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Unimolecular Reaction Rate Theory

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With 1 Figure

1. Introduction

This contribution summarizes the unimolecular reaction rate theory as developed by RICE, RAMSPERGER, KASSEL and MARCUS (RRKM-theory) and especially reviews the treatment given in three earlier publications [*1–3*].

The RRK-theory of the 1920's was based on the hypothesis of LINDEMANN, that in unimolecular reactions there is a time lag for every active molecule. It was postulated that active molecules (i.e. molecules that have a critical amount of energy or more in certain internal degrees of freedom) either decompose or isomerize after a definite time (time lag) unless they are deactivated by a molecular collision. The existence of a time lag was explained by the assumption that the energy contained in the internal degrees of freedom – or some part of this energy – had to accumulate into one certain degree of freedom (critical oscillator concept). The time lag also was considered to be a function of the amount of energy surpassing the critical energy. A discussion of the RRK-theories is given in the book of BENSON [*4*]. An excellent summary of the RRK, SLATER and RRKM-theories, as well as of related topics, has been given by RICE [*5*]. Relevant experimental data are described in a number of articles [*2, 6, 7*], each of which contains many references to the literature. Of particular note also is a recent book by BUNKER [*8*].

2. The Specific Rate Constant

The RRKM-theory gives a better description than the earlier theories of the quasi-unimolecular rate constant $k_{uni} \equiv -[A]^{-1} \cdot d[A]/dt$ as a function of pressure without using an adjustable parameter. The theory is based on a reaction sequence

$$A + M \rightleftharpoons A^* + M \tag{1}$$

$$A^* \xrightarrow{k_{EJ}} A^+ \tag{2}$$

$$A^+ \longrightarrow \text{products} \tag{3}$$

where M is any third body capable of deactivating an activated molecule, A^*. (A list of notations is given in the appendix.)

The activated complex, A^+, is treated like a molecular species. It possesses 3n−4 rotational and vibrational degrees of freedom (for a non-linear polyatomic activated complex with n atoms) and one internal translation. Reactions in which bonds are formed as well as broken are usually expected to involve rigid activated complexes (e.g. the isomerization of cyclopropane to give propene). Reactions involving only a dissociation for which the reverse reaction of recombination requires no activation energy are expected to involve loose activated complexes (e.g. the dissociation of ethane into methyl radicals). In such a loose activated complex the separating particles are assumed to rotate relatively freely, being held only by loose bonds. By contrast, a rigid complex normally has no new internal rotations, and indeed has about the same extension in space as the reactant in its vibrational and rotational ground state.

In the RRK-theory the number of internal degrees of freedom effective in transferring energy to the "critical oscillator" was an adjustable parameter. This number was found by fitting the calculated curves $\log k_{uni}$ versus $\log p$ to the experimental curves. In the RRKM-theory we distinguish from the outset "adiabatic" and "active" degrees of freedom. Only the active degrees of freedom are active in intramolecular energy transfer. All vibrations are assumed to be active, since anharmonicity effects are important and no severe restrictions should be imposed by momentum conservation laws.

Because of the increased separation distance the centrifugal potential facilitates reaction – especially for reactions with loose activated complexes – in any given rotational state of the molecule. We ignore Coriolis effects and denote by J the totality of quantum numbers that are approximately conserved on forming A^+ from A^*. Thus J is the quantum number of the adiabatic degrees of freedom which, in applications, have usually been taken to be the external rotations of the molecule. The energy for these degrees of freedom changes from E_J to $E_J^\dagger$. When J refers only to rotations, the difference $E_J - E_J^\dagger$ represents the change in centrifugal potential and we have the following energy balance (compare fig. 1):

$$E_a + E^+ + E_J^\dagger = E + E_J \tag{4}$$

$$E^+ = E_t^+ + E_n^+ \tag{5}$$

k_{EJg}, the specific rate constant for a dissociation (isomerization) by a particular reaction path, can be derived in the following manner: consider an energetic molecule A^* whose energy of the active modes is in an interval $(E, E + dE)$ and whose adiabatic modes are in a state J. The statistical equilibrium probability of finding such a molecule as an activated complex

