C lie on the y-z plane and that A approaches B–C along the z axis.

Table R3.C-4 Initial Conditions to Start the Trajectory

Initial Conditions

Specified Initial Conditions, r_o, b, □, J

The following variables are chosen randomly: R_{BC}, □, □, and □

Location of C wrt B	Angular momentum of B–C
$Q_1^\circ = R_{BC}\sin\square\cos\square$	$P_1 = P(\sin\square\cos\square + \cos\square\cos\square\sin\square)$
$Q_2^\circ = R_{BC}\sin\square\sin\square$	$P_2 = \square P(\cos\square\cos\square \,\square\, \sin\square\cos\square\sin\square)$
$Q_3^\circ = R_{BC}\cos\square$	$P_3 = P\sin\square\sin\square$
	where[4] $P = \sqrt{J(J+1)}\,\dfrac{\hbar}{R_+}$

The center of mass lies in x–y plane. Location of A wrt center of mass of B–C

$Q_4^\circ = 0$	$P_4 = 0$
$Q_5^\circ = b$	$P_5 = 0$
$Q_6^\circ = \square\left(r_o^2 \,\square\, b^2\right)^{1/2}$	$P_6 = \square_{A,BC}U_R$

with r_o the initial distance between A and the center of mass of BC

Here, $\hbar$ is Plank's constant divided by 2□, and R_+ is the turning point radius shown in Figure R3.C-7. We choose the value of r_o as small as possible to save computing time but not so small as to experience any potential interactions between the A and BC molecules. A schematic of the initial conditions and the orientation is shown in Figure R3.C-6.

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[4] Steinfeld, Loc cit., p. 265.

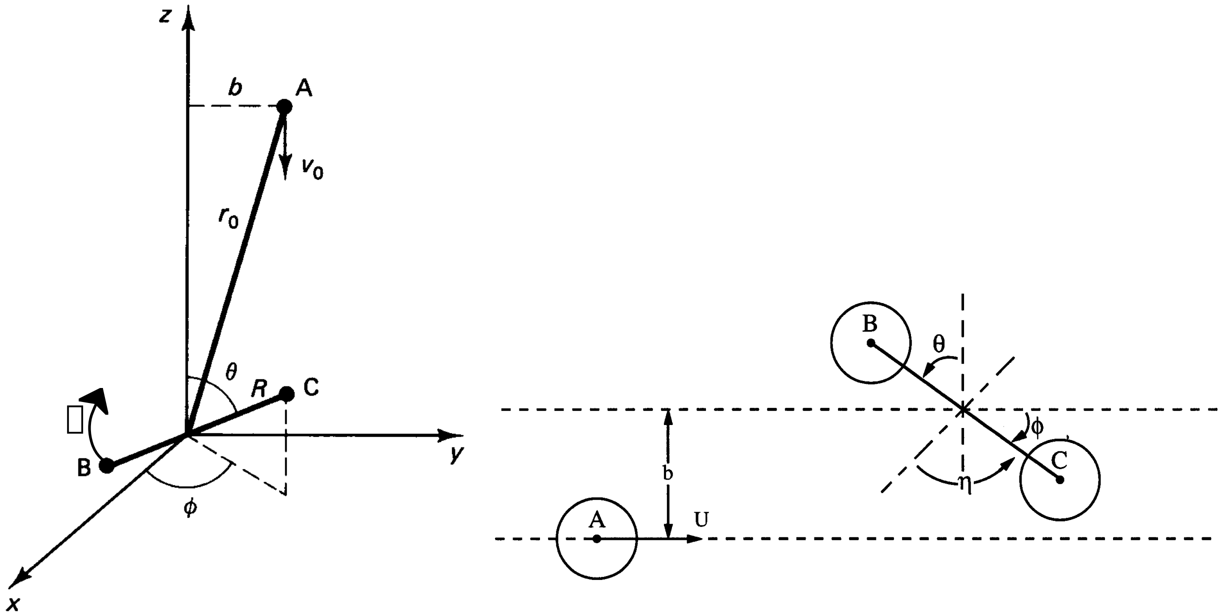
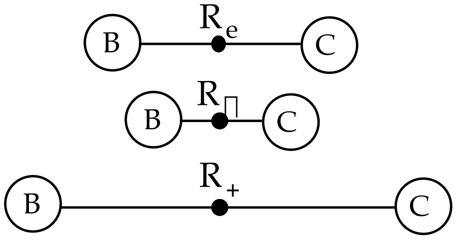


Figure R3.C-6 Reactive trajectory. Courtesy of Steinfeld et al., (Upper Saddle River, NJ: Prentice Hall, 1989) p. 264, with $v_0 = U = U_R$ in our notation.

Comments on the Initial Conditions

A few comments about the Monte Carlo choice of the distance, R_{BC}, between the B and the C molecule.



$R_□ < R < R_+$

Figure R3.C-7 Turning points of H–H vibration.

