DYNAMICAL BOTTLENECKS
AND SEMICLASSICAL TUNNELING PATHS
FOR CHEMICAL REACTIONS

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ABSTRACT

The principles of variational transition state theory and multidimensional semiclassical tunneling approximations are discussed, and recent tests and applications are summarized.

RÉSUMÉ

Les principes de la théorie variationnelle du complexe activé et les approximations semi-classiques de l'effet tunnel à plusieurs dimensions sont discutés. On présente également des vérifications et des applications de ces méthodes.

1. Introduction

The calculation of chemical reaction rates by quantum mechanics involves several difficulties. In the first place, we must calculate the potential energy surface, for which high-order configuration interaction in a space defined by a very extended basis set may be important for significant quantitative features ([1-3]). Secondly, the internuclear motion problem for a chemical reaction involves rearrangement scattering theory ([4]), which involves special difficulties associated with imposing asymptotic boundary conditions in two or more nonorthogonal coordinate systems. Third, chemical reaction rates involve a thermal average over reactive events occurring at many total energies and out of many initial states. Fourth, the thermal reaction rate is very sensitive to the threshold energy region, and this region is especially difficult to treat accurately. Transition state theory is an approximate dynamical method that has many convenient features for overcoming these difficulties. With regard to the first difficulty, transition state theory has the advantage that it requires knowledge of only a localized portion of the potential energy surface. Secondly, transition state theory does not require the imposition of boundary conditions on continuum wave functions at all; it reduces the reaction rate to a quasiequilibrium calculation involving molecular partition functions. Third, transition state theory may be formulated to yield thermally averaged reaction rates directly, and in fact it takes its simplest form when this is done. Even more important may be a fourth advantage, namely that the fundamental assumption of transition state theory is best justified in the threshold region, at least in classical mechanics.

In recent years our research group has made a systematic effort to study the validity of transition state theory ([5]). We have found that the conventional theory is sometimes remarkably accurate, but in many other cases it leads to large errors. Fortunately we have found that a much more reliable theory that has many of the advantages of conventional transition state theory can also be formulated, and it can be applied to practical problems with an effort that is much closer to that required for conventional transition state theory than to that required for full quantal dynamics calculations. This lecture provides an overview of the new theory and summarizes tests of the theory published since our 1984 review ([5a]). The two most important features in the improved approach to transition state theory are the variational determination of the transition state ([6-9]) and the incorporation of tunneling contributions by multidimensional semiclassical approximations ([10-16]).

Before proceeding to the main line of development it is useful to point out that many people have contributed to improving the theory. The seminal contributions of Eyring and Wigner to the formulation of conventional transition state theory are well known, and hundreds of later contributions that lead to improved understanding could be cited easily. For the work to be discussed in this lecture though, it is especially relevant to mention a few key contributions that provided an invaluable background for the approach discussed here. One important idea discussed below is the variational optimization of transition states, and in this regard one can single out the very stimulating way in which Keck and Anderson formulated classical variational transition state theory as a basis for the sampling of phase in trajectory calculations ([17,18]). Another central idea is vibrational adiabaticity, many of whose detailed consequences for chemical dynamics were first elucidated by Marcus ([19,20]). The stimulating attempts by Miller ([21]) and Pechukas ([22]) to devise a useful quantum mechanical version of transition state theory provided useful clues to the limitations of more approximate ways to incorporate quantal effects in transition state theory. A key element in the ability to successfully incorporate such effects has been the development of reasonably accurate ways to accound for multidimensional effects in semiclassical tunneling calculations, and some key advances in this regard were made by Marcus, Coltrin and Babamov ([10,14]). The extension of reaction path concepts to polyatomic systems has been facilitated by the systematic formulation of a general reaction-path Hamiltonian by Miller, Handy and Adams ([23]). Our own work ([24,25]) on variational transition state theory and semiclassical tunneling approximations for chemical

reactions has benefited greatly from the contributions of these workers.