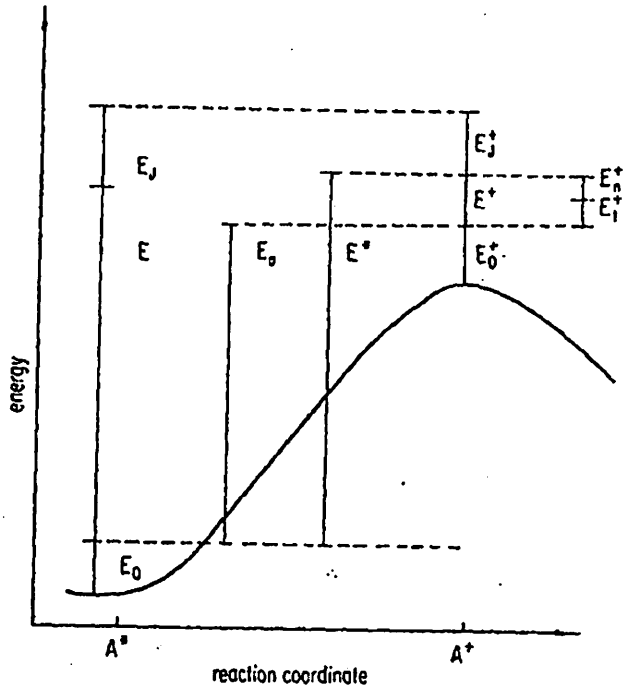

Fig. 1. Energy diagram for an unimolecular process

A^+ having an internal translational momentum in the range $(p, p + dp)$, being in a state n of the active degrees of freedom and in an interval $(q, q + dq)$ and formed by a given path, is given by the ratio of the quantum states of this A^+ and of A^* namely by

$$\frac{dq \cdot dp}{b} \frac{\Omega^+(E_n^+)}{\Omega^*(E)\, dE}, \tag{6}$$

since $dq \cdot dp/h$ is the number of internal translational quantum states in $dq\, dp$. The corresponding probability per unit interval along q is obtained by dividing by dq. The contribution of these states of A^* to the specific unimolecular reaction rate constant, k_{EJg}, is obtained by multiplying the resulting ratios by the velocity $\dot{q}$. The coordinate q is taken to be Cartesian, so that $\dot{q}$ equals p/m where m is an effective mass. Since $d(p^2/2m)$ equals dE, and since k_{EJg} equals the above rate expression summed over all accessible n, we obtain

$$k_{EJg} = \sum_{E_n^+ \leqslant E^+} \Omega^+(E_n^+) / \{b\, \Omega^*(E)\}. \tag{7}$$

A concept of equilibrium for reactants with activated complexes moving in the forward direction along the reaction coordinate is embodied in equations (2), (6) and (7). It is discussed for a quite different case – bimolecular reactions – in the "Remarks on Generalization of Activated Complex Theory" (R. A. MARCUS, this book).

Equation (7) is the contribution for a given reaction path. There may be one or more reaction paths which are "geometric isomers" of each other. For each such path there may be a further degeneracy: a path may have an optical isomer [9]. Optically isomeric reaction paths can be detected by drawing a picture of the chemical migration of the atoms and seeing if the resulting figure has an optical isomer. Paths which are geometrically isomeric usually have different A^+'s and may lead to different products; so we have to sum over rather than to multiply by the number of such paths and obtain

$$k_{EJ} = \sum_g \alpha_g \sum_{E_n^+ \leqslant E^+} \Omega^+(E_n^+) / \{h\,\Omega^*(E)\}, \tag{8}$$

where α_g and Ω^+ depend on g.

Because of symmetry restrictions some rotational states may be absent in A^*, or in A^+ or in both. On making the usual approximation employed in a classical description of rotational partition functions the absence of certain rotational states in A^* or A^+ is accounted for by introducing symmetry numbers: $\Omega^+ = W^+/\sigma^+$; $\Omega^* = W^*/\sigma^*$.

