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Theoretical
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Perspective

Perspective on "The activated complex in chemical reactions"

Eyring H (1935) J Chem Phys 3: 107

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Abstract. A general theory of the absolute rates of chemical reactions proved to be an elusive goal for nineteenth century chemists. This goal would only be achieved through a combination of statistical mechanics with the new quantum mechanics of the early twentieth century, when the insights of Henry Eyring and his contemporaries lead to the absolute rate equation that we are only now beginning to rigorously evaluate. The conceptual focus of absolute rate theory is the transition state (or activated complex), the window through which the future plunges into the past, and this is still the foundation of our understanding of chemical reaction rates as we enter the new millennium.

Key words: Transition state theory – Absolute rate theory – Chemical kinetics

1 Introduction

The great achievement of fundamental chemical theory of the nineteenth century was the conceptualization of bulk matter in equilibrium through thermodynamics and statistical mechanics. The early twentieth century brought an understanding of the periodic table and the behavior of individual molecules through quantum mechanics. The transition-state theory (TST) of Henry Eyring [1] combined these two theories to provide the fundamental conceptual framework for our understanding of the rates of chemical reactions. Very few single articles have had such a dramatic impact on chemistry. This paper is the starting point for any qualitative or quantitative discussion of bulk chemical reaction rates. Our concept of the nature of the transition state (TS) has evolved somewhat, but it is still a dividing surface separating products from reactants: "the now and the here – through which all future plunges into the past" [2].

The absolute rate of a chemical reaction is a problem first addressed in the middle of the last century, but it was the insights of Eyring and his contemporaries in the 1930s that lead to the equation that we are only now beginning to rigorously evaluate. I shall give just enough selective history to set the scene for Eyring's work and to present these ideas in the context in which they were introduced. Then I shall give a selective sampling of the path down which Eyring sent us – a path that promises unimagined new discoveries well into the next millennium.

2 Background

The temperature dependence of rate constants was examined by Wilhelmy as early as 1850 [3], but it was not until 1889 that the correct equation,

$$k_{\mathrm{rate}}(T) \approx A \exp(-\Delta E^{\ddagger}/kT) \ , \tag{1}$$

for the basic temperature dependence was proposed by Arrhenius [4]. The development of the theory of chemical kinetics then focused on the preexponential factor, A, and the activation energy, $\Delta E^{\ddagger}$. The simple interpretation of the Arrhenius equation assigned A to the collision frequency and $\Delta E^{\ddagger}$ to the minimum energy required for a successful (i.e. reactive) collision. It gradually became clear that nature was a good bit more subtle and thus far more interesting than this very simple suggestion.

A macroscopic thermodynamic understanding of the preexponential factor was greatly advanced by the work of Kohnstamm and Scheffer [5], who introduced the concept of the Gibbs free energy of activation. A complementary molecular understanding came from the collision theory approach of McC Lewis [6], which is rather remarkable for its simplicity. If a "collision" between molecules A and B is defined as the two molecules coming within $(r_A + r_B)$, the sum of the radii, then each molecule of A with relative velocity v_{AB} will sweep out a cylinder of length $v_{AB}\,dt$ and cross section $\pi(r_A + r_B)^2$. The mean relative velocity, v_{AB}, had been calculated 50 years earlier by Maxwell and Boltzmann [7]:

$$v_{AB} = [8kT/\pi\mu_{AB}]^{1/2} \ , \tag{2}$$

where the reduced mass, μ_{AB}, is $m_{\mathrm{A}}m_{\mathrm{B}}/(m_{\mathrm{A}}+m_{\mathrm{B}})$. The number of B molecules in the collision cylinder is then

$$\mathrm{d}N_{\mathrm{B}} = [N_{\mathrm{B}}/V]\pi(r_{\mathrm{A}}+r_{\mathrm{B}})^2\left[\frac{8kT}{\pi}\left(\frac{m_{\mathrm{A}}+m_{\mathrm{B}}}{m_{\mathrm{A}}m_{\mathrm{B}}}\right)\right]^{1/2}\mathrm{d}t \qquad (3)$$

and so the total rate of collisions per unit volume for all A molecules is

$$\frac{\mathrm{d}(N_{\mathrm{coll}}/V)}{\mathrm{d}t} = [N_{\mathrm{A}}/V][N_{\mathrm{B}}/V](r_{\mathrm{A}}+r_{\mathrm{B}})^2 \times\left[8\pi kT\left(\frac{m_{\mathrm{A}}+m_{\mathrm{B}}}{m_{\mathrm{A}}m_{\mathrm{B}}}\right)\right]^{1/2} \qquad (4)$$

giving the collision theory rate constant

$$k_{\mathrm{rate}}(T) = (r_{\mathrm{A}}+r_{\mathrm{B}})^2\left[8\pi kT\left(\frac{m_{\mathrm{A}}+m_{\mathrm{B}}}{m_{\mathrm{A}}m_{\mathrm{B}}}\right)\right]^{1/2} \times\exp(-\Delta E^{\ddagger}/kT)\ . \qquad (5)$$

