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Metastable lifetimes and fast chemical reactions

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Abstract. We point out that, using the first-passage time formalism, it is now possible to calculate metastable lifetimes in the limit of the free energy barrier which is *small* compared to thermal energies. This opens the possibility of calculating rates for fast chemical reactions. Possible experimental checks include explosive branching reactions, decreasingly stable molecular series, and bistable molecular isomers.

Keywords. Metastable lifetimes; fast chemical reactions; first-passage time formalism; non-Arrhenius reaction rates.

1. First-passage-time formalism and low-barrier limit

Kramers (1940), motivated by the need to calculate chemical reaction rates, considered the now classic problem of escape of a Brownian particle across a potential barrier in one dimension. The barrier, in chemical language, corresponded to the free energy cost of forming an activated complex, with the energy supplied thermally. The Brownian position variable was some reaction coordinate x (figure 1),

$$\text{energy} + A + B \rightarrow (AB)^* \rightarrow C + D. \tag{1}$$

These ideas were generalized to several variables, $x \rightarrow (x_1 \ldots x_n)$ by several authors (Brinkman 1956; Landauer and Swanson 1961; Langer 1969) independently. The barrier now becomes a 'saddle' in n dimensions, with a metastable and an unstable well on either side. The Brownian particle jiggles around thermally in the metastable well, and at some time jumps over the saddle on the free energy surface, to the globally stable minimum.

In all dimensions n, the calculation gave an Arrhenius-type expression for the reaction rate R,

$$R = \omega\, e^{-\beta \Delta F}, \tag{2}$$

where ω is the attempt frequency, $\beta = (k_B T)^{-1}$ the inverse temperature, and ΔF the free energy difference between the metastable minimum and the saddle point. The Kramers-type calculations involved the assumption of a quasithermal distribution and a slow leakage of probability over the saddle, enabling a calculation of the steady probability current flow, and hence an evaluation of the *rate*. The 'slow-leakage' condition implied a small rate R, and hence a high barrier/low noise condition,

$$\Delta F / k_B T \gg 1 \tag{3}$$

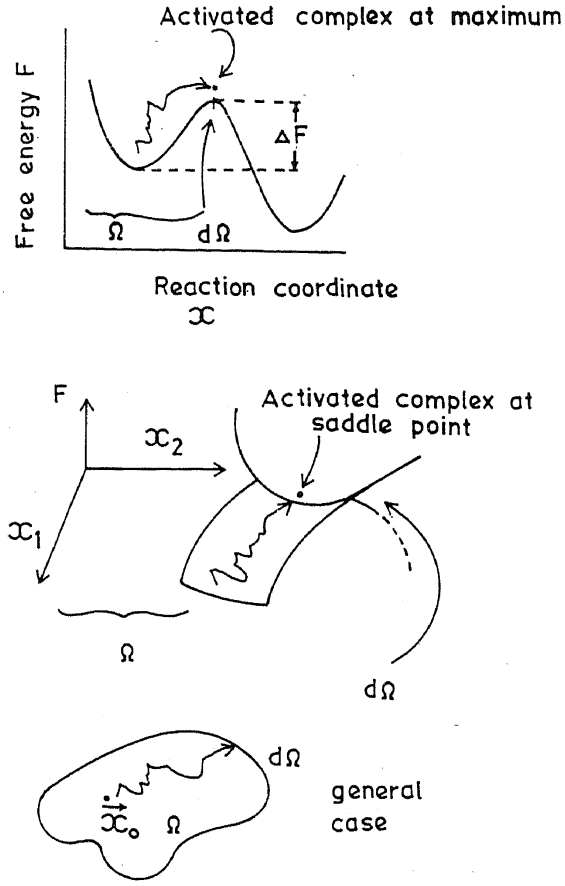

Figure 1. Barrier escape of a Brownian 'particle'.