3. The First Order Rate Expression

The equilibrium probability of finding an A^* with an energy of the active modes in the range $(E, E + dE)$ and with adiabatic modes in the state J is $P^0_{EJ}\,dE$ where

$$P^0_{EJ} = P^{-1}\,\Omega^*(E) \exp\left[-(E + E_J)/kT\right]. \tag{9}$$

$\Omega^*(E)$ counts all states per unit of energy and therefore includes the degeneracy factor. We denote by ω the specific collisional deactivation probability assuming a strong collision mechanism for deactivation (a single collision removes enough energy to deactivate every A^*). Considering very high pressures, where $\omega \gg k_{EJ}$, the rate of activation can be calculated. Using the equilibrium expression for A and A^* this rate equals the rate of collisional deactivation $\omega\,P^0_{EJ}\,dE[A]$. Since the rate of formation of A* thus calculated will be assumed to hold also for lower pressures, it is implicitly taken for granted that equilibrium conditions are preserved for all molecules with energies smaller than E_a in their active modes. By using steady state arguments for A^* under conditions where $\omega \gg k_{EJ}$ no longer is true one can show that the concentration of each A^* is a fraction $\omega/(\omega + k_{EJ})$ of the equilibrium concentration. Thus the unimolecular reaction rate constant is obtained by summing $k_{EJ}\,P^0_{EJ}\,dE\,\omega/(\omega + k_{EJ})$ over all E and J:

$$k_{uni} = \int_E \sum_{J=0}^{\infty} k_{EJ}\,P^0_{EJ}\,dE / (1 + k_{EJ}/\omega). \tag{10}$$

By substituting (8) and (9) and using (4) one obtains

$$k_{\mathrm{uni}} = \frac{kT}{hP} \int_{E^+=0}^{\infty} \sum_{J=0}^{\infty} \frac{\sum_g \left(\frac{\alpha_g}{\sigma^+}\right) e^{-E_a/kT} \sum_{E_n^+ \leq E^+} W^+(E_n^+)\, e^{-\frac{(E^+ + E_J^+)}{kT}}}{(1 + k_{EJ}/\omega)} \frac{dE^+}{kT}. \tag{11}$$

The k_{uni} for formation of a particular product by a particular path g is obtained from (11) by deleting the $\sum_g$ in (11) but not in (8). In the case of an isomerization to form B from A, B^* may reform A^* before being deactivated. A correction can be easily introduced to correct for such situations [3].

4. The Density of Energy States

For numerical calculations the evaluation of the numbers of states per unit energy becomes important. In most cases an exact calculation is only necessary for the activated complex. As for this complex internal energies are small in systems with thermal activation, quantum restrictions can not be neglected; with growing internal energies the contributions to the integral in (11) quickly become negligible. For the evaluation of $W^*(E)$, which appears in k_{EJ} and therefore also in k_{uni}, useful approximations have been found [10]. The semiclassical expression for the case that only vibrations are taken to be active is given by [11]:

$$W^*(E) = [E + E_0]^{s-1} / \{\Gamma(s) \prod_{i=1}^{s} (h\nu_i^*)\}. \tag{12}$$

The s normal vibrations have frequencies ν_i^*. A better approximation is attained by

$$W^*(E) = [E + aE_0]^{s-1} / \{\Gamma(s) \prod_{i=1}^{s} (h\nu_i^*)\}, \tag{13}$$

where a is a quantity smaller than unity depending weakly on the energy E and approaching unity for large energies.

If there are t active rotations in A the energy E is distributed between these and the active vibrations:

$$W^*(E) = \int_{x=0}^{E} W_v^*(E - x)\, W_r^*(x)\, dx. \tag{14}$$

This leads to an expression corresponding to equation (13):

$$W^*(E) = P_R (E + aE_0)^{s+t/2-1} / \{(RT)^{\frac{t}{2}} \Gamma\left(s + \frac{t}{2}\right) \prod_{i=1}^{s} (h\nu_i^*)\}. \tag{15}$$

Similarly active rotations in A^+ have been shown to factor the expression $1/\sigma_2^+ \sum_{E_n^+ \leq E^+} W^+(E_n^+)$ into terms corresponding to partitioning of E^+ among the active rotations and vibrations of A^+ [1].