The preexponential factor is often called the collision frequency and is abbreviated $\mathcal{Z}_{\mathrm{AB}}$. In order to achieve even qualitative agreement with experiment, it was necessary to introduce an empirical "steric factor", $\mathscr{P}_{,\mathrm{AB}}$, which is generally between 0.01 and 1.0, but occasionally is outside this range:

$$k_{\mathrm{rate}}(T) = \mathscr{P}_{\mathrm{AB}}\mathcal{Z}_{\mathrm{AB}}\exp(-\Delta E^{\ddagger}/kT)\ . \qquad (6)$$

The mathematical problem was thus reduced to the very physical problem of understanding why most collisions between molecules with sufficient energy to react nevertheless do not lead to chemical reaction.

By 1914 Marcelin [8] had shown that the Arrhenius equation could be derived from statistical mechanics. However, the nature of both the preexponential factor, A, and the activation energy, $\Delta E^{\ddagger}$, remained undetermined until 1919 when Herzfeld [9] derived the correct form of A for the dissociation of a diatomic molecule:

$$k_{\mathrm{rate}}(T) = (kT/h)Q_{\mathrm{vib}}^{-1}\exp(-\Delta E^{\ddagger}/kT)\ . \qquad (7)$$

The first understanding of the real nature of $\Delta E^{\ddagger}$ can be traced to Tolman's proof that the activation energy is the difference between the energy of the activated state necessary for reaction and the average energy of the reactant molecules [10, 11].

The formalism for the quasiseparation of nuclear coordinates from electronic coordinates was introduced by Born and Oppenheimer in 1927 [12]. However, it was the 1929 paper by London [13] and the 1931 paper by Eyring and Polanyi [14] that introduced the potential-energy surface (PES) for a chemical reaction and thus created the conceptual framework for modern kinetic theory. The following year Pelzer and Wigner [15] identified the saddle point on the PES as the TS. The stage had been set.

3 Henry Eyring's TST

Eyring formulated absolute reaction rates "in terms of quantities which are available from potential energy surfaces" [1]. He defined the "activated complex" (we now prefer transition state) as "a saddle point with positive curvature in all degrees of freedom except the one which corresponds to crossing the barrier [i.e. the reaction path] for which it is of course negative." He assumed that once the forces between atoms have been treated quantum mechanically, the reaction rate can then be calculated by the methods of statistical mechanics. The fundamental idea was to treat the molecular flux from reactants to products as a one-dimensional problem along the reaction path by taking an ensemble average over all other degrees of freedom.

The partition function for the forward motion along the reaction path (rp) is

$$\frac{\mathrm{d}Q}{\mathrm{d(rp)}} = \left(2\pi\mu_{\mathrm{rp}}kT\right)^{1/2}/2h\ . \qquad (8)$$

Eyring multiplied this sum of states by the average velocity along the reaction path

$$\langle p/\mu_{\mathrm{rp}}\rangle = \int_0^{\infty}(p/\mu_{\mathrm{rp}})\exp[-(p^2/2\mu_{\mathrm{rp}}kT)]\mathrm{d}p \Bigg/ \int_0^{\infty}\exp[-(p^2/2\mu_{\mathrm{rp}}kT)]\mathrm{d}p = \left[2kT/\pi\mu_{\mathrm{rp}}\right]^{1/2} \qquad (9)$$

to obtain the flux (frequency factor) along the reaction path

$$\frac{\mathrm{d}N_{\mathrm{rp}}}{\mathrm{d}t} = kT/h\ . \qquad (10)$$

He performed an ensemble average over all remaining coordinates to obtain the total flux through the dividing surface:

$$\frac{\mathrm{d}N^{\ddagger}}{\mathrm{d}T} = (kT/h)N_{\mathrm{A}}N_{\mathrm{B}}\left(Q^{\ddagger}V/Q_{\mathrm{A}}VQ_{\mathrm{B}}V\right)\exp(-\Delta E_0^{\ddagger}/kT)\ , \qquad (11)$$

