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## Liquid-phase chemical reactions, the pathways for important rare events

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**Abstract.** Chemical dynamics is the dynamics associated with the chemical rearrangements of atoms to form products from reactants. Such processes are infrequent but the important ones to understand are the kinetics of chemistry. Transition state theory provides a classical perspective with which one may focus on these rare but important events. Through two examples, this paper describes some of what can be learned with this perspective and its dynamical and quantum-mechanical generalizations.

This paper outlines our recent work on the dynamical and quantum-mechanical generalizations of classical transition-state theory. The work is well described in the current and forthcoming literature [1-3], so this review is purposely brief.

I deal first with classical theory. On the usual time scales of molecular dynamics, chemical rearrangement of atoms are rare events. Transition state theory and its generalizations address the dynamics of such events—the infrequent transitions between long-lived stable or nearly stable states. For chemical reactions in liquids, the stable states coincide with reactant and product potential wells. The potential barrier that separates them is the bottleneck which makes transitions infrequent. This is because the probability of visiting the barrier is low. For equilibrium considerations, it is virtually an irrelevant region of configuration space. For the dynamics of chemical reactions, however, this bottleneck is of central importance; it is the transition state for the reaction.

The theory of liquid-phase chemical dynamics is therefore closely tied to the study of the general barrier-crossing problem [4]. A qualitative solution to this problem in its simplest classical context was developed long ago, perhaps first by Kramers [5]. In recent times, many advances beyond this understanding have arisen from the ability to discuss specific barrier crossings through exact numerical trajectory calculations. Such studies are made feasible with non-Boltzmann sampling techniques (e.g., umbrella sampling) which can highlight infrequent or rare dynamical events [6]. The techniques work by examining transition states and the trajectories that pass through them. Without these methods, statistically meaningful studies of infrequent barrier crossings in complex systems would be impossible even with the most powerful imaginable computers.

The precise procedures employed in these examinations are intimately related [7] to transition state theory (an approximation to the dynamics), and also to the rigorous calculation of a chemical rate constant,  $k$  [7, 8].

One important conclusion drawn from detailed trajectory studies of chemical reactions is that solvent effects are highly system specific. Quantitative aspects including the general functional form of  $k$  compared with quantities like solvent pressure or density seem to defy general descriptions. This lack of universality may be disappointing, but it does seem intrinsic to the nature of chemical dynamics.

An illustration is provided by the liquid-phase chair-boat isomerization of cyclohexane. In 1979 and 1980 [9], we predicted that unimolecular processes such as isomerizations in liquids will often occur in the so-called 'energy diffusion' regime where rates are accelerated by the application of solvent pressure. This acceleration was subsequently observed experimentally for cyclohexane [10], though the interpretation remained unsettled until our recent theoretical analysis of specifically that system [3, 11]. In these recent calculations we find that a significant fraction of trajectories passing over the barrier are temporarily on vague tori and are not rapidly trapped in the product region without the influence of the solvent. The introduction of a solvent will cool down or stabilize these activated trajectories and therefore lead to an enhancement of the rate.

Transient non-chaotic behaviour of this sort can be expected in any polyatomic system. The detailed way in which it appears, however, will vary significantly from one molecule to another; and how it occurs will strongly influence, for example, the solvent pressure dependence of  $k$ . Specifically for cyclohexane, detailed trajectory calculations are in agreement with experimental observations [10], while to date, analytical treatments [12] based upon overly general dynamical assumptions have proved incorrect.

It is worth keeping in mind that issues concerning classical dynamics are of a detailed quantitative nature. The statistical transition-state theory is already a nearly complete story if one is simply interested in the absolute value of the rate constant. Information of a more detailed nature involving the specific dynamical pathways is accessed through the interpretation of experiments like those which measure the pressure dependence of the rates.