The distance R can only take on value between the maximum and minimum points of the vibration, $R_\pm$. That is

$$R_- \leq R \leq R_+$$

We calculate the values R_- and R_+ by knowing at the turning points where the oscillation changes direction and R_+ and R_-, where all the vibration energy is potential vibrational energy. That is, the molecules are in their most compressed state, R_-, or their most extended state, R_+. The potential energy is given by a Morse function D_{BC} [1 – exp [–□□$_{BC}$(R–R_e)]^2 where □$_{BC}$, D_{BC}, and R_e are the appropriate values for H_2. The quantum mechanical energy for the BC molecule in the □ and J quantum state is Equation 15 of article by Karplus et al.†

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† Karplus, et al., loc. cit.

$$E_{\nu,J} = \sum_{i=1} \left[G_i \left(\nu + \frac{1}{2}\right)^i + \sum_{i=1} F_{ij} \left(\nu + \frac{1}{2}\right)^{j-1} \left[J(J+1)\right]^i \right] \qquad \text{(R3.C-19)}$$

The constants in this equation (e.g., G_1, I_{11}) are given for H_2 in Table I in Karplus. By equating equations (R3.C-19) and (R3.C-20) we can find the roots of the equation for R to determine the turning points, R_+ and R_-. There is no angular momentum along the bond direction.

$$\frac{J(J+1)\hbar^2}{2\mu_{BC}R^2} + D_{BC}\left[1 - \exp\left[-\beta_{BC}(R - R_e)\right]\right]^2 = E_{\nu,J} \qquad \text{(R3.C-20)}$$

This calculation is tedious and difficult so we just need to accept that we can find the roots and "move on." Figures R3.C-8, and R3.C-9 show the results of the calculations we just outlined.

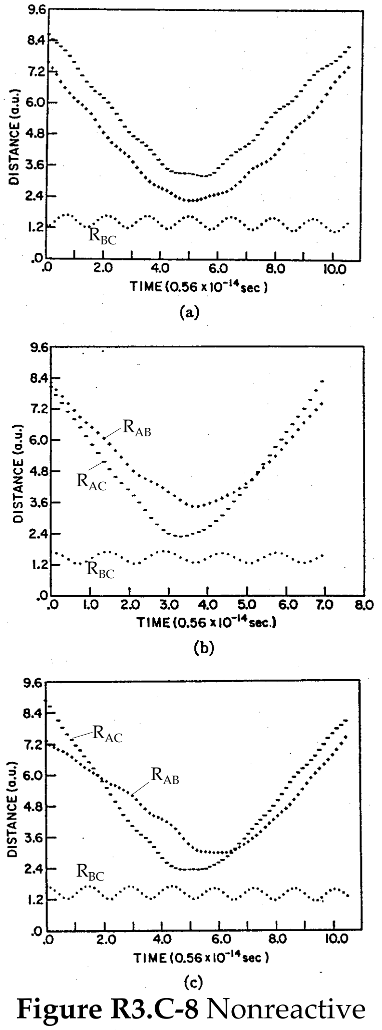


Figure R3.C-8 Nonreactive Trajectories

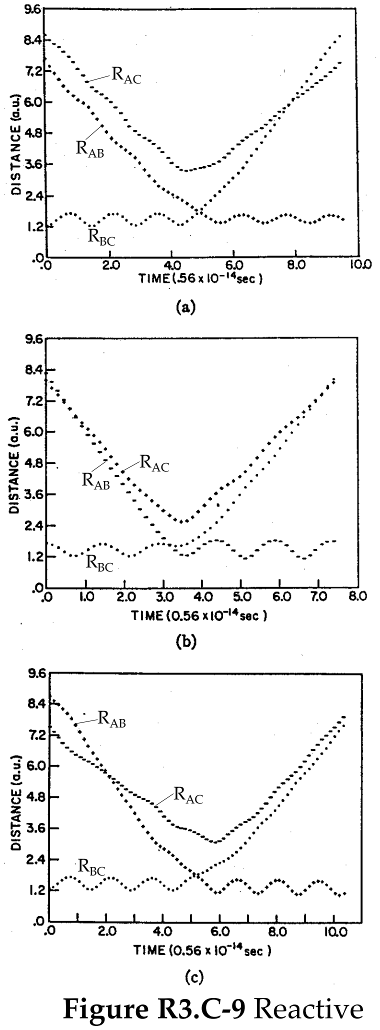


Figure R3.C-9 Reactive trajectories

Figures R3.C-8 and R3.C-9, Courtesy of American Chemical Society, Karplus et al., loc. cit., p. 3259.

	Figure 8			Figure 9		
	(a)	(b)	(c)	(a)	(b)	(c)
$U \times 10^{-6}$ cm/s	1.32	1.96	1.18	1.32	1.96	1.18
J	0	2	5	0	2	5
ν	0	0	0	0	0	0

One notes from Figures R3.C-8 (b) and (c) that the B-C molecule is rotating as evidenced by the fact that the R_{AB} and R_{AC} trajectories cross. On the other hand, for the case of no rotation, $J = 0$ in Figure (a), they do not cross. By the two crossings of R_{AB} and R_{AC} in Figure 8 (c) , one observes a faster rotation speed than Figure 8(a) where $J = 2$. In Figure R3.C-9 (a), we see that while B-C is not rotating before reaction, the AC molecule is rotating after reaction, as evidenced by the crossing of the R_{AC} and R_{BC} trajectories. The time of the trajectory calculation is $4\text{–}8 \times 10^{-14}$s, the $\nu = 0$ vibration period is 0.5×10^{-14}s, the rotational period for $J = 1$ is 20×10^{-14}s and for any quantum number J is $[27 \times 10^{-14}/J[(J+1)]^{1/2}]$s.