2. Theory

The textbook view of conventional transition state theory is focussed on a quasiequilibrium between activated complexes and reactants. Thus an atom transfer is considered to proceed in two steps as follows

$$A + BC \rightleftharpoons ABC^+ \rightarrow AB + C \qquad (1)$$

Here A, B and C are atoms or groups of atoms, and ABC^+ is an activated complex or transition state. (The two words are synonyms). The transition state theory rate constant at temperature T is written as

$$k(T) = \kappa(T) \frac{\tilde{k}T}{h} K^+(T) \qquad (2)$$

where $K^+(T)$ is the equilibrium constant for the bimolecular first step in (1), and $\tilde{k}T/h$ (where $\tilde{k}$ is the Boltzmann constant and h is Planck's constant) is a collection of kinematic constants associated with the unimolecular second step. The activated complex is not a real bound species, but rather a mathematical construct defined in terms of the properties of a saddle point, which is the highest energy point on the minimum energy path from reactants to products. One degree of vibration of the saddle point species, that directed along the reaction coordinate, is unbound and hence is removed from consideration in calculating $K^+(T)$. The factor $\kappa(T)$ in eq. (1) is called the transmission coefficient. Usually it is set equal to unity, but in principle it contains our best attempt to correct for any known inadewuacies in the theory. For example, since transition state theory does not include tunneling, $\kappa(T)$ can be used to correct the theory for tunneling contributions. We will consider tunneling below, but temporarily we set $\kappa(T) = 1$.

The equilibrium constant in (1), even though it involves a mathematically defined species that is missing one degree of freedom, can be related to a standard-state free energy change, $\Delta G^{+,0}(T)$, by a well known thermodynamic relation, yielding

$$k(T) = \kappa(T) \frac{\tilde{k}T}{h} K^0 \exp[-\Delta G^{+,0}(T)/RT] \qquad (3)$$

where K^0 is the reciprocal of the standard state concentration and R is the gas constant. Because of the mathematical character of ABC^+, we are not dealing with a true equilibrium and hence we call $K^+(T)$ a quasiequilibrium constant, and eq. (3) is called the quasithermodynamic formulation of transition state theory. $\Delta G^{+,0}(T)$ is called the standard-state free energy of activation (or the standard-state Gibbs activation energy according to the IUPAC recommendations on nomenclature). The free energy change in eq. (3) can be evaluated by statistical mechanics yielding

$$k^+(T) = \kappa(T) \frac{\tilde{k}T}{h} \frac{Q(T)}{\Phi^R(T)} e^{-V^+/RT} \qquad (4)$$

where $Q^+(T)$ is the transition state partition function (still missing one degree of freedom). Φ^R is the reactant partition function per unit volume, and V^+ is the classical barrier height, i.e., the potential energy at the saddle point minus that for equilibrium reactants.

The above equations may be given a simple dynamical interpretation, as follows. In a classical mechanical world the rate constant calculated by eqs. (2)-(4) equals the equilibrium one-way flux through a phase space hypersurface that passes through the saddle point and is perpendicular to the omitted degree of freedom of the transition state, i.e., to the reaction coordinate. The phase space hypersurface will be called the transition
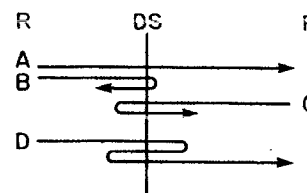

Fig. 1. — Schematic view of representative trajectories in a canonical-ensemble. R denotes reactants' side of the transition-state dividing surface (DS), and P denotes products'side.

state dividing surface, or, for short, the transition state. At equilibrium the forward and reverse fluxes through any surface that divides reactants from products are the same, so we associate eqs. (2)-(4) with the equilibrium flux through the dividing surface in the direction from reactants to products. We now make the fundamental assumption of classical transition state theory, namely that trajectories passing through the transition state dividing surface originated from equilibrated reactants without having previously reached this surface and will proceed to products that relax without returning to it. With this assumption, the local equilibrium flux through the transition state in the product direction equals the net rate of reaction in a system with equilibrated reactants and no products. This is called the local-equilibrium rate constant. Deviations of phenomenological, i.e., measured, rate constants from local-equilibrium ones are believed small for gas-phase bimolecular reactions ([26,27]); in fact most experimental measurements of gas-phase bimolecular rate constants are carried out in the very early stages of reaction (i.e., with no products present) and in a large excess of inert gas that fixes the temperature.