5. The Influence of Centrifugal Potential

We now consider the influence of changing centrifugal potential on the unimolecular reaction rate. Taking (15) as the approximation for the density of energy states we define

$$F = \frac{W^*(E^* + E_J^\dagger - E_J)}{W^*(E^*)} = \left(1 - \frac{E_J - E_J^\dagger}{E^* + a E_0}\right)^{s+t/2-1}. \tag{16}$$

For rigid activated complexes E_J and $E_J^\dagger$ are normally about equal and F is very close to unity. For loose activated complexes leading to a dissociation, E_J and $E_J^\dagger$ differ primarily for two rotations in which the two resulting fragments are treated as the "atoms" of a diatomic molecule. The mean value of $E_J - E_J^\dagger$ can be shown to be pressure insensitive and to equal $(I^+ - I)/IRT/2I$ where l is the number of adiabatic rotations and I^+/I is the ratio of the moments of inertia for these rotations [3]. The value of k_{EJ} is relatively insensitive to fluctuations of $E_J - E_J^\dagger$ about this mean, and the corresponding value of k_{EJ} obtained by making this replacement for $E_J - E_J^\dagger$ is denoted by k_a; for the given value of E^+

$$k_a = \sum_g \frac{\alpha_g \sigma^*}{\sigma^+} \left[\sum_{E_n^+ \leqslant E^+} W^+(E_n^+)\right] \Big/ \{h F W^*(E^*)\}, \tag{17}$$

where

$$F = W^*\{E^* - l R T(I^+ - I)/2I\}/W^*(E^*). \tag{18}$$

For the dissociation of ethane into methyl radicals and dissociation of N_2O_5 into NO_2 and NO_3 F has been calculated to be about 0.8 and 0.4, respectively, at $E^* = E_a$ [3].

Upon introducing (17) into (11) and integrating over J one finds

$$k_{\text{uni}} = \frac{kT}{hP} \sum_g \frac{\alpha_g P_1^\dagger e^{-E_a/kT}}{\sigma_2^\dagger} \int_{E^+=0}^{\infty} \frac{\sum_{E_n^+ \leqslant E^+} W^+(E_n^+)\, e^{-\left(\frac{E^+}{RT}\right)}}{1 + k_a/\omega} \frac{dE^+}{kT}. \tag{19}$$

In (19) the properties of A^+ (e.g. α_g, E_a, $P_1^\dagger$, W^+ and $\sigma_2^\dagger$) may depend on the path g.

6. Concluding Remarks

The high pressure value of k_{uni}, given by (20), is obtained from (19) by setting $\omega = \infty$, interchanging order of summation and integration ($E^+ = E_n^+$ to ∞, and then $E_n^+ = 0$ to ∞), integrating and summing.

$$k_{\text{uni},\infty} = \frac{kT}{h} \sum_g \frac{\alpha_g P^+}{P} \exp(-E_a/kT). \tag{20}$$

This expression can be used to discuss statistical factors in reaction rates. An alternative group theoretical description of the statistical effect has been given by other authors [12]. It should be noted that equation (20) is equivalent to that derived previously by EYRING [13].

If one wants to calculate k_{uni} as a function of pressure, the Arrhenius activation energy E_∞ must be known for the homogeneous reaction and the properties of the activated complex must be chosen in a reasonable manner. This choice is guided by the knowledge of the vibrational frequencies (and the properties of the internal rotations) for the reacting molecules and the product molecules and by the knowledge of the experimental value of $k_{\text{uni},\infty}$ which must agree with the value calculated from equation (20).

Appendix

NOTATIONS:

A, A^*, A^+ = reactant, active molecule (an A with enough energy to react), and the activated complex.

E_0, E_0^+ = zero-point energy of A, A^+.

E, E^+ = energy of the active modes of A^* and of A^+, respectively.

E_J, E_J^+ = energy of adiabatic modes of A^* and of A^+, respectively.