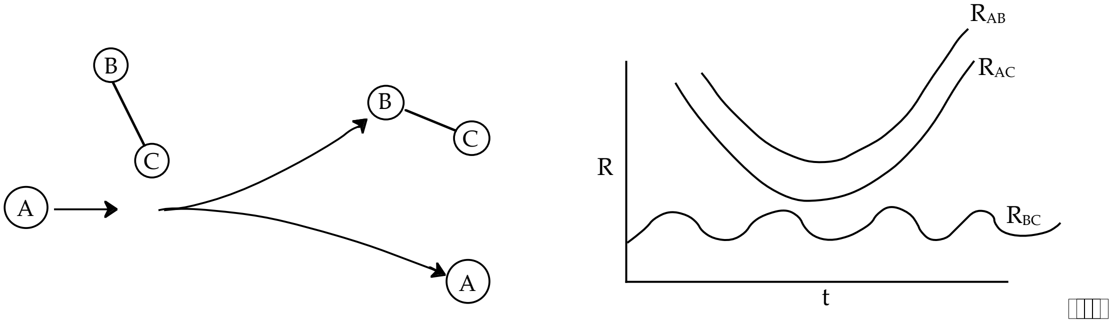
IV. CALCULATING THE REACTION CROSS SECTION

For a specified set of conditions, we now simply run a simulation and see whether or not a reaction occurs. Then we repeat for the same specified conditions but different Monte Carlo chosen values. A number of trajectories were calculated for the specified parameters [V_R, J, ν, b] using Monte Carlo techniques to calculate many trajectories similar to those shown in Figures R3.C-8 and R3.C-9. We keep track of the number of trajectories (simulations) that react, N_R, and those that don't react. We then take the ratio of those trajectories that resulted in reaction to all the trajectories carried out, N, to calculate the reaction probability

$$P_r\left[U,\nu,J,b\right] = \lim_{N\to\infty}\left[\frac{N_r\left(U,\nu,J,b\right)}{N\left(U,\nu,J,b\right)}\right] \qquad \text{(R3.C-21)}$$

We sum the AB reactions and AC reaction to get N_r.

No reaction



Reaction

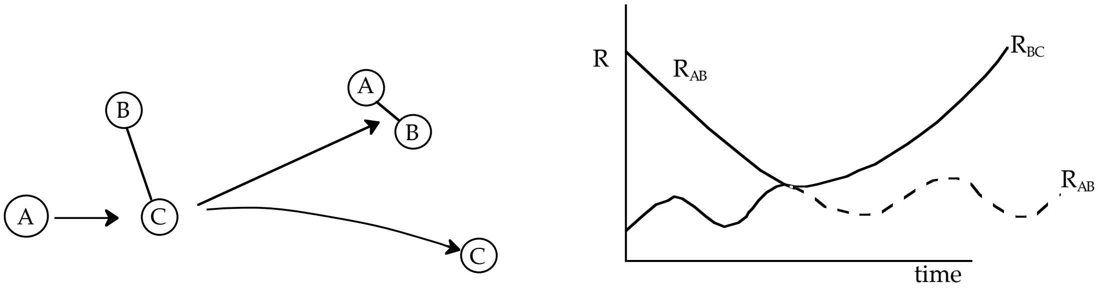


Figure R3.C-10 Molecular Trajectories.

Now vary one of the specified parameters by running a number of Monte Carlo simulations for each value of that parameter. First, b was varied while holding U, , and J constant. A number of simulations (trajectories) are carried out for each value of b in order to calculate P_r at that value of b. Then b is increased and the simulations repeated to again calculate P_r at another value of b. The results of the calculation are shown in Figure R3.C-11. For two different velocities. One notes that even for a head-on collision ($b = 0$), the probability is not 1.0. Taking into account orientation effects, and that the offset impact parameter, b, of A, relative to the center of mass of BC is greater than 1.85 au, then no reaction will occur.

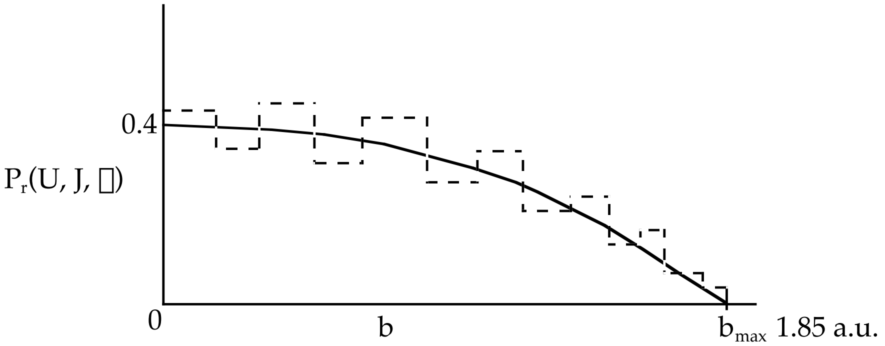
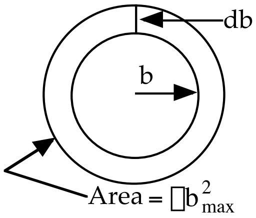


Figure R3.C-11 Probability of reaction as a function of the impact parameter. [Note 1 a.u. = 59.9 pm and 1 hartree (htr) = 627 kcal]. Courtesy of American Chemical Society, Karplus et al., loc. cit., p. 3259.

The dashed lines represent the actual calculated values of P_r while the curve represents the smoothed values. We note there is a maximum value of the impact parameter, b_{max}, above which no reaction will take place.

The Reaction Cross Section, S_r

The reaction cross section, S_r, is the probability of reaction, P_r and the cross section πb^2. In differential form S_r is a function of the relative velocity and the rotational and vibrational quantum numbers ν and J.



$$dS_r = P_r 2\pi b db$$

where b goes between zero and b_{max}

$$S_r(U,J,\nu) = \int_0^{b_{max}} P_r(U,J,\nu,b) 2\pi b db \qquad \text{(R3.C-22)}$$

We are going to make an approximation to simplify the calculations. The approximation is that the curve in Figure R3.C-11 can be approximated by a cosine function, namely

$$P_r = a\cos\left(\frac{\pi b}{2b_{max}}\right) \qquad \text{(R3.C-23)}$$

Both a and b_{max} increase in velocity as shown in Table R3.C-5.