What if trajectories recross the transition state dividing surface? Then the calculated rate constant is too large. This can be seen most clearly by a diagram. Consider Figure 1. This shows a schematic representation of four trajectories, and we consider an ensemble of eight trajectories consisting of these four and their time reverses. For discussion sake suppose that these trajectories constitute a canonical ensemble at the temperature of interest. Neglecting nonequivalent weighting factors for the various trajectories (again, only for discussion purposes; these weights are correctly included in actual calculations), the local flux through the transition state toward products is eight (one each from A, B, and C, two from D, and one each from the time reversed versions of B, C, and D) whereas the net reactive flux in the forward direction is two (A and D). Clearly the local flux toward products is always greater than or equal to the net reaction rate. It is also easy to see that if all trajectories crossed the transition state only once, transition state theory would be exact (in a classical world), e.g., if the canonical ensemble consisted only of A and its time reverse, both the actual rate and the transition state approximation to the rate would be one.

The above argument leads to a fundamental theorem : Classical transition state theory with a unit transmission coefficient agrees with exact classical dynamics if and only if all trajectories through the dividing surface cross it only once. We also have corollary 1 — if trajectories do recross the transition state, classical transition state theory with unit transmission coefficient overestimates the classical equilibrium rate — and corollary 2 — the best transition state dividing surface can be found variationally. In other words, since classical transition state theory for any choice of transition state dividing surface provides a strict bound on the

classical local-equilibrium rate constant, the choice of dividing surface that gives the minimum rate constant is the best. We have implicitly assumed here that transition state rate constants can be calculated even for transition states that are not located at saddle points. This is called generalized transition state theory or GTST.

To calculate GTST rate constants practically we define a reaction coordinate s that measures distance along the minimum energy path (MEP). We put the origin ($s = 0$) at the saddle point and define the positive progress direction as that leading from reactants to products (i.e., we put reactants at $s = -\infty$ and products at $s = +\infty$). At each point, labelled by s, along the reaction path we define a generalized transition state as a coordinate space hypersurface, locally flat and perpendicular to the reaction path but curved elsewhere if necessary to ensure that it divides reactants from products. The free energy change in passing from reactants to such a generalized transition state is computed strictly analogously to $\Delta G^{+,0}$ (T) and is called $\Delta G^{GT,0}$ (T,s) where, to make the superscript less cumbersome, GTST is shortened to GT. By corollary 2 the best estimate of the rate constant is

$$k^{CVT}(T) = \min_{s} \frac{\tilde{k}T}{h} K^0 \exp[-\Delta G^{GT,0}(T,s)/RT] \quad (5)$$

where CVT denotes canonical variational transition-state-theory. In practice, in order to treat the threshold as accurately as possible, we use a dividing surface that depends on total energy as well as coordinates; this introduces a (generally small) correction into the above scheme and results in a rate constant called k^{ICVT} (T), where I denotes improved ([24e,24f]).

So far we have discussed the reaction using classical mechanics. Classically the partition functions used to evaluate $\Delta G^{GT,0}$ (T) are phase space integrals. To introduce quantum effects we first replace these phase space integrals by quantal partition functions, i.e., sums of Boltzmann factors for discrete states. Since the reaction coordinate is missing in the generalized transition state, it remains classical at this stage. We quantize it by introducing a ground-state transmission coefficient κ^G (T). This is defined by

$$\kappa^G(T) = k^G_{quantal}(T)/k^{ICVT,G}(T) \quad (6)$$

where $k^{ICVT,G}$ (T) is what k^{ICVT} (T) reduces to if only the ground state is included in the internal partition functions, and $k^G_{quantal}$ (T) is our best estimate of the true ground-state rate constant. We estimate $k^G_{quantal}$ (T) by semiclassical methods that are consistent with ICVT in that they reduce κ (T) to unity in the high-temperature limit, where reaction-coordinate motion is effectively classical. Since κ (T) differs from unity only at lower temperatures it is reasonable to base it on the ground state.