An alternative formalism, based on conditional probabilities, is the 'first-passage time' formalism (Stratonovich 1963). As the name implies, it involves considering a random variable $\mathbf{x} = (x_1 \ldots x_n)$ inside some region Ω (metastable well), placed initially at $x_0 \in \Omega$. The random variable crosses the boundary $\partial\Omega$ in a mean first passage time $T_p(\mathbf{x}_0)$. The formalism expresses the mean first passage time $T_p(\mathbf{x})$ as the solution to a differential equation:

$$L_{\mathbf{x}}^{+} T_p(x) = -1, \tag{4}$$

where

$$L_{\mathbf{x}}^{+} = \sum_{i=1}^{n} D \frac{\partial^2}{\partial x_i^2} - A_i(x) \frac{\partial}{\partial x_i}. \tag{5}$$

Here D is the diffusion constant $= C_0 k_B T$ (C_0 = constant), and $\mathbf{A}(\mathbf{x})$ is the deterministic force $\mathbf{A}(\mathbf{x}) = C_0 \nabla_{\mathbf{x}} F(\mathbf{x})$. Thus the free energy surface $F(\mathbf{x})$, containing the metastable minimum in Ω and the saddle point on the boundary $\partial\Omega$, determines the FPT. The boundary condition is $T_p(x \in \partial\Omega) = 0$, as is physically reasonable: any point starting on the boundary has already 'passed', so the passage time is zero. The passage time calculation is then a boundary value problem, involving the solution of a differential equation.

A calculation of the FPT in n-dimensional yields the Kramers expression (2) (with $\partial\Omega$ suitably defined). This is obtained starting from an *exact* expression for

$T_p(\mathbf{x}_0)$ in terms of a ratio of volume (Ω) to surface ($\partial\Omega$) integrals, and then using the sharp-peaking approximations based on (2) (Schuss and Matkowsky 1979).

The stationary probability $P_0(\mathbf{x})$ satisfies the Fokker-Planck equation $L_x P_0(\mathbf{x}) = \dot{P}_0(\mathbf{x}) = 0$. Thus from (4), the identity $\int d^n x\, P_0(\mathbf{x})\,(L_x^+ T_p(\mathbf{x}) + 1) = 0$ holds exactly. The separation $T_p(\mathbf{x}) = v(\mathbf{x}, \mathbf{x}_0)\, T_p(\mathbf{x}_0)$; $v(\mathbf{x}_0, \mathbf{x}_0) = 1$, $v(\mathbf{x} \in \partial\Omega; \mathbf{x}_0) = 0$, plus partial integration yields (Schuss and Matkowsky 1979),

$$T_p(\mathbf{x}_0) = \frac{\int_\Omega P_0(\mathbf{x})\, d^n x}{-\int_{\partial\Omega} d^{n-1} x\, P_0(\mathbf{x})\, D\hat{n} \cdot \nabla_x v(\mathbf{x}, \mathbf{x}_0)}, \tag{6}$$

where $\hat{n}$ is the outward normal to the boundary $\partial\Omega$. Since $P_0(\mathbf{x}) = \exp[-\beta F(\mathbf{x})]$, sharp-peaking assumptions, for $\Delta F/k_B T \gg 1$ yield (2), with ω in terms of the free energy curvature matrix at the metastable minimum. The function v is a solution of $L^+ v \simeq 0$, and can be evaluated in a systematic expansion in $k_B T/\Delta F$. For the one-dimensional case (Gilmore 1979), (4) is exactly soluble, and one can examine the opposite *low barrier/high noise* limit (Agarwal and Shenoy 1981),

$$\Delta F/k_B T \ll 1. \tag{7}$$

One finds that if μ is some control parameter that shrinks the barrier $\Delta F(\mu)$ to zero at some $\mu = \mu_c$, $\Delta F(\mu_c) = 0$, then the FPT varies as a *power* of the barrier, or of the control parameter difference, $\mu - \mu_c$. Thus

$$T_p \sim [\Delta F(\mu)]^{\text{power}} \sim (\mu - \mu_c)\,\theta_p, \tag{8}$$

where the exponent θ_p in the one-dimensional case is $\theta_p = \frac{1}{2}$ (Agarwal and Shenoy 1981).

Since (6) is *exact*, one can handle the low-barrier/high-noise limit (7) for a *general* dimension n of the reaction coordinate space (Shenoy 1984) with θ_p depending on the nature of the free energy surface and boundary $\partial\Omega$ defined (nature of reactants and activated complex). This means that *fast* chemical reaction times can in principle be handled if the free energy surface is known. [For a two-mode ring laser (Shenoy and Agarwal 1984), $n = 4$ and one finds $\theta_p = 2$. This has been verified by Monte Carlo simulations (Murthy and Shenoy 1986, unpublished) confirming the formalism].

Of course the control parameter μ that shrinks the barrier is more easily obtained in examples from physics (pressure, temperature, laser pump parameter for saturable absorber). By varying μ rapidly enough, one can prepare a non-equilibrium population in the metastable well, and watch it decay. It is this preparation of the metastable state and possibility of a first-order phase transition which is the problem, in the chemical case. But one can find some possible chemical examples where these ideas can be tested and short reaction times predicted.