Table R3.C-5 Effect of Approach Velocity on Probability Parameters

U (cm/s $\times 10^6$)	a	b_{max} (a.u.)
0.78	0	0
0.93	0.26	0.95
1.17	0.39	1.85
1.32	0.42	2.00
1.95	0.61	2.50

For the curve shown for $U_R = 1.17 \times 10^6$ cm/s in Figure PRS.3-11

$$P_r = 0.39\sin\left(\frac{\pi b}{(2)(1.85)}\right)$$

Translational Energy

We now will vary the relative velocity U and again calculate a reaction probability P_r as a function of b for each U. Using the cosine approximation, Equation (R3.C-23) we can determine a and b_{max} for the chosen value of U. The reaction smoothed probability is shown as a function b for two different relative velocities in Figure R3.C-12

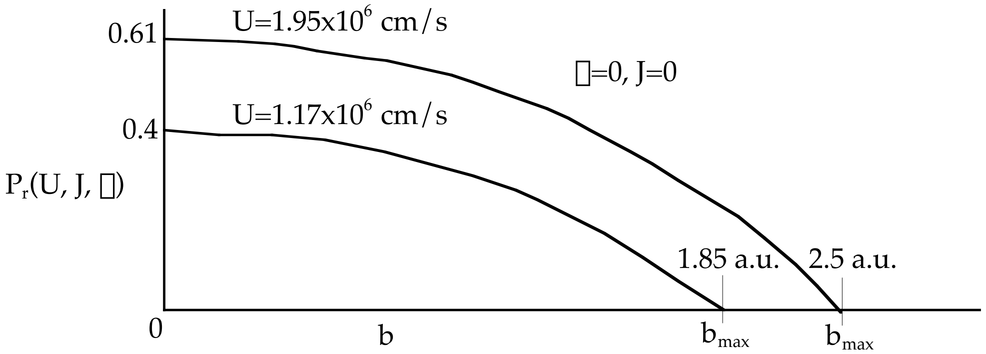


Figure R3.C-12 Reaction probability as a function of impact parameter for two different relative velocities.

We need to specify the vibration and rotation energies, i.e., quantum number, ν and J, when carrying out these calculations.

From Figure R3.C-12, we see that as the velocity increases to 1.95 cm/s, both a and b_{max} increase. Substituting for P_r using Equation (R3.C-23) into Equation (R3.C-22) we

$$S_r = 2\pi \int_0^{b_{max}} a \cos \frac{\pi b}{2b_{max}} \, b\,db$$

$$\text{Let } \alpha = \frac{\pi b}{2b_{max}}, \text{ then } b = \frac{2b_{max}\alpha}{\pi}, \text{ and } db = \frac{2b_{max}}{\pi} d\alpha$$

Substituting for b and for db

$$S_r = \frac{8ab_{max}^2}{\pi} \int_0^{\pi/2} \alpha \cos \alpha \, d\alpha$$

Integrating by parts

$$\boxed{S_r = \frac{8ab_{max}^2}{\pi}\left[\frac{\pi}{2} - 1\right] = 1.45ab_{max}^2 \,(\text{a.u.})^2} \qquad \text{(R3.C-24)}$$

Now the reaction cross section, $S_r(U,J,\nu)$, can be found as a function of the relative velocity for which one can determine the corresponding relative transition energy, E_R

$$E_R = \frac{1}{2\mu}U^2$$

Equation (R3.C-24) can be used to calculate the reaction cross section at any relative velocity. For example, when $U_R = 1.17 \times 10^6$ cm/s, $a = 0.39$, and $b = 1.85$ a.u., then

$$S_r = (1.45)(0.39)(1.85)^2 = 1.94(\text{a.u.})^2$$

when $U = 1.91 \times 10^6$ cm/s, $a = 0.61$ and $b_{max} = 2.5$ a.u., then

$$S_r = 5.45(\text{a.u.})^2$$

We continue in this manner to choose U, vary b, and find P_r as a function of b to obtain a and b_{max} and arrive at Figure R3.C-12. One notes from this figure that while the cross section at $U_R = 1.17 \times 10^6$ cm/s for which $S_r = 1.94$ (a.u.)^2 agrees with the simulation. The value at $U = 1.95 \times 10^6$ cm/s of $S_r = 4.4$ (a.u.)^2 is different from the value of 5.45 (a.u.)^2 just calculated. The reason for this discrepancy is that we used the cosine function to approximate the P_r very b curve rather than, say, fitting (P_r vs. b) with a polynomial or plotting the "data" as bP_r as a function b and multiplying the area under the curve by 2π to get S_r. This technique, while more tedious and labor intensive, would give a more accurate value than the cosine approximation.

$$S_r = 2\pi \int_0^{b_{max}} \left(P_r b\right) db$$

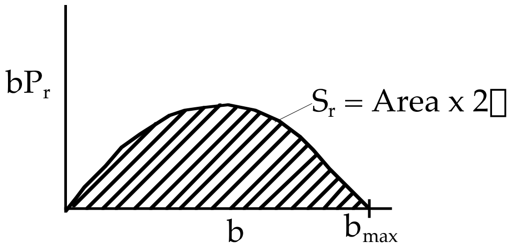


Figure R3.C-13 Determining the reaction cross section.