As just mentioned, we estimate $k^G_{quantal}$ (T) semiclassically. In one dimension the semiclassical wave function is given by exp (iS/h) where S is an action integral given by

$$S = \int^x \{2\mu[E - V(x')]\}^{1/2} dx' \quad (7)$$

where x is the coordinate, V (x) is the potential, and E is the energy. In tunneling regions the action integral is imaginary and the wave function decays exponentially. For a many-body system the one-dimensional action integral becomes an integral along a path through a multidimensional space. Since the tunneling probability is proportional to $|\psi|^2$ on the other side of the barrier, the dominant contribution to the tunneling comes from
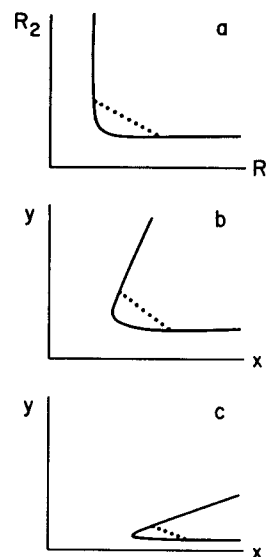

Fig. 2. — Minimum energy path (solid) and typical tunneling path (dotted) for A + BC → AB + C : (a) vs. R (A—B) and R (B—C), (b) vs. two mass-scaled cartesian coordinates for a typical case of B heavier than A and C, (c) same as b for central atom much lighter than A and C.

a tunneling path along which the imaginary action integral is a minimum. In the semiclassical limit the tunneling probability is simply exp ($-2|S|/h$) where S is the imaginary action integral for the dominant tunneling path. In order to analyze the integral in the simplest possible terms we scale the coordinates so that μ is the same in all directions (so that $(2\mu)^{1/2}$ in the multidimensional analog of (7) may be pulled out of the integral); this simply requires multiplying the cartesian coordinates of each atom by the square root of its mass. In the new coordinate system the minimization of the imaginary action integral involves a compromise between paths with small barriers and short tunneling lengths.

At this point we must consider the curvature of the MEP. Figure 2a, which is schematic, shows a typical plot of the MEP and also of a possible tunneling path. Both paths are shown as functions of the bond coordinates. Parts b and c show the same paths in mass-scaled coordinates for transfer of a heavy atom (part b) and a light atom (part c). In general, even for polyatomic A, B, and C, the angle, in the multidimensional mass-scaled coordinate system, between the reactant portion of the MEP and the product portion is given by

$$\beta = \arctan\left(\frac{m_{ABC}m_B}{m_A m_C}\right)^{1/2} \quad (8)$$

where m_X is the mass of X. This is called the skew angle. As discussed above the optimum tunneling path results from a compromise between a short path and a low barrier. As the tunneling path deviates more and more from the MEP, the potential energy (barrier) tends to increase. For heavy B the optimum path, i.e., the one with the minimum imaginary S, usually involves only a little corner cutting, whereas for light B, because of the small skew angle and large resulting reaction-path curvature, a small increase in the potential results in a more significant path-shortening factor, and corner cutting may be severe. We have developed approximations to calculate S by one-dimensional quadratures along multidimensional tunneling paths for the small-curvature ["small-curvature semiclassical adiabatic ground-state" transmission coefficient, κ^{SCSAG} (T)] and large-curvature ["large-curvature ground-state" transmission coefficient, κ^{LCG} (T)] limits and also for the

general case 12, 15, 16. In the latter case we consider a one-parameter sequence of tunneling paths between the MEP and the "straight-across path" (which connects the two translational turning points by a straight line through the mass-scaled cartesian system), and we find the least-(imaginary)-action one numerically. This yields the "least-action ground state" transmission coefficient, κ^{LAG} (T). The LCG and the LAG approximations also include contributions from paths with termini farther out than the translational turning points for the given energy.

The final rate constant is written

$$k^{ICVT/G}(T) = \kappa^G(T)\, k^{ICVT}(T) \qquad (9)$$

We have also extended these methods to predict rate constants for state-selected vibrationally excited reactants ([24b,24g,25s]).

3. Testing

It was of course not clear without testing that the predictions of this method would be accurate. Since comparisons to experiment involve uncertainties due to the generally unknown potential energy surface we tested the theory extensively against accurate quantal calculations by performing ICVT/G calculations for the same potential energy surface as used for the quantal study. Unfortunately many of the quantal studies are for reduced dimensionality (collinear collisions), but the few available three-dimensional quantal studies led to a similar conclusion as the one-dimensional tests, namely the ICVT/G predictions are remarkably accurate, typically within a factor of two or better, often much better ([5]).

