RRKM REACTION RATE THEORY FOR TRANSITION STATES OF ANY LOOSENESS ☆

David M. WARDLAW [1] and R.A. MARCUS
Arthur Amos Noyes Laboratory of Chemical Physics [2], *California Institute of Technology, Pasadena, California 91125, USA*

Received 6 July 1984; in final form 19 July 1984

Unimolecular rate theory for various types of reactions is implemented for any looseness of transition state. Quantum states are counted for all but the "transitional" modes, their phase space being counted via Monte Carlo sampling. The rate constant k_{EJ} is then weighted with the initial E and J distributions.

1. Introduction

In the transition-state theory of chemical reactions the position of the transition state along the reaction coordinate is frequently readily identifiable, for example when the potential-energy surface for the reaction has a pronounced saddle point. In this case the transition state is often chosen to be a hypersurface passing through the saddle point so as to separate the reactant and product valleys ‡.

In reactions such as bond fissions, the reverse reaction of free-radical recombination, or some ion–molecule reactions, there is little or no potential-energy barrier along the reaction coordinate. However, one may define a dividing surface such that the available phase space on it, restricted by any constants of the motion, is a minimum [2]. This dividing surface is then the transition state [2] and it depends on any constants of the motion, such as, for an isolated molecule or pair of molecules in the gas phase, the total energy E, the total angular momentum J and its component J_Z along a space-fixed axis. In practical applications of this criterion (or in a quantum treatment) it is common to choose as a dividing surface a hypersurface in *coordinate* space such that the number of available classical (or quantum) states N_{EJ} for motion on the hypersurface, is a minimum when plotted versus the reaction coordinate [3–5]. (This criterion was noted in ref. [5], which mistakenly attributed it to Bunker. However, Bunker and Pattengill [6] minimized a density of states for RRKM theory rather than N_{EJ}, which is not quite correct but gives essentially the same result.)

For bond-fission reactions the main difficulty in calculating N_{EJ} lies in the "transitional" degrees of freedom, namely those vibrations, rotations, and hindered rotations in the dissociating reactant which become free rotations and orbital motions of the separating products. In the transition-state region these modes may display large-amplitude anharmonic motion and may be strongly coupled to each other. The calculation of their quantum energy levels and the associated sum of states becomes very complicated indeed. In this Letter we treat the transitional modes in a way which affords computational tractability and which makes use of coordinates designed to facilitate the analysis. Namely, action–angle coordinates related to those used for bimolecular collisions [7] are introduced for these modes. Next, a classical Monte Carlo calculation of the available phase space is made, including quantum corrections if needed. The remaining coor-

☆ This research was supported by a grant from the National Science Foundation.
[1] NSERC of Canada Postdoctoral Research Fellow.
[2] Contribution No. 7061.
‡ Sometimes, as in the transfer of a light particle, such as an H atom or proton between two heavy particles, the system may by-pass the saddle-point region because of the large curvature of the conventional reaction path. A treatment of such cases is given in ref. [1].

dinates are treated via the usual quantum count [8].

The procedure, choice of variables, and some results are given below. The present work extends in a practical way that which we have given earlier [9,10] in which the transition states were assumed to be "tight" or "loose" in actual applications. Monte Carlo calculations of phase-space volumes have been used in completely classical calculations of numbers of states, densities of states, or unimolecular reaction rate theory [11–14]. Both rotating [11] and non-rotating [12–14] systems have been so studied, although for the rotating systems [11] the ensembles used were not J-fixed. A comparison between classical and quantal counts for separable [12] and non-separable [13] systems has also been given.

2. Theory

The rate constant k_{EJ} for the unimolecular decomposition or isomerization of a molecule with total energy in the center-of-masss frame E and specified J is given in RRKM theory [9] by

$$k_{EJ} = N_{EJ}/h\rho_{EJ} , \tag{1}$$

where N_{EJ} is the number of quantum states of the transition state having an energy less than or equal to E in the degrees of freedom orthogonal to the reaction coordinate and at the given J; ρ_{EJ} is the density of states of the dissociating or isomerizing molecule. Tunneling corrections along the reaction coordinate [5,15,16] (eq. (4) of ref. [16]) and reaction path degeneracy [5,10,16,17] can be introduced into N_{EJ} if needed. A unimolecular rate constant at any pressure is obtained from eq. (1) in the standard way by suitably weighting the Es and Js (eq. (4) of ref. [10]). In the center-of-mass system the modes are subdivided into "transitional" modes and the remaining coordinates, thereby yielding the following expression for N_{EJ}:

$$N_{EJ} = \int_0^{E'} N_v(E' - \epsilon)\Omega_J(\epsilon)\mathrm{d}\epsilon , \tag{2}$$

where $\Omega_J(\epsilon)\mathrm{d}\epsilon$ is the number of states of the transitional modes for the given J when their total energy lies in $(\epsilon, \epsilon + \mathrm{d}\epsilon)$. $N_V(E' - \epsilon)$ is the number of quantum states in the remaining coordinates having an energy less than or equal to $E' - \epsilon$, E' being the available energy, i.e. E minus the potential-energy minimum at the given value of the reaction coordinate and minus the zero-point energy of the modes included in N_V. The two types of coordinates are taken to be uncoupled from each other in eq. (2), apart from an indirect coupling via the dependence of the molecular constants on the reaction coordinate.

To obtain N_{EJ} we define two sets of body-fixed coordinate axes, each fixed in a separating fragment [7,18]. The origin of each coordinate system is located at the center of mass of that fragment. If either fragment has some symmetry, its coordinate axes are chosen to coincide with the symmetry axes. Using the action–angle coordinates of polyatomic species [7,18] referred to earlier to represent the phase space of the transitional modes, Ω_J and then N_{EJ} is calculated as a function of R, the separation distance of the fragments' centers of mass. Our use of action–angle rather than Cartesian coordinates is a matter of convenience rather than of necessity, chosen so as to enhance the sampling in the Monte Carlo calculation of Ω_J and to minimize the dimensionality of the phase-space integral. These coordinates are also suitable for a scattering description of the process and, as such, are useful in describing the separated-product properties as well as exit-channel effects.

In the case of a reaction such as $H_2O_2 \rightarrow 2OH$, action variables, written throughout in units of h as j_1, j_{1z} j_{1z}, j_{2z}, l and l_z, and their conjugate angles can be used [7,18] to specify the relative orientations of all the atoms. j_1 and j_2 are the individual rotational angular momentum actions of fragments 1 and 2, j_{1z} and j_{2z} are their space-fixed z components, and l and l_z are the orbital angular momentum action of the fragments and its z component, respectively. However, we choose to make a canonical transformation [18] [‡2] to the action variables J, J_Z, j_1, j_2, l, k and their respective conjugate angles α, β, α_1, α_2, α_l, α_k, where k is an intermediate angular momentum action associated with a vector sum $|j_1 + j_2|$, and J corresponds to $|k + l|$. (J now denotes an action variable rather than the angular momentum, from which it differs by a factor or 2π.) The transformation between action–

[‡2] A different but related angular momentum coupling scheme is used in ref. [7] because of the different application involved.

angle and internal-type coordinates, in which the potential is usually given, is similar to that described in ref. [7] and is given elsewhere [19]. (In the case of a dissociation of a polyatomic molecule into non-linear fragments there are two additional action variables involved in the description of the transitional modes, namely the component κ_i of each j_i along the body-fixed z axis of fragment i. In such cases there are six transitional degrees of freedom, apart from those associated with J and J_Z.)

For a system described by the above variables, such as $H_2O_2 \rightarrow 2OH$, we have

$$\Omega_J(\epsilon) = (2J+1) \times \int \ldots \int \mathrm{d}j_1 \mathrm{d}j_2 \mathrm{d}l \mathrm{d}k \mathrm{d}\alpha_1 \mathrm{d}\alpha_2 \mathrm{d}\alpha_l \mathrm{d}\alpha_k \delta(\epsilon - H_{\mathrm{cl}}) , \quad (3)$$

where H_{cl} is the classical Hamiltonian for the transitional modes, and is given below. The factor $2J+1$ arises from the J_Z multiplicity. The limits on the angle variables are 0 to 1. The angular momentum action variables are restricted by energy conservation and by the triangle inequalities: $|j_1 - j_2| \leqslant k \leqslant j_1 + j_2$ and $|k - l| \leqslant J \leqslant k + l$. The relative positions of all the particles are independent of the overall orientation of the set of atoms and so the integrand cannot depend on J_Z, β, and α [19]. H_{cl} is taken to be