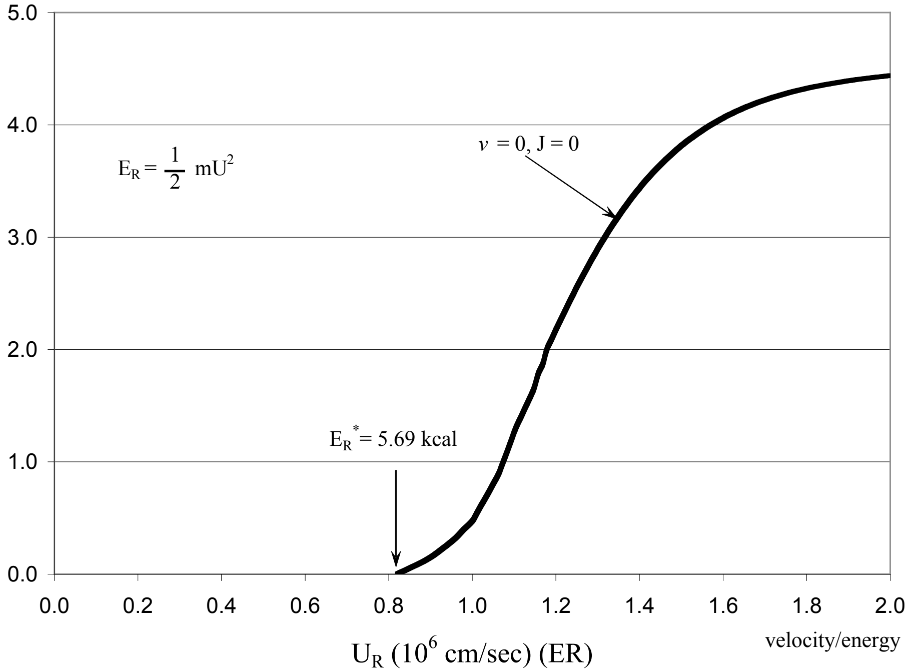


Figure R3.C-14 Reaction cross section as a function of relative velocity. Here 1 atomic unit ≡ 1 a.u. = 0.59 Å = 59 pm a_0^2 = (1 a.u)^2. Courtesy of American Chemical Society, Karplus et al., loc. cit., p. 3259.

We note $S_r = 0$ until we reach $E_R^* = 5.69$ kcal.[5] This energy is threshold kinetic energy necessary for the molecules A and BC to react. If the relative velocity U is such that the threshold energy is not exceeded, no reaction will occur. Now let's look at the effect of some of the parameters, namely ν and J, on the reaction cross section.

Rotational Energy

A approaches the BC molecule and reacts to form A–B and C. The rotational energy of the BC molecule is

$$E_{rot} = \frac{J(J+1)\left(\frac{h}{2\pi}\right)^2}{\underset{\text{moment of inertia}}{2I}} \text{ , } J = \text{Rotational quantum number} \qquad \text{(R3.C-25)}$$

We now carry out a number of realizations and mark down those runs that result in reaction (e.g., Figure R3.C-9) and those that do not result in reaction (e.g., Figure R3.C-8) to arrive at Figure R3.C-11. Figure R3.C-14 shows the results of the calculations that give the reaction cross section as a function of relative velocity (kinetic energy $\left(\frac{1}{2}\mu U^2\right)$) for the case $J = 0$ and $\nu = 0$.

Now let's change J and vary U (i.e., E_R) to calculate the reaction cross section.

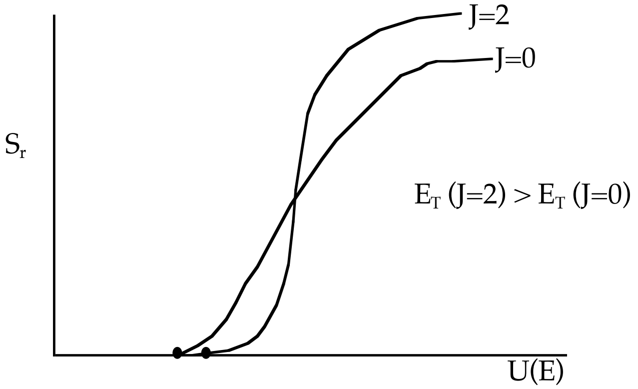


Figure R3.C-15 Effect of rotation quantum number on reaction cross section.

We see that both the threshold kinetic energy, E_T, and the limiting cross section at high kinetic energies increase with increasing rotation quantum number (frequency) For $J = 2$, the rotation period is 11.1×10^{-14}s compared with the interaction time of 10^{-14}s. At low kinetic energies the increased rotational energy makes it more difficult to react (steric effects). Also at higher kinetic energies the increased rotational energy increases the reaction cross section. However, the rotational energy is not available for crossing the potential energy barrier, $V(R_{AB}, R_{BC}, R_{AC})$.

Vibrational Energy

The vibrational energy is[†]

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[5] Karplus, et al, loc. cit.

[†] See most any Physical Chemistry textbook, e.g., Atkins, P.A. Physical Chemistry 6th Ed. W. H. Freemand & Co. NY (1997).

$$E_{vib} = \left(\frac{1}{2} + \nu\right) h v_o \qquad \text{(R3.C-26)}$$

ν = vibrational quantum number, v_0 is the frequency of vibration, and h is Plank's constant.

$$\text{Zero point energy } \nu = 0$$

$$E_o = \frac{1}{2} h v_0 = 6.2 \text{ kcal}$$

The vibrational energy contributes to the kinetic to supply the energy to pass over the barrier. However, not all the vibrational energy is available for reaction. Now lets change ν and vary U (E_R) and calculate the reaction cross section as shown in Figure R3.C-16

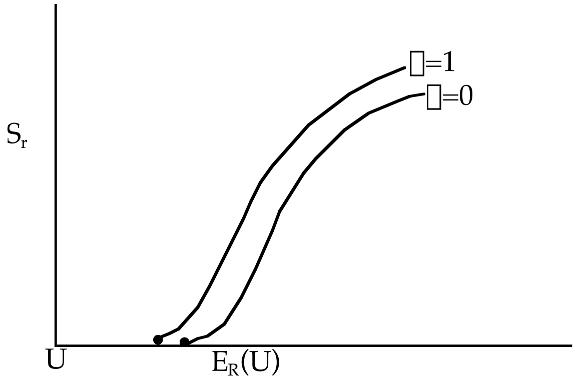

Figure R3.C-16 Effect of vibrational quantum number on reaction cross section.