2. Possible chemical examples

2.1 *Explosive branching reactions*

Hydrogen and oxygen, under high temperatures and pressures, undergo a chain of reactions (Alberty 1983).

$H_2 + O_2 \xrightarrow{\text{wall}} 2OH$	initiation
$OH + H_2 \longrightarrow H_2O + H$	propagation
$H + O_2 \longrightarrow OH + O$	branching
$O + H_2 \longrightarrow OH + H$	
$H + \text{wall} \longrightarrow$	termination.

The branching reaction is explosive, for a range of temperatures and pressures. Figure 2 gives a rough 'Phase diagram', with rapid reactions occurring as the boundary is crossed. Thus, at $T = 550°C$ for $P < 100$ Pa the reaction is slow, while for $P = 100$ Pa the reaction is fast. Similarly for $P > 1{\cdot}33 \times 10^4$ Pa it is slow while for $P = 1{\cdot}3 \times 10^4$ Pa it is fast.

Since one has a parameter (in fact, two) to control ΔF, that shrinks at the boundary, one could in principle calculate reaction rates close to the boundary, given a knowledge of the hydrogen-oxygen atom free-energy surface.

2.2 *Decreasingly stable molecular series*

The basic problem, as stated, is to have some method of decreasing the free-energy barrier for the decay of a metastable state.

One could take a metastable molecule, and excite it by a laser, say to decreasingly stable molecular levels, measuring the decay times from the (increasingly) excited states (see figure 3a). The control μ is the laser frequency. If the energy surface in three dimensions is known, e.g., by quantum mechanical calculation, and if the decay is classical (no tunnelling-through), then the low-barrier decay time could be calculated.

Alternatively, one could consider decreasingly stable molecular series, prepared separately, with known (decreasing) activation barriers for dissociation (figure 3b). The control parameter μ is the molecular tailoring. The dissociation time could be measured and compared with theory.

2.3 *Bistable molecular isomers*

Molecular isomers are known, where two distinct forms have the same energy, with a barrier to the deformation of any isomer into another.

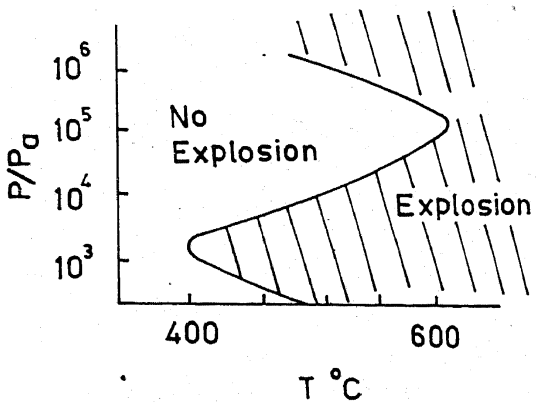

Figure 2. Pressure versus temperature stability diagram for hydrogen and oxygen.

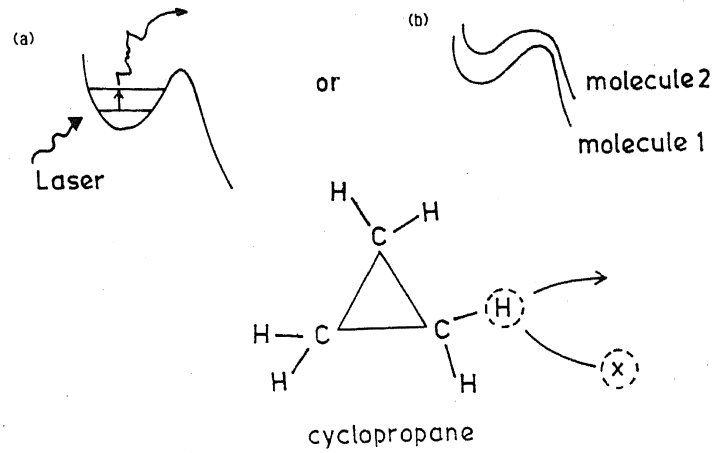

Figure 3. Effective barrier lowering through excitation.