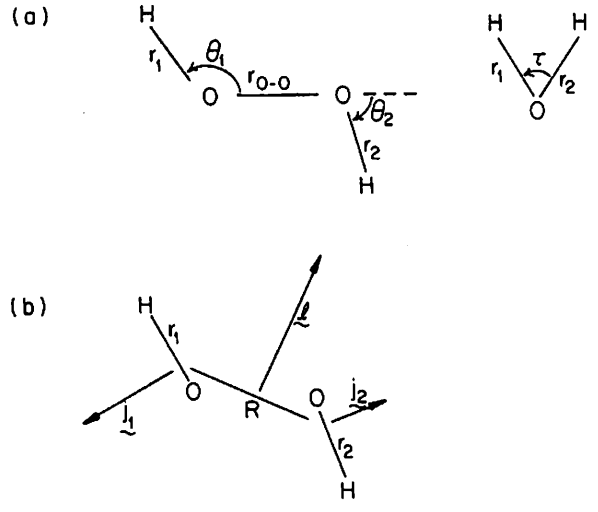

Fig. 1. (a) The O–O and O–H bond lengths (r_{O-O}, r_1, r_2), bending angles (θ_1, θ_2), and the torsional angle for H_2O_2. (b) Angular momenta for fragment rotations and relative motion of HO...OH, and distance between the centers of mass, R.

$$H_{\mathrm{cl}} = \frac{j_1^2}{2\mu_1 r_1^2} + \frac{j_2^2}{2\mu_2 r_2^2} + \frac{l^2}{2\mu R^2} + V_{\mathrm{t}}(r_{O-O}, \theta_1, \theta_2, \tau) , \quad (4)$$

where μ_i is the reduced mass of fragment i, and μ is the reduced mass for the relative motion of the two fragments. H_{cl} is specified by the variables (R, r_1, r_2, J, j_1, j_2, l, k, α_1, α_2, α_l, α_k). The potential V_{t} for the transitional modes is modeled in the example below for H_2O_2 to be function of the internal coordinates r_{O-O}, θ_i and τ, in fig. 1a. The two other coordinates there, r_1 and r_2, correspond to OH vibrations and are therefore included in $N_V(E' - \epsilon)$. The reaction coordinate R and several angular momenta involved in the description of H_2O_2 are depicted in fig. 1b. The functional form used for V_{t}, together with numerical constants, are given elsewhere [19].

From eq. (2) and (3) one obtains

$$N_{EJ} = (2J+1) \times \int \ldots \int N_V(E' - H_{\mathrm{cl}}) \mathrm{d}j_1 \mathrm{d}j_2 \mathrm{d}l \mathrm{d}k \, \mathrm{d}\alpha_1 \, \mathrm{d}\alpha_2 \, \mathrm{d}\alpha_l \mathrm{d}\alpha_k , \quad (5)$$

where N_V is zero unless $E' > H_{\mathrm{cl}}$. The Monte Carlo evaluation of this integral involves random selection of the angles in the (0,1) interval and random selection of the angular momenta subject to the constraints described above.

3. Results

In developing and assessing the present method three bond-fission reactions were examined using model potential-energy surfaces: $NO_2 \rightarrow NO + O$, $H_2O_2 \rightarrow 2OH$, and $C_2H_6 \rightarrow 2CH_3$, having 2, 4 and 6 transitional modes, respectively. For each system N_{EJ} was calculated over a range of Es and Js, and in each case the transition-state location $R^\dagger$ defining the minimum in the N_{EJ} versus R curve was readily identifiable. $N_{EJ}(R^\dagger)$ was obtained to within a variance of $\approx$1% for NO_2 and H_2O_2, and $\approx$3% for C_2H_6 with uniform Monte Carlo sampling. The relative computation times to obtain N_{EJ} for each of the three systems were found to be essentially independent of E and J. Computation times for systems larger than ethane will be approximately the same as that for

