Lecture 2: Chemical Reaction Rate Theory, continued

In the last class, we considered a unimolecular reactions of the form

$$A \rightleftarrows B \tag{1}$$

where k_{BA} and k_{AB} are the forward and reverse rate constants, respectively.

We then derived the exact quantum mechanical rate expression in the flux-side formulation:

$$k_{\mathrm{BA}} = \frac{1}{x_{\mathrm{A}}} \lim_{t \to \text{``}\infty\text{"}} \tilde{C}_{fs}(t), \tag{2}$$

where $t \to$ “∞" indicates that plateau region of the TCF after dynamical recrossing, the Kubo-transformed flux-side time correlation function is

$$\tilde{C}_{fs}(t) = \mathrm{Tr}\left\{\rho_0 \tilde{F}(0) h_{\mathrm{B}}(t)\right\}, \tag{3}$$

and in the classical mechanical limit, this correlation function becomes

$$C_{fs}^{(\mathrm{cl})}(t) = \langle \delta(q_0 - q^*) \dot{q}_0 h_{\mathrm{B}}(q_t) \rangle_0, \tag{4}$$

A. Transition State Theory

The central assumption of transition state theory (TST) is that once the system reaches the “transition state" (i.e., the location of the dividing surface, $q(\mathbf{r}) = q^*$, that separates the reactant from the product), then it proceeds to the product without any dynamical recrossing. Considering this statement in the context of the flux-side formulation of the rate, it is clear that the TST approximation corresponds to the $t \to 0^+$ limit of the rate expression.

B. Classical TST

Taking the $t \to 0^+$ limit of the rate expression leads to the classical mechanical expression for the TST rate,

$$k_{\mathrm{BA}}^{(\mathrm{TST})} = \frac{1}{x_{\mathrm{A}}} \lim_{t \to 0^+} C_{fs}^{(\mathrm{cl})}(t) = \frac{1}{x_{\mathrm{A}}} \lim_{t \to 0^+} \langle \delta(q_0 - q^*) \dot{q}_0 h_{\mathrm{B}}(q_t) \rangle_0, \tag{5}$$

This can be simplified by considering the term

$$\lim_{t\to 0^+}\delta(q_0-q^*)h_\mathrm{B}(q_t) = \lim_{t\to 0^+}\delta(q_0-q^*)\Theta(q_t-q^*) \tag{6}$$

$$= \lim_{t\to 0^+}\delta(q_0-q^*)\Theta(q_0+\dot{q}_0 t-q^*) \tag{7}$$

$$= \lim_{t\to 0^+}\delta(q_0-q^*)\Theta(\dot{q}_0 t) \tag{8}$$

$$= \delta(q_0-q^*)\Theta(\dot{q}_0) \tag{9}$$

Using this result, we can express the classical flux-side correlation function in terms of the classical phase-space distribution

$$\lim_{t\to 0^+} C^{(\mathrm{cl})}_{fs}(t) = \lim_{t\to 0^+}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} d\mathbf{p}_0\int_{-\infty}^{\infty} d\mathbf{r}_0 e^{-\beta H(\mathbf{p}_0,\mathbf{r}_0)}\delta(q_0-q^*)\dot{q}_0 h_\mathrm{B}(q_t) \tag{10}$$

$$= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} d\mathbf{p}_0\int_{-\infty}^{\infty} d\mathbf{r}_0 e^{-\beta H(\mathbf{p}_0,\mathbf{r}_0)}\delta(q_0-q^*)\dot{q}_0\Theta(\dot{q}_0) \tag{11}$$

$$= \frac{1}{2\pi\hbar}\int_{0}^{\infty} d\mathbf{p}_0\int_{-\infty}^{\infty} d\mathbf{r}_0 e^{-\beta H(\mathbf{p}_0,\mathbf{r}_0)}\delta(q_0-q^*)\dot{q}_0 \tag{12}$$

$$= \frac{1}{2\pi\beta\hbar}\int_{-\infty}^{\infty} d\mathbf{r}_0 e^{-\beta V(\mathbf{r}_0)}\delta(q_0-q^*) \tag{13}$$

$$\equiv \frac{1}{2\pi\beta\hbar}e^{-\beta F(q^*)}, \tag{14}$$

where in the last line we have introduced the notation for the free energy surface as a function of the reaction coordinate, $F(q)$, evaluated at the dividing surface. We thus arrive at the final expression for the classical TST rate,

$$k^{(\mathrm{TST})}_\mathrm{BA} = \frac{1}{x_\mathrm{A}}\frac{1}{\beta h}e^{-\beta F(q^*)} \tag{15}$$

The major advantage of this result is that an often-useful approximation to the rate is obtained exclusively from statistical quantities - no dynamics required!