Since our last review ([5g]) we have continued to test the methods in several new studies.

In the first ([25a]) we showed that the accuracy is improved for both thermal and state-selected rates if anharmonic corrections to stretching vibrations are computed by the WKB method rather than by the Morse model used for earlier studies.

In another test ([25b]) we considered a collinear reaction for which k^{ICVT} (T) differs greatly from conventional transition state theory but tunneling is negligible. Over a range of a factor of ten in temperature, 100-1 000 K, the errors in conventional transition state theory varied from 1.7×10^4 to 19, whereas those in ICVT varied from 0.77 to 1.42. Even at 40 K, where conventional transition state theory overestimated the exact result by over ten orders of magnitude, ICVT remained accurate within a factor of 3. This is a very important test case because it shows the validity of the ICVT dynamical bottlenecks even for a case with very large reaction-path curvature where the dividing surface must also be very curved.

We also considered an H-atom transfer that is dominated by tunneling, namely collinear Cl + HBr → HCl + Br on a model high-barrier (11 kcal/mol) potential energy surface ([25i]). This is an interesting case because for temperatures below 400 K the reaction is dominated by tunneling into a vibrationally excited state of HCl. We found that the accuracy of the ICVT/LAG method for this reaction is very good. It leads to errors of a factor of 1.55 or less for the 200-1 000 K temperature range, and the error increases to a factor of 1.88 at 2 400 K.

Very recently it has been possible to greatly extend the number of comparisons of our approximate methods to accurate quantal studies for three-dimensional reactions, and we have reported several new such tests,

bringing the total number of three-dimensional tests to nine ([25o]). The only temperature for which comparisons are possible for all nine cases is 300 K. At this temperature the average discrepancy between the ICVT/LAG results and the accurate quantal ones is only 12 %. Furthermore in only one case is the discrepancy large than 26 %.

Two additional sets of tests have been performed for rate constants of state-selected vibrationally excited molecules by comparison of our approximate results to accurate quantal calculations for a collinear reactions. The first set was performed for the reactions of H, D, and T with vibrationally excited F_2 ([25q]). The ICVT/LAG results agree with the accurate quantal ones within 10 % or better for all three reactions for the whole temperature range examined, 300-1 260 K. The second set of tests involved the reaction of O with vibrationally excited H_2 and the backward reaction of H with vibrationally excited OH on three quite different potential energy surfaces ([25s]). In this case we proposed a new model in which reaction is assumed to be vibrationally adiabatic only over the partial reaction path (PRP) up to the first occurrence in proceeding from reactants to products of an appreciable local maximum in the reaction-path curvature. The average errors in both the forward and backward PRP-ICVT/LA rate constants were less than a factor of two.

4. Applications

We have performed several additional applications to three-dimensional hydrogen atom transfer reactions since the review of Ref. 5g. These include the reactions F + H_2, D_2, and HD ([25c,25e,25h,25t]) and OH + H_2 ([25d]); Cl + H_2, both for thermal kinetic isotope effects ([25f]) and for state-selected vibrationally excited H_2 ([26q]); H + H_2 and D + H_2, again both thermal rate constants ([25r]) and those for state-selected vibrationally excited H_2 ([25g,25r]); and O + H_2, HD, and D_2, for thermal rate constants ([25m,25p,25v]) and for state-selected vibrationally excited H_2 ([25n]). We also made applications Mu + F_2 ([25u]), Cl_2 ([25u,25w]), and Br_2 ([25w]) and to hydride transfer in nicotinamide adenine dinucleotide analogs ([25x]).

Two newer areas of application are to surface diffusion and reactions of polyatomics. In the former we reported calculations for diffusion of H, D, and T on the (100) face of Cu ([25j,25l,25n]). For reactions of polyatomics we have reported a preliminary study of $CH_3 + H_2 \rightarrow CH_4$ + H ([24h]).

Several of the above applications were discussed at the symposium.

5. Acknowledgments

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Presented at the 9th International Symposium on Gas Kinetics, Bordeaux 20-25 July 1986.