At higher vibrational states the threshold energy decreases while the limiting value of S_r increases. However, Karplus notes that too few vibrational states were simulated to reach a definitive conclusion.

Figure R3.C-17 shows the reaction cross as a function of kinetic energy for the hard sphere and line of center models along with the results of molecular dynamics calculations.

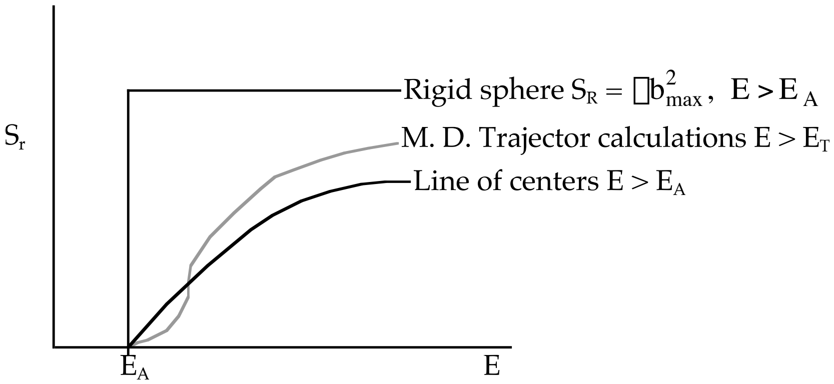

Figure R3.C-17 Comparison of models.

A discussion of the reaction cross section for the rigid sphere model and for line of centers model is given in Professional Reference Shelf 3A. We see the molecular dynamics (M.D.) trajectory for $\nu = 0$ and $J = 0$ gives a reaction cross section that falls between these two models.

V. RATE OF REACTION

Knowing the reaction cross section we can now proceed to calculate the overall rate of reaction, $-r_A$. The differential rate of reaction $d[-r_A(J,\nu)]$ of species A, which has a velocity V_A and a concentration $d\hat{C}_A$, with species BC, which has a concentration of $d\hat{C}_{BC}$ that has velocity V_B and is the ν vibrational state and the J rotational state, is

$$d\left[-r_A(J,\nu)\right] = \overbrace{dS_r}^{P_r\,2\pi b\,db}\ N_{Avo}U\left[d\hat{C}_A(V_A)\right]\left[d\hat{C}_{BC}(J,\nu,V_{BC})\right] \quad \text{(R3.C-27)}$$

$$\text{(mole A/s/dm}^3\text{)}$$

where

$-r_A(J,\nu)$ = Rate of reaction of A with BC molecules in the J rotational state and ν vibrational state (mol A/dm^3/s)

U = Relative velocity $(V_A - V_{BC})$ (dm/s)

$d\hat{C}_A$ = Concentration of A molecules with velocities between V_A and $(V_A + dV_A)$

= $C_A f(V_A) dV_A$ (mol/dm^3)

C_A = The total concentration of A molecules (mol A/dm^3)

$f(V_A)$ = Distribution of molecular velocities of molecule A, similar for BC molecules BC (c.f. Equation (R3.C-27)).

$d\hat{C}_{BC}$ = Concentration of BC molecules with rotational state J, vibrational state ν, and velocities between V_{BC} and $(V_{BC} + dV_{BC})$ (mol/dm^3)

$d\hat{C}_{BC}$ = $C_{BC}(J,\nu) f_{BC}(V_{BC}) dV_{BC}$ (mol/dm^3)

$C_{BC}(J,\nu)$ = $C_{BC}F_{BC}(J,\nu)$ (mol/dm^3) = concentration of BC molecules in J rotational state and ν vibrational state (mol BC/dm^3)

C_{BC} = The total concentration of all B–C molecules (mol/dm^3), and

$F_{BC}(J,\nu)$ = The fraction of B–C molecules in the J rotational state and the ν vibrational state

The distribution functions in the above equations are for velocity

$$f_i dv_i = \left(\frac{m_i}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-m_i v_i^2}{2k_B T}\right) dv_i \quad \text{(R3.C-28)}$$

for rotation and vibration

$$F_{BC} = f_J\,\frac{(2J+1)\ e^{-(E_{\nu,J}/k_B T)}}{Q_{J,\nu}} \quad \text{(R3.C-29)}$$

where $Q_{J,v}$ is the rotational-vibrational partition function, f_J is the statistical weight, and

$$E_{\nu,J} = \sum_{i=1}\left[G_i\left(\nu+\frac{1}{2}\right)^i + \sum_{i=1} F_i\left(\nu+\frac{1}{2}\right)^{i-1}\left(\frac{J}{J+1}\right)^i\right] \quad \text{(R3.C-30)}$$

and the values of G_i and F_i are given in the article by Karplus et al.[6]

Calculating the Total Rate

First we integrate Equation (R3.C-27) over all velocities so that velocity is incorporated in the rate and it is now only a function ν and J.

$$-r_A(\nu,J) = C_A C_{BC} F_{BC}(\nu,J) \underbrace{\int_0^\infty \int_0^\infty U S_r(\nu,J,V_R) f_A dV_A f_{BC} dV_{BC}}_{k_{\nu,J}} \qquad \text{(R3.C-31)}$$

$$-r_A(\nu,J) = k_{\nu,J} F_{BC}(\nu,J) C_A C_B \qquad [U \equiv V_R] \qquad \text{(R3.C-32)}$$