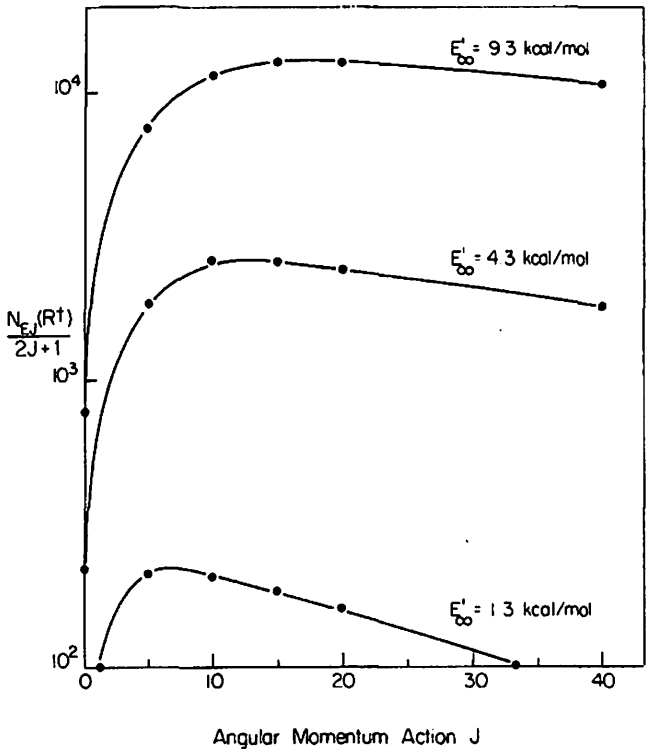

Fig. 2. Semilog plot of $N_{EJ}(R^{\dagger})/(2J+1)$ versus J (in units of h) for various values of E'_{∞}, the energy available to the system at $R = \infty$. The calculations are given for $R = R^{\dagger}$; the value of $R^{\dagger}$ varies with E and J and is in the range 3.0–3.75 Å.

ethane since the number of transitional modes is the same. Thus, large systems and large Es are readily treated.

A sample of the results is presented in fig. 2, where $N_{EJ}/(2J+1)$ is plotted versus J for three values of available product energy. One sees that the ordinate depends strongly on J at small J and that it undergoes a maximum with increasing J at high Js. Quantum corrections can be introduced as needed. When there are many accessible quantum states in each zeroth-order transitional degree of freedom, the quantum correction is negligible. This situation occurs when the transition state is loose or when the available ϵ is high enough. One can estimate quantum counts using a method such as Doll's [12] or using the frequencies of the transitional modes obtained from the power spectrum [20] of a typical trajectory for H_{cl} in eq. (4). One can also adapt quantum Monte Carlo methods [21] to a microcanonical ensemble to obtain a quantum correction for the transitional modes. From the typical value of $\int \Omega_J(\epsilon')\mathrm{d}\epsilon'/(2J+1)$, integrated from 0 to ϵ, one can roughly estimate whether quantum corrections are needed or not. When this value is of the order of unity or less, they certainly are needed. (See for example refs. [12,13].)

In subsequent papers [19] results such as those in fig. 2 are compared with those for simple models, e.g., the loose and tight transition states. Also explored there are the dependence of N_{EJ} and of $R^{\dagger}$ on the large-R behavior of the potential-energy surface, the calculation of unimolecular and bimolecular rate constants, energy disposal cross sections, the "transition-state switching" topic in ion–molecule reactions [21] and the approximation of minimizing an appropriate ensemble-weighted average of k_{EJ}, instead of minimizing N_{EJ} for each E and J. Comparison will also be made with a statistical "adiabatic channel" model [17]. Some features of the present method for obtaining k_{EJ} are its simplicity, rapidity of computation and, particularly, its use of actual potential-energy surfaces as they become available.

References

[1] V.K. Babamov and R.A. Marcus, J. Chem. Phys. 74 (1981) 1790;
V.K. Babmov, V. Lopez and R.A. Marcus, J. Chem. Phys. 78 (1983) 5621; 80 (1984) 1812;
B.C. Garrett, D.G. Truhlar, A.F. Wagner and T.H. Dunning, J. Chem. Phys. 78 (1983) 4400;
D.K. Bondi, J.N.L. Connor, B.C. Garrett and D.G. Truhlar, J. Chem. Phys. 78 (1983) 5981.