E_a = energy of A^+ in its lowest vibrational, rotational and translational state minus that of A in its lowest state. (Hence, E_a also equals the activation energy at 0 °K).

E^* = $E_a + E^+$.

k_{EJ} = specific rate constant for molecules with energy E in their active modes and in quantum state J of their adiabatic modes (eq. 2).

k_{EJg} = specific rate constant as before, but only for a particular reaction path.

q, p = reaction coordinate and its conjugate momentum.

E_t^+ = internal translational energy of A^+; $E_t^+ = p^2/2m$.

E_n^+ = energy of the active vibrations and rotations of an A^+ in quantum state n.

g = label for a geometrically isomeric path.

α_g = number of optically isomeric reaction paths for each geometrically different path leading from the initial A molecule (or A isomer if there is more than one) through A^+ to the given product.

$\Omega^+(x)$ = number of states of active modes of A^+ (formed by a given path) in an energy interval $(x, x + dx)$.

$\Omega^*(y)$ = number of states of A^* per unit energy, when the energy of the active modes is y (energy density at y).

$W^+(x), W^*(y)$ = number of such states of A^+ and A^* when symmetry numbers are ignored.

$W_v^*(y), W_r^*(y)$ = number of rotational and vibrational states per unit of energy.

σ^*, σ^+ = symmetry numbers of A^* and A^+.

σ_2^+ = symmetry number for the active rotations of A^+.

P, P^+ = partition function of all the rotational and vibrational modes of A and A^+, respectively.

P_1, P_1^+ = partition functions of the adiabatic modes of A and of A^+.

P_2, P_2^+ = partition functions of the active modes of A and of A^+. $P = P_1 \cdot P_2$, $P^+ = P_1^+ P_2^+$.

P_R = rotational partition function for active rotations of A.

ω = the specific collisional deactivation probability, which is for a strong collision mechanism equal to the probability of a collision per unit of time and hence approximately proportional to the total pressure.

References

1. MARCUS, R. A.: J. Chem. Phys. 20 359 (1952).
2. WIEDER, G. M., and R. A. MARCUS: J. Chem. Phys. 37, 1835 (1962).
3. MARCUS, R. A.: J. Chem. Phys. 43, 2658 (1965).
4. BENSON, S. W.: The Foundations of Chemical Kinetics. New York: McGraw Hill, 1960.
5. RICE, O. K.: contribution in "Energy Transfer in Gases, 12th Solvay Congress. New York: Interscience Publishers 1962.
6. RABINOVITCH, B. S., and D. W. SETSER: Advances in Photochem. 3, 1 (1964).
7. RABINOVITCH, B. S., R. F. KUBIN, and R. E. HARRINGTON: J. Chem. Phys. 38, 405 (1963).
8. BUNKER, D. L.: Theory of Elementary Gas Reaction Rates. Braunschweig: Pergamon Press 1966.
9. MARCUS, R. A.: J. Chem. Phys. 43, 1598 (1965).
10. RABINOVITCH, B. S., and R. W. DIESEN: J. Chem. Phys. 30, 735 (1959); WHITTEN, G. Z., and B. S. RABINOVITCH: J. Chem. Phys. 38, 2466 (1963); 41, 1883 (1964); SCHLAG, E. W., and R. A. SANDSMARK: J. Chem. Phys. 37, 168 (1962); THIELE, E: J. Chem. Phys. 39, 3258 (1963); HAARHOFF, P. C.: Mol. Phys. 7, 101 (1963); LIN, S. H., and H. EYRING: J. Chem. Phys. 43, 2153 (1965).
11. MARCUS, R. A., and O. K. RICE: J. Phys. & Colloid Chem. 55, 894 (1951).
12. SCHLAG, E. W.: J. Chem. Phys. 38, 2480 (1963); SCHLAG, G. W., and G. L. HALLER: 42, 584 (1965); cf. BISHOP, D. M., and K. J. LAIDLER: 42, 1688 (1965).
13. GLASSTONE, S., K. J. LAIDLER, and H. EYRING: The Theory of Rate Processes. New York-London: McGraw Hill 1941.

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