The rate, $-r_A(\nu,J)$ in Equation (R3.C-32), is only for those reactions with vibrational ν and rotation states J. The total rate of reaction is found by summing overall vibrational and rotational states

$$\boxed{-r_A = \sum_{\nu,J} \left[-r_A(\nu,J)\right]} \qquad \text{(R3.C-33)}$$

$$-r_A = \sum F_{BC}(\nu,J) k_{\nu,J} C_A C_{BC} = k(T) C_A C_{BC} \qquad \text{(R3.C-34)}$$

$$k = \sum F_{BC}(\nu,J) k_{\nu,J} \qquad \text{(R3.C-35)}$$

A comparison of the theoretical and calculated values of the specific reaction rate is shown in Table R3.C-6.

$$k(T) = \sum_{J,\nu} k_{J,\nu} F_{BC}(J,\nu) = Q_{J,\nu}^{-1} \left[\sum_{J,\nu} f_J (2J+1) \exp\left(\frac{-E_{J,\nu}}{kT}\right) N_{Avo} \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \left(\frac{\mu_{A,BC}}{kT}\right)^{\frac{1}{2}} \right.$$

$$\left. \times \int_0^\infty S_r(U_B,J,\nu) \times \exp\left(-\frac{\mu_{A,BC} U_R{}^2}{kT}\right) U_R{}^3 dU_R \right] \qquad \text{(R3.C-36)}$$

Equation (R3.C-36) is Equation 41 in the article by Karplus et al.[7] N_{Avo} is Avogadro's number.

After carrying out the Monte Carlo Simulations for all specified variables b, U (i.e., E_{AC}), J, and ν at a given temperature we use Equation (R3.C-36) to calculate the specific rate k(T) next. The temperature was changed (e.g., from 300 to 500K) and the specific reaction rate recalculated. The results of some of these of the calculations are shown in Table R3.C-6.

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[6] Karplus, et al., loc. cit.; also see K. J. Laidler *Chemical Kinetics*, 3rd ed. (New York: Harper Collins, 1987) p. 449-558.

[7] Karplus, et al., loc. cit.

Table R3.C-6 k(T) Values from M.D. Calculations and Experiment.[a,h]

T(K)	k(T) □ 10^{-11} from least-squares fit[b] $\frac{\text{cc}}{\text{mole} \bullet \text{s}}$	k(T) □ 10^{-11} from calculated points[c] $\frac{\text{cc}}{\text{mole} \bullet \text{s}}$	k(T) □ 10^{-11} from experiment $\frac{\text{cc}}{\text{mole} \bullet \text{s}}$
300	0.0018	0.002008	0.0014–0.0020 [d]
500	0.225	0.23	.□□
700	2.01	2.04	2.49–4.99 [e,g]
900	7.3	7.38	7.6–15.2 [f,g]
1000	11.69	11.78	11.0–22.0 [f,g]

[a] All values of k(T) is units of cubic centimeters per mole•second.

[b] Calculated by Eq. (41) with S_r given by Eq. (43) and Table II of Karplus' paper

[c] Calculated by Eq. (C-36) with computed values of S_r.

[d] K. Geib and P. Harteck, Z. Physik Chem. Bodenstein Fastband 849 (1931).

[e] M. van Meersche, Bull. Soc. Chim. Belges 60, 99 (1951).

[f] A. Farkas and L. Farkas, Proc. Roy. Soc. (London) A152, 124 (1935).

[g] G. Boato, G. Careri, A. Cimino, E. Molinari, and G. G. Volpi, J. Cl. Phys. 24, (1956), p. 783, have suggested that the values of van Meersche and Farkas and Farkas should be multiplied by 0.5 to correct for the present oxygen in the reaction mixture. Since this point has not been settled unequivocally, we list the range corresponding to 0.5 times the measured value to measured value.

[h] Table R3.C-6 Courtesy of *ACS*, Karplus, et al., loc. cit.

Looking at the specific reaction rates k in Table R3.C-6 we see

	Theory	Experiment
T = 300	$k = 0.00185\ \text{cm}^3/\text{s}\bullet\text{mol}$	$0.0017–006\ \text{cm}^3/\text{s}\bullet\text{mol}$
T = 1000	$k = 11.5\ \text{cm}^3/\text{s}\bullet\text{mol}$	$11–22\ \text{cm}^3/\text{s}\bullet\text{mol}$

We can use the theoretical values of k(T) predicted in Table R3.C-2 to determine the activation energy. A plot of ln k vs. 1/T is shown in Figure R3.C-17.

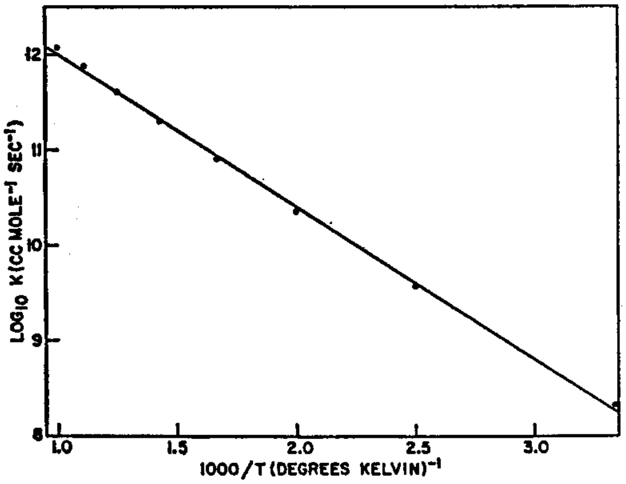

Figure R3.C-18 Using molecular dynamics to predict activation energy. Courtesy of Karplus et al., *J. Chem. Phys.* **43**, 1965, p. 3259.