[2] E. Wigner, J. Chem. Phys. 5 (1937) 720; Trans. Faraday Soc. 34 (1938) 29;
J. Horiuti, Bull. Chem. Soc. Japan 13 (1938) 210;
J.C. Keck, J. Chem. Phys. 32 (1960) 1035; Advan. Chem. Phys. 13 (1967) 85;
D.G. Truhlar, W.L. Hase and J.T. Hynes, J. Phys. Chem. 87 (1983) 2664, and references therein.

[3] W.L. Hase, J. Chem. Phys. 57 (1972) 730; 64 (1976) 2442;
B.C. Garrett and D.G. Truhlar, J. Chem. Phys. 70 (1979) 1593.

[4] M. Quack and J. Troe, Ber. Bunsenges. Physik. Chem. 81 (1977) 329;
J. Troe, J. Chem. Phys. 75 (1981) 226; 79 (1983) 6017.

[5] R.A. Marcus, J. Chem. Phys. 45 (1966) 2630.

[6] D.L. Bunker and M. Pattengill, J. Chem. Phys. 48 (1968) 772.

[7] A.F. Turfa, D.E. Fitz and R.A. Marcus, J. Chem. Phys. 67 (1977) 4463;
A.F. Turfa, W.-K. Liu and R.A. Marcus, J. Chem. Phys. 67 (1977) 4468.

[8] P.J. Robinson and K.A. Holbrook, Unimolecular Reactions (Wiley–Interscience, New York, 1972);
W. Forst, Theory of unimolecular reactions (Academic Press, New York, 1973).
[9] R.A. Marcus, J. Chem. Phys. 20 (1952) 359;
R.A. Marcus and O.K. Rice, J. Phys. Colloid Chem. 55 (1951) 894.
[10] R.A. Marcus, J. Chem. 43 (1965) 2658; 52 (1970) 1018.
[11] D.L. Bunker, J. Chem. Phys. 40 (1964) 1946;
S.C. Farantos, J.N. Murrell, and J.C. Hadjuk, Chem. Phys. 68 (1982) 109.
[12] J.D. Doll, Chem. Phys. Letters 72 (1980) 139;
L.B. Bhuiyan and W.L. Hase, J. Chem. Phys. 78 (1983) 5052.
[13] D.W. Noid, M.L. Koszykowski, M. Tabor and R.A. Marcus, J. Chem. Phys. 72 (1980) 6169;
M.V. Berry, Ann. Phys. 131 (1981) 163.
[14] J.E. Adams, J. Chem. Phys. 78 (1983) 1275.
[15] W.H. Miller, J. Am. Chem. Soc. 101 (1979) 6810.
[16] R.A. Marcus, J. Chem. Phys. 45 (1966) 2138.
[17] M. Quack and J. Troe, Ber. Bunsenges. Physik. Chem. 78 (1974) 240.
[18] D.M. Wardlaw, Ph. D. Thesis, University of Toronto (1982).
[19] D.M. Wardlaw and R.A. Marcus, J. Chem. Phys., to be submitted for publication.
[20] D.W. Noid, M.L. Koszykowski and R.A. Marcus, J. Chem. Phys. 67 (1977) 404;
M.L. Koszykowski, D.W. Noid and R.A. Marcus, J. Phys. Chem. 86 (1982) 2113;
D.M. Wardlaw, D.W. Noid and R.A. Marcus, J. Phys. Chem. 88 (1984) 536.
[21] J.A. Barker, J. Chem. Phys. 70 (1979) 2914;
D. Chandler and P. Wolynes, J. Chem. Phys. 74 (1981) 4078;
K.S. Schweitzer, R.M. Stratt, D. Chandler and P.G. Wolynes, J. Chem. Phys. 75 (1981) 1347;
R.M. Stratt, J. Chem. Phys. 77 (1982) 2108;
D. Thirumalay, E.J. Bruskin and B.J. Berne, J. Chem. Phys. 79 (1983) 5063;
J.D. Doll and D.L. Freeman, J. Chem. Phys. 80 (1984) 2239;
D.L. Freeman and J.D. Doll, J. Chem. Phys. 80 (1984) 5709.
[22] W.J. Chesnavich, L.M. Bass, T. Su and M.T. Bowers, J. Chem. Phys. 74 (1981) 2228;
M.T. Bowers, M.F. Jerrold, W. Wagner-Redeker, P.R. Kemper and L.M. Bass, Faraday Discussions Chem. Soc. 75 (1983) 57.