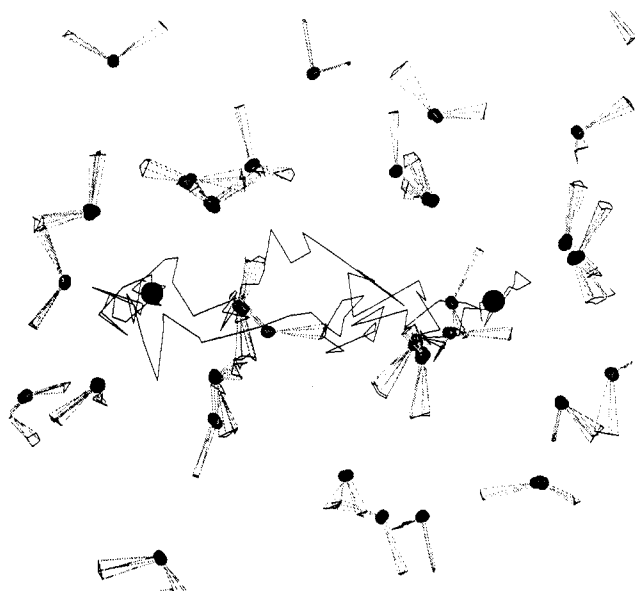
I now turn to quantum theory. In the quantum realm, something more comes into play. The positions of particles can never be certain and focusing attention on one precise configuration, such as a transition state, cannot be totally correct. Nevertheless, Voth, Miller and I have been able to derive a quantum-mechanical generalization of the transition-state-theory perspective [1]. Like its classical counterpart, the new theory provides a reasonable means of estimating rate constants from entirely statistical considerations. Further, like its classical counterpart, this quantum transition-state theory provides the basis for importance sampling with which exact quantum-dynamical calculations are now feasible.

How is this done? We begin with a suggestion from Gillan [13]: Rather than consider particle positions, focus instead on the *centroid* of Feynman's imaginary time quantum paths. Gillan noted that by computing the reversible work to move this centroid from a stable state to a bottleneck, one has, in effect, determined the activation free energy for a barrier crossing which includes the instanton or WKB tunnelling factor [14]. Hence, the probability distribution for the reaction coordinate centroid appears to be the appropriate quantum-mechanical version of the Arrhenius exponential factor.

One may make this appearance more vivid with explicit model calculations. Included among such calculations, we have arrived at a corrected version of Wolynes's [15] quantum-mechanical Grote-Hynes theory [16]. These theories describe barrier

crossing in terms of a linear model—an inverted parabolic barrier with linear coupling to a stable harmonic bath. Our version is distinguished from earlier work on this model in that it provides a variational procedure which avoids the unphysical divergences present in the straightforward quantum-mechanical treatment. Ours also provides a means of estimating the parameters to be used when applying the harmonic model to anharmonic systems. For further developments along these lines, see [23].

A stationary phase argument provides a rationale for why the centroid is the appropriate quantity to consider. This argument leads naturally to an important formal result—a rigorous and computationally feasible algorithm for computing rate constants for quantum systems.



**Figure 1.** A transition state from the simulated aqueous  $\text{Fe}^{2+}$ – $\text{Fe}^{3+}$  electron transfer. The centroid of the electron path is midway between the two irons. The two larger dark circles are the irons 5.5 Å apart, and the jagged lines connecting them are one path of the resonating electron. The Feynman paths of the quantized water molecules show the librations. Only a few of the hundreds of simulated waters are depicted. Those drawn with darker shade are the nearest neighbour ligands, each iron being six-fold coordinated.

The aqueous ferrous–ferric electron transfer provides an illustration of this approach. In the electron transfer process, the electron tunnels between the two iron ions. As delineated by Marcus [17], the transfer is made possible by rearrangements of the surrounding water molecules. Specifically how these rearrangements occur can be discerned by detailed calculations, those of the type we have carried out considering two iron ions, an electron and hundreds of water molecules [2, 18]. In particular, we have analysed the reversible work necessary to move the electron path centroid from one iron to the midpoint between the two. With the electron centroid at the midpoint, a resonant state has been prepared where the electron tunnels between the two redox sites. (For an asymmetric system, the transition state would be located

with the centroid displaced from the midpoint.) Notice that in this procedure [19], the electron's position plays the role of the reaction coordinate—a perspective that might be contrasted with the classical description of electron transfer [17]. In the limit of the small electron-tunnelling amplitude, the centroid method referred to here is closely related to the stationary-phase imaginary-time evaluation of the golden rule approximation to the rate constant [20].

In doing this, we have discovered something quite remarkable about the dominant pathways to electron transfer: Not only does the electron tunnel; liquid water tunnels too. Without classically forbidden nuclear configurations, electron transfer in water would occur at a rate two orders of magnitude slower than it actually does. There is also a significant isotope effect in changing the solvent from H<sub>2</sub>O to D<sub>2</sub>O, and our theoretical calculations are in agreement with experimental observations of this effect. The water motions involved in the tunnelling are librations—*collective* librations of hundreds of water molecules, the same fast motions responsible for the rapid time scales for hydrating electrons [21], and the same motions that quickly accommodate photochemically induced non-equilibrium charge distributions [22]. Figure 1 taken from a representative transition-state configuration in our Monte Carlo runs illustrates these motions.

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