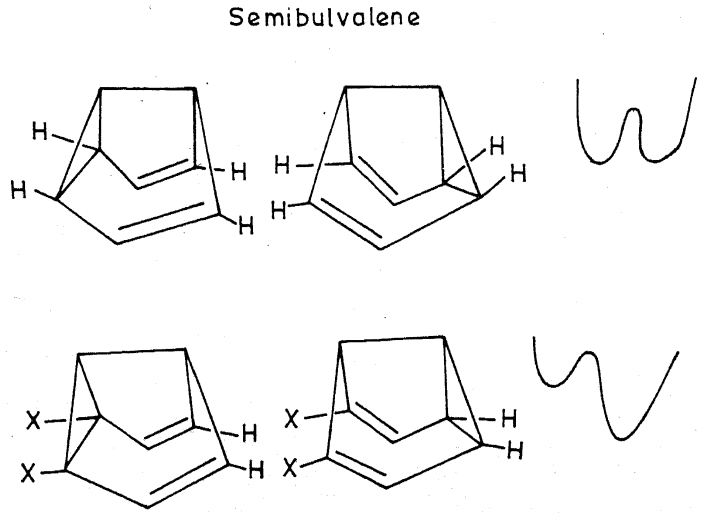

Figure 4. Asymmetric barriers by substitution.

(i) Semi-bulvalene is an example (figure 4), with hydrogen atoms attached to an organic ring with bonds connecting the points of attachment. One can replace the hydrogen by a complex X that strains this configuration, so that the two configurations shown (figure 4) have different energies, and a reduced free energy barrier ΔF. $\Delta F \sim 5$ kcal/mole (say) $\sim 0{\cdot}2$ eV, corresponding to $\Delta F/k_B T \sim 8$. This is still high but with judicious 'doping of the molecule, if one were to get $\Delta F/k_B T < 1$, one might be in the power-law regime of decay times.

One could prepare the non-equilibrium populations in the metastable well by laser irradiation at a frequency destroying the major (more stable) molecular species.

Alternatively, one could add the complex X to replace the H, and cool suddenly. If the reaction adding X proceeds faster than the hop-over, one will have a non-equilibrium 50-50 population of the X-compound, that will then decay to the unequal fractions dictated by the thermodynamics.

(ii) Acetaldehyde is another example, existing in the two states shown in figure 5. The unequal reaction rates indicated by the arrows imply that the free energy

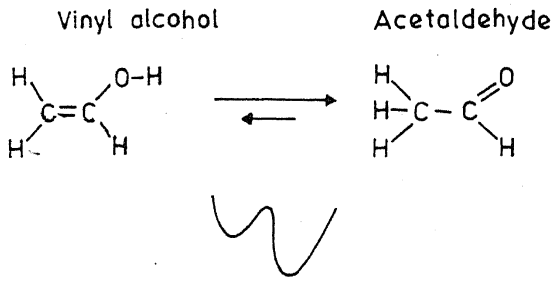

Figure 5. Asymmetric barriers in isomers.

barrier is asymmetric. The required non-equilibrium population could be created by laser pulses at frequencies that suddenly destroy the single C–C bond, leaving a non-equilibrium molecular form as dominant.

2.4 *Electron transfer reactions*

These involve electron pull-offs like

$$A + Cr^{2+} = Cr^{3+} + (e^{-}A)$$

and would cost, in terms of energy, typically of the order of 0·1–1 eV. One might think of the capturing molecule A as a film on an anode in a solution with Cr^{2+} ions. The barrier might conceivably be reduced by the applied voltage.

3. Conclusions

In conclusion, fast metastable decay times can in principle be calculated by recent formal developments. The problem is then to find chemical examples where a non-equilibrium population can be prepared in a metastable well with a free-energy barrier that is small compared to thermal energies. Some examples have been suggested. More work on the application of these ideas would clearly be worthwhile.

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References

Agarwal G S and Shenoy S R 1981 *Phys. Rev.* **A23** 2719
Alberty R A 1983 *Physical chemistry* (New York: John Wiley)
Brinkman H C 1956 *Physica* **22** 149
Gilmore R 1979 *Phys. Rev.* **A20** 2510
Kramers H A 1940 *Physica* **7** 284

Landauer R and Swanson J A 1961 *Phys. Rev.* **121** 1668
Langer J S 1969 *Ann. Phys.* (*NY*) **54** 258
Schuss Z and Matkowsky B 1979 *SIAM J. Appl. Math.* **35** 604
Shenoy S R and Agarwal G S 1984 *Phys. Rev.* **A29** 1315
Shenoy S R 1984 *Phys. Rev.* (*Rapid Commun.*) **A30** 2849
Stratonovich R L 1963 *Topics in the theory of random noise* (New York: Gordon and Breach)