where $Q^{\ddagger}$, Q_{A}, and Q_{B} are the partition functions of the TS and the reactants, and $\Delta E_0^{\ddagger}$ is the energy of the TS elative to the reactants. Eyring's "barrier height", $\Delta E_0^{\ddagger}$, included the change in quantum mechanical zero-point energy. His TS partition function, $Q^{\ddagger}$, includes all degrees of freedom except the reaction path, which was treated separately. Eyring's final expression for the absolute rate constant was

$$k_{\mathrm{rate}}(T) = (kT/h)\left(Q^{\ddagger}/Q_{\mathrm{A}}Q_{\mathrm{B}}\right)\kappa(E)\exp(-\Delta E_0^{\ddagger}/kT)\ , \qquad (12)$$

where $\kappa(E)$ is the "transmission coefficient" (vide infra).

The TST rate equation has the appearance of an equilibrium expression; however, all that is really necessary for the validity of Eq. (12) is that the reactants are at thermal equilibrium (thus defining the temperature, T) and that a sufficient number of A and B molecules pass through our "window", or "dividing surface", to give a statistically valid sample of the phase space around the TS. It is of no consequence that few of them may return to the reactant side. Eyring allowed for such recrossing through a factor equal to the reciprocal of the average number of crossings (our κ), but assumed that "the barriers are so flat near the top that tunneling may be neglected without appreciable error." We shall follow Wigner [16] and include tunneling through the energy-dependent transmission coefficient, $\kappa(E)$:

$$k_{\mathrm{rate}}(T) = (kT/h)\left(Q^{\ddagger}/Q_{\mathrm{A}}Q_{\mathrm{B}}\right) \times \int_{0}^{\infty} \kappa(E)\exp(-E/kT)\mathrm{d}(E/kT) \ . \qquad (13)$$

Note that Eq. (13) reduces to Eq. (12) if we return to the classical approximation for the transmission coefficient, $\kappa(E)$:

$$\kappa_{\mathrm{classical}}(E) = \left\{ \begin{matrix} 0\colon E < \Delta E_0^{\ddagger} \\ 1\colon E > \Delta E_0^{\ddagger} \end{matrix} \right\} \ . \qquad (14)$$

If we include quantum interference so that $\kappa(E)$ can be less than 1 for $E > \Delta E_0^{\ddagger}$, then we have also included one-dimensional recrossing in $\kappa(E)$. This requires solution of the one-dimensional Schrödinger equation along the reaction path, rather than just integrating $\exp(-2\pi\{2\mu_{\mathrm{rp}}[V(r_{\mathrm{rp}}) - E]\}^{1/2} r_{\mathrm{rp}}/h)$ over the region with $V(r_{\mathrm{rp}}) > E$.

Although in his original paper [1], Eyring only allowed that "tunneling may occasionally play some role", we can more easily describe the pervasive influence of TST if we include quantum mechanical tunneling in our reference equation. Regrettably, Eq. (13) does not provide a clear intuitive picture of the role of the barrier height, but the additional complexity is necessary to describe both the low-temperature rates of hydrogen-transfer reactions (i.e. tunneling) and the general effects of recrossing.

Simultaneous with Eyring's work, Evans and Polanyi [17] developed equivalent rate equations, but Eyring and Wynne-Jones [18] immediately extended TS to solutions by connecting with the macroscopic thermodynamic quantities $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, thus providing the link from molecular collision theory all the way to these phenomenological macroscopic quantities.

4 The impact of TST on chemical kinetics

Eyring's TST has provided the basic conceptual framework for the interpretation of the rates of nearly all chemical reactions on a bulk scale. He quickly applied his new theory to homogeneous gas-phase thermochemical reactions, photochemical reactions, heterogeneous catalysis, and reactions in solution [19]. He even considered such topics as viscosity and diffusion [19].

The greatest impact so far has been as a qualitative interpretive tool, rather than the achievement of the original goal of a quantitative theory of absolute rates. In his original paper Eyring stated: "The calculation of the concentration of activated complexes is a straightforward statistical problem, given the moments of inertia of the complex and the vibrational frequencies. This information is given with sufficient accuracy, even by our very approximate potential surfaces, to give good values for the partition functions." Even Eyring could be completely wrong. The ab initio calculation of the partition functions has proven difficult, but the ab initio calculation of the barrier heights – until very recently – appeared impossible.