C. Quantum TST?

The natural way forward to obtain the quantum mechanical TST rate is to similarly consider the $t\to 0^+$ of the quantum mechanical flux-side rate expression

$$k^{(\mathrm{TST})}_\mathrm{BA} = \frac{1}{x_\mathrm{A}}\lim_{t\to 0}\tilde{C}_{fs}(t) \tag{16}$$

However, as emphasized in the previous lecture, since $\tilde{C}_{fs}(t)$ is a time-derivative of an autocorrelation function, we have

$$\tilde{C}_{fs}(t) = -\tilde{C}_{fs}(-t), \tag{17}$$

such that $\tilde{C}_{fs}(t)$ is an odd (and real and continuous) function of time. Therefore,

$$k_{\mathrm{BA}}^{(\mathrm{TST,QM})} = 0. \tag{18}$$

For this reason, it has been argued by some that unlike classical mechanics, quantum mechanics does not have a well-defined TST limit for the rate.

As a pragmatic approach to including quantum effects in a TST rate expression, one can simply include quantum effects through the calculation of the TST rate in Eq. 15, except with the free energy value obtained from the quantum mechanical expectation value. This approach assumes that motion along the reaction coordinate is separable from motion on the dividing surface, treating the former as classical and the latter as quantum mechanical. Alternative treatments remove this assumption of separability and include tunneling along the reaction coordinate.[1–4]

1. W. H. Miller, J. Chem. Phys. 61, 1823 (1974).
2. G. A. Voth, D. Chandler and W. H. Miller, J. Chem. Phys. 91, 7749 (1989).
3. W. H. Miller, Y. Zhao, M. Ceotto and S. Yang, J. Chem. Phys. 119, 1329 (2003).
4. T. J. H. Hele and S. C. Althorpe, J. Chem. Phys. 138, 084108 (2013).

D. Computational advantage of the flux-side formulation: The Bennett-Chandler Approach

As emphasized in the last class, the characterization of the reaction rate in terms of the side-side correlation function,

$$\tilde{C}_{h_{\mathrm{A}}h_{\mathrm{A}}}(t) = x_{\mathrm{A}}^2 + x_{\mathrm{A}}x_{\mathrm{B}}e^{-t/\tau}, \tag{19}$$

requires the dynamics to be run for exponentially long times in order to extract the exponential decay associated with the reaction rate. We now illustrate that the flux-side correlation function substantially reduces the length of time for which the correlation functions need to be propagated.

For simplicity, we consider the classical limit, rearranging the classical flux-side rate expression

$$k_{\mathrm{BA}}^{(\mathrm{cl})} = \frac{1}{x_{\mathrm{A}}} \lim_{t\to\text{``}\infty\text{"}} \langle \delta(q_0 - q^*)\dot{q}_0 h_{\mathrm{B}}(q_t)\rangle_0 \tag{20}$$

$$= \left(\frac{\langle \delta(q_0 - q^*)\rangle_0}{x_{\mathrm{A}}}\right)\left(\lim_{t\to\text{``}\infty\text{"}} \frac{\langle \delta(q_0 - q^*)\dot{q}_0 h_{\mathrm{B}}(q_t)\rangle_0}{\langle \delta(q_0 - q^*)\rangle_0}\right) \tag{21}$$

where the first term in the final result is a purely statistical quantity ($\propto e^{-\beta F(q^*)}$) and the second term includes all of the dynamical recrossing. Specifically, the second term specifies that trajectories should be started from the classical Boltzmann distribution restrained to the dividing surface, and then the initial velocities should be correlated with h_{B} for the time-evolved trajectory. The beauty of this Bennett-Chandler approach is the dynamics need only be evolved for long enough for the molecule to leave from the dividing surface and thermalize in the reactant or product region. This occurs on the molecular timescale, rather than the exponentially long timescale of thermal activation of the barrier crossing event, a huge savings!

E. Factors that influence dynamical recrossing

In the classical limit, it is natural to quantify dynamical recrossing across the dividing surface in terms of the transmission coefficient

$$\kappa(t) = \frac{C_{fs}^{(\mathrm{cl})}(t)}{C_{fs}^{(\mathrm{cl})}(0)} \tag{22}$$

such that

$$\lim_{t\to\text{``}\infty\text{"}} \kappa(t) = \frac{k_{\mathrm{BA}}^{(\mathrm{cl})}}{k_{\mathrm{BA}}^{(\mathrm{TST})}} \tag{23}$$

The amount of observed recrossing follows from both physical features of the system (such as the amount that motion along the reaction coordinate is coupled to the other degrees of freedom), as well as the choice of the dividing surface for the system. The latter point is clear upon realizing that both the quantum reaction rate (Eq. 2) and the classical reaction rate (Eq. 4) are independent of the choice of the dividing surface (so long as it successfully divides the thermally accessible regions associated with the reactant and product). In fact, it is clear from the Bennett-Chandler expression for the rate (Eq. 21) that if the dividing surface were to be shifted in position, the dynamical recrossing term precisely compensates for the term that describes the Boltzmann probability of reaching the dividing surface. Since the Boltzmann weight varies exponentially with the dividing surface, we expect that the transmission coefficient becomes vanishingly small as we place the dividing surface away from the maximal free energy along the reaction coordinate. In this sense, the classical (and quantum) rates are invariant to the choice of dividing surface, but calculating the dynamical recrossing contribution to the rate is much easier if the dividing surface is located near the free-energy maxima.