From the slope, we find $E_A = 7.4$ kcal/mole

$$k = Ae^{-E_A/RT}$$

with

$$A = 4.3 \times 10^{13}\ \frac{\text{cm}^3}{\text{mol} \bullet \text{s}} = 4.3 \times 10^{10}\ \frac{\text{dm}^3}{\text{mol} \bullet \text{s}}$$

which is in excellent agreement with the experimental values.

A plot of the values in Table PRS.C3-5 in the form of ln k(T) versus 1/T will yield an activation energy of 7.4 kcal/mol, which is very close to the experimental value of 7.5 kcal/mol. We see there is excellent agreement of both the frequency factor, A, and the activation energy, E_A, between the theory and experiment. We also note the differences in the values of the following energies.

A summary of all the energies obtained from the literature or by calculation is given in Figure R3.C-19.

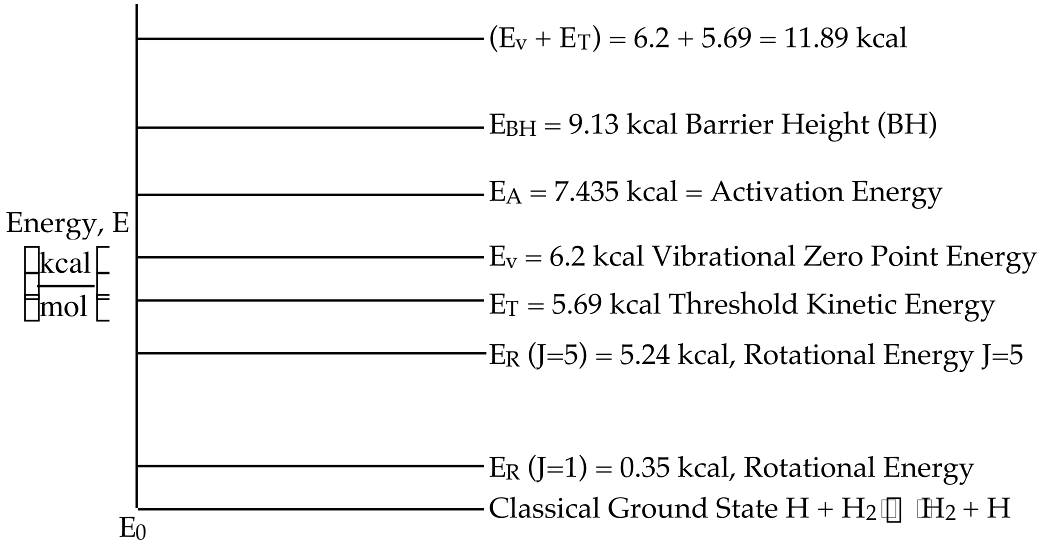

Figure R3.C-19—Comparison of energies.

The barrier height = 9.2 kcal
The minimum kinetic energy (MKE) = 5.7 kcal
The ground state vibrational energy (GSV) = 6.2 kcal
The ground state vibration energy + MKE = 6.2 + 5.89 = 11.89 kcal
The activation energy = 7.5 kcal

One notes that the activation energy is less than the barrier height, which is a result of quantum mechanical tunneling. One also notes that not all the ground state vibrational energy is available to be added to the translational energy to cross the energy barrier.

CLOSURE

The equation of motion for molecules A and BC were coupled with potential energy surface to calculate trajectories of the A and BC molecules. The reaction probability was calculated by counting up the number of trajectories that resulted in reaction and dividing by all the trajectory trials. Below a threshold value of the translational kinetic energy no reaction occurs. There is also a maximum value of the impact parameter above which no reaction will occur, owing to steric effects. The reaction probability only reaches a value of 0.6, even for head-on collisions (b-0) and very large translational kinetic energies. The reaction cross can be calculated from the impact parameter and relative velocity for given values of the vibrational and rotational quantum numbers. It was found to have a sigmodal shape, increasing as the kinetic energy (velocity) increased. The threshold kinetic energy decreased with increasing vibration quantum numbers and increased with increasing rotational quantum numbers.

The characteristic times are the rotational vibrational period for $J = 1$ (19×10^{-4}s) and for $J = 5$ (4.9×10^{-14}s) the vibration period (0.5×10^{-14}s) the time of interaction is (10^{-14}s) and the time of the trajectory calculation (between 4 and 8×10^{-14}s). We note that the rotational period is an order of magnitude greater than the interaction time, while the vibrational period is the same order as the interaction time.

The minimum kinetic energy 5.69 kcal is not sufficient to cross the potential energy barrier of 9.13 kcal and requires some of the vibrational energy from the BC molecules. The sum of the threshold (i.e., minimum energy necessary for reaction) of 5.69 kcal and the □ = 0 vibrational state energy of 6.2 kcal gives a total energy of 11.89 kcal, which is greater than barrier height of 9.13 kcal. The difference between 11.89 and 9.13 indicates that not all the vibational energy is available for reaction. None of the rotational energy is available for reaction.

The rate constants k(T) were calculated as a function of temperature from first principles with no adjustable parameters. When the ln k was plotted as a function of 1/T, the activation energy was found to be 7.4 kcal/mol, which is in excellent agreement with the experimental value of 7.5 kcal/mol. The fact that the activation energy is smaller than barrier is a consequence of quantum mechanical tunneling.

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