In spite of these difficulties in quantitative implementations, TST has nevertheless provided a framework for understanding even the most complicated reactions. TST immediately provided a deeper understanding of collision theory. The collision theory rate in Eq. (5) can be recovered by evaluating Eq. (12) for the reaction of two point particles (i.e. $Q_{\mathrm{rot}} = Q_{\mathrm{vib}} = Q_{\mathrm{elec}} = 1$) to form a linear TS (i.e. $Q_{\mathrm{rot}\|\mathrm{rp}} = Q_{\mathrm{vib}} = Q_{\mathrm{elec}} = 1$). Comparison of Eq. (6) with the general form then reveals the nature of the steric factor:

$$\mathscr{P}_{\mathrm{AB}}(\mathrm{TST}) = \frac{Q^{\ddagger}_{\mathrm{rot}\|\mathrm{rp}} Q^{\ddagger}_{\mathrm{vib}} Q^{\ddagger}_{\mathrm{elec}} \kappa(E)}{(Q_{\mathrm{rot}}Q_{\mathrm{vib}}Q_{\mathrm{elec}})_{\mathrm{A}}(Q_{\mathrm{rot}}Q_{\mathrm{vib}}Q_{\mathrm{elec}})_{\mathrm{B}}} \ , \qquad (15)$$

where $Q^{\ddagger}_{\mathrm{rot}\|\mathrm{rp}}$ is the partition function for rotation about the reaction path coordinate. The portion of the entropy of activation arising from the translational partition functions was included in Eq. (5), so the dominant additional entropy effect in Eq. (15) is the reduced rotational freedom in the TS, i.e. $Q^{\ddagger}_{\mathrm{rot}\|\mathrm{rp}} \ll (Q_{\mathrm{rot}})_{\mathrm{A}}(Q_{\mathrm{rot}})_{\mathrm{B}}$. Hence, the steric factor is indeed an appropriate description of $\mathscr{P}_{,\mathrm{AB}}$.

Until fairly recently, successful applications of TST have treated the barrier height, $\Delta E_0^{\ddagger}$, as an adjustable parameter. Nevertheless, our basic understanding of general homogeneous and heterogeneous catalysis and even enzyme active sites is based on qualitative considerations of the role of the TS. Qualitative estimates of variations in zero-point energies and in vibrational and rotational partition functions can be based on experience and analogy. Our ability to anticipate the qualitative effect of substituting deuterium for hydrogen has led to a whole industry of mechanistic studies through isotopic substitution [20].

We can expect the new millennium to spawn a new age of routine quantitative absolute rate predictions based on the confluence of chemically accurate ab initio electronic structure theory with continued refinement of Eyring's TST.

5 The evolution of absolute rate theory

Refinements in Eyring's TST have been driven both by developments in electronic structure theory and by progress in understanding how to apply this emerging computational technology to the prediction of chemical reaction rates. A very thorough recent review of the current status of TST gives the informed perspective of the primary contributor to these modern refinements [21]. Our starting point is the PES, which we can now routinely generate from first principles.

5.1 Ab initio PESs

The journey of the PES from the highly speculative semiempirical formulations of London, Eyring, and

Polanyi [13, 14] to the firm reality of modern ab initio electronic structure theory began with the molecular orbital concepts introduced by Mulliken [22] (1966 Nobel Prize in Chemistry). These ideas were developed into a practical computational method on the new digital computers by Roothaan [23]. Early calculations were severely limited by the difficulty in evaluating integrals over Slater-type orbitals (due to the cusp at each nucleus) [24], until Boys demonstrated the advantages of Gaussian basis sets [25]. At this point Pople released the computer program Gaussian 70, which has evolved into a very comprehensive and widely used computer program [26], implementing his model chemistry concept [27], for which he was to share the 1998 Nobel Prize in Chemistry. The model chemistry concept of Pople provided a well-defined broad approach to general classes of problems, thereby removing the arbitrariness of ad hoc decisions for each particular case. Improvements in both computer hardware and computational methodology have each increased the speed of ab initio calculations by a factor of about 10^4 since those early days (based on the author's timing comparison of 24 h for a minimum basis set self-consistent-field calculation on ethane in 1964 versus 8 ms for the same calculation today). The combined effect has made ab initio theory into a practical tool for chemical predictions.

Among many other developments important in achieving the current state of the art in computational quantum chemistry, we should recognize the transplanting of coupled-cluster methods from nuclear physics by Bartlett and Purvis [28], providing a manageable approximation to full configuration interaction calculations. The development of systematic sets of atomic basis functions by Dunning [29] has provided a tool to probe convergence to the complete one-electron basis-set limit, which can be compared to results obtained from the efficient implementation of explicit functions of interelectronic coordinates by Kutzelnigg and Klopper [30].

In a complementary development, very rapid, if inexact, evaluations of a PES are now possible through the density functional theory methods developed by Hohenberg and Kohn [31], Kohn and Sham [32], Lee et al. [33a], Parr and Yong [33b], and Becke [34], for which Kohn shared in the 1998 Nobel Prize in Chemistry.

5.2 Evaluation of $Q^\ddagger$

It is the genius of TST that only the saddle point of the PES need be examined. At low pressure, we can use the ideal gas partition functions for translational motion:

$$Q_{\text{trans}} = V\left(2\pi mkT/h^2\right)^{3/2} \quad , \tag{16}$$

The geometry of the saddle point provides the moments of inertia, I_j, required for evaluation of the rigid rotor rotational partition functions

$$Q_{\text{rot}} = 2\pi\left(\frac{4\pi}{\sigma}\right)\prod_j\left(\frac{2\pi I_j kT}{h^2}\right)^{1/2} \tag{17}$$

which are valid except at very low temperatures. The vibrational partition functions are a bit more problematic. The stretching and bending frequencies, ν_j, are generally large enough that the harmonic oscillator partition functions

$$Q_{\text{vib}} = \prod_j\left[1 - \exp(-h\nu_j/kT)\right]^{-1} \tag{18}$$

provide an adequate approximation; however, the torsional modes (especially torsion of one reactant with respect to the other) should be treated as free or hindered rotors [35].

The previous discussion presumes that we know the geometry of the TS and the second derivative of the energy with respect to each of the vibrational normal modes. Since the TS is a stationary point the first derivative of the energy with respect to each coordinate must vanish. Hence, both problems require knowledge of the derivatives of the energy with respect to the positions of the nuclei.

5.3 Analytical derivatives

The farsighted development of methods to calculate the analytical derivatives of the ab initio energy with respect to the Cartesian coordinates of the nuclei by Pulay [36] played a key role in the practical implementation of TST. Further developments by Handy and Schaefer [37a] Schlegel et al. [37b], and Johnson and Frisch [38], among others greatly expanded the number of ab initio methods for which these derivatives were available. The tools to evaluate the partition functions were at hand, but first we must locate the TS.

5.4 Locating TSs

Once these derivatives are available, efficient and reliable algorithms are still required for locating the TS and in the case of variational TST (VTST) for obtaining a portion of the reaction path. The former was often a rather frustrating search requiring a guess for the reaction path along which a maximum energy point was determined. Once the TS was located, "reaction-path following" was more routine, being essentially a matter of starting off in the direction of negative curvature of the PES and following the energy gradient to reactants and products.

Finding the geometry of a stable molecule is quite straightforward, since following the energy gradient is sufficient to guarantee eventual convergence to the nearest local minimum on the PES. Saddle points provide a more interesting challenge, for which the quadratic synchronous transit (QST) algorithms of Peng and Schlegel [39] represent a dramatic improvement over previous methods, and finally give us a tool, making TS geometry optimizations relatively routine.

5.5 Variational transition-state theory

We can trace the origins of VTST all the way back to Wigner [40], but this acronym is now generally associated with the modern development that has been dominated by Truhlar [41].

The exact quantum mechanical absolute rate constant can, in principle, be obtained as a Maxwell–Boltzmann average over the state-to-state reaction cross sections [42]. The rate is also given by the net flux through any surface in phase space dividing products from reactants. VTST seeks the best such window for the plunge from reactants into products. This is the surface giving the minimum one-way forward flux, so the two-dimensional recrossing we ignore must also be a minimum, the sum being constant. Recognizing that Eyring's TST includes the effects of both the zero-point energy and the entropy of activation through the partition functions, it is clear that the forward flux depends on the Gibbs free energy, $\Delta G_0^{\ddagger}(T)$, at the TS. We should therefore select the TS as the point along the reaction path at which the Gibbs free energy is a maximum. The tunneling is then determined by the solution of the one-dimensional Schrödinger equation along the reaction path, with a potential-energy function given by $G(T, r_{\mathrm{rp}})$. This is what Truhlar describes as canonical zero curvature (ZC) VTST [43]. Note that the geometry of the TS is now a function of both the temperature and the isotopes of the atoms, in contrast to the saddle point on the Born–Oppenheimer PES.

VTST is especially important for reactions without a saddle point on the Born–Oppenheimer PES, such as radical recombination reactions. The free energy of activation for such reactions is often dominated by entropic effects.

5.6 Reaction-path curvature

If the reaction path coordinate were truly separable from the other coordinates, then classical recrossing of the barrier would not occur and our $\kappa(E)$ would give the exact quantum mechanical recrossing rate. Unfortunately, this situation is impossible. For example, if our chemical reaction is

$$A - B + C \quad \rightarrow \quad A + B - C \tag{19}$$

then the initial reaction path must be $r_{\mathrm{AB-C}}$, the distance from the center of mass of AB to C, while the final reaction path must be $r_{\mathrm{A-BC}}$, the distance from A to the center of mass of BC. The resulting curvature of the reaction path is the primary underlying reason why TST cannot be exact for such a reaction. This curvature necessarily couples the reaction path to the other coordinates and thus leads to corner cutting (i.e. finding a shorter path not quite traversing the saddle point) [44], bob sledding (i.e. riding up the sides of the exit channel) [45], and two-dimensional corrections to recrossing. Refined versions of TST designed for both small [46] and large curvature [47] have been developed. The largest curvature in mass-weighted coordinates corresponds to the transfer of a light atom (i.e. hydrogen) between two heavy atoms – precisely the situation where tunneling will be most important. However, canonical ZC-VTST is certainly adequate for reactions not involving hydrogen.

5.7 Unimolecular reactions

The rate of a unimolecular reaction can depend upon both the rate at which collisions provide the required activation energy and the rate at which this energy can be funneled into the reaction coordinate and used to cross the dynamical bottleneck. The crossing of the dynamical bottleneck is properly described by Eyring's TST (or generalizations thereof). The intramolecular energy transfer is usually described by the exchange of energy between coupled harmonic oscillators using the unimolecular rate theory developed by Rice, Ramsperger, Kassel, and Marcus [48]. In the high-pressure limit, the reaction is slow compared to the collision rate and so the reactants maintain a Boltzmann energy distribution, but most unimolecular reactions are studied experimentally under conditions where corrections for non-Boltzmann behavior are required.

5.8 Recent progress in barrier heights

For a long time, it was not possible to assess the accuracy of TST. The early PESs were more a result of speculation than firm knowledge, so discrepancies with experiment were impossible to interpret. Two developments have dramatically altered this impasse.

The first is the refinement of quantum dynamics to accurately determine the rate constant that results from a given PES [49–51], thereby providing an evaluation of the various levels of TST that does not rely on the availability of an accurate PES.

The second breakthrough is our rapidly developing ability to remove inaccuracies in the ab initio PES as the bottleneck in the predictive ability of absolute rate theory. The benchmark paper by Diedrich and Anderson [52] on H_3 set a new standard of accuracy for a PES. Having at least one PES accurate to ±0.01 kcal/mol allows us to begin the task of objectively evaluating the reliability of methods applicable to larger systems – without reference to problems in the interpretation of experimental rates. Klopper et al. [53] have recently reviewed the state of the art for ab initio calculations on systems with up to about five atoms. An accuracy of ±0.2 kcal/mol is now practical. This error in calculated barrier heights corresponds to an error of ±40% in the rate constant at room temperature. Disagreement with experiment by more than a factor of 2 can then be attributed to a deficiency in the flavor of TST that is employed. The recent compilation of articles on computational thermochemistry by Irikura and Frurip [54] gives a very useful overview of the current state of computational methodology for larger systems. We can anticipate very rapid progress in this area over the next few years.

6 Summary and conclusions

The 1935 paper by Eyring represents the successful conclusion of a long search for a quantitative theory of chemical kinetics, providing the link from the microscopic world of the quantum mechanics of single molecules to the macroscopic world of the rates of chemical reactions in bulk matter. TST forms the very core of our conceptual framework for understanding chemical reactions – whether in the gas phase, on surfaces, in solution, or even in the active sites of enzymes.

The extreme sensitivity of chemical reaction rates to small changes in the PES confined early applications to semiempirical qualitative interpretations of experimentally measured rates. It is in this interpretive role that TST has had such a pervasive influence in chemistry. As our ability to calculate accurate PESs and to carry out quantum dynamics calculations has improved, the role of TST has evolved. Refinements in TST and in our ability to generate chemically accurate PESs are opening a new era in which we shall predict the rates of chemical reactions from first principles.

We can be confident that various incarnations of Eyring's TST will continue to provide the foundation for our qualitative and quantitative understanding of chemical reaction rates throughout the next century.

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