RRK theory

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1 Isomerization reactions as a test of theories of unimolecular reactions

Gas-phase unimolecular reactions have played a pivotal role in theoretical chemical kinetics because they are, on the surface at least, so simple. And yet, it is surprisingly difficult to reconcile theory and experiment, even for these simplest of chemical reactions. It would also seem that isomerization reactions would be particularly simple since the reactants and products are similar in size and complexity. In this case, we would expect that collisional activation and deactivation would be similarly effective, whether the reactant collides with another molecule of reactant or with the product, or indeed with an activated reactant molecule. In this case, the Lindemann mechanism reads

$$\mathrm{A} + \mathrm{X} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{X},$$
$$\mathrm{A}^* \xrightarrow{k_2} \mathrm{P},$$

where X can be either A, A^* or P. Clearly, $[\mathrm{X}] = a_0$ is a constant, with a_0 the initial concentration of A. Applying the steady-state approximation, we get a reaction rate

$$v = \frac{k_1 k_2 a_0}{k_{-1} a_0 + k_2}[\mathrm{A}].$$

In other words, we should observe first-order behavior, with an effective rate constant k that depends on a_0 as follows:

$$k = \frac{k_1 k_2 a_0}{k_{-1} a_0 + k_2}. \tag{1}$$

If we take the reciprocal of this equation, we have

$$\frac{1}{k} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1 a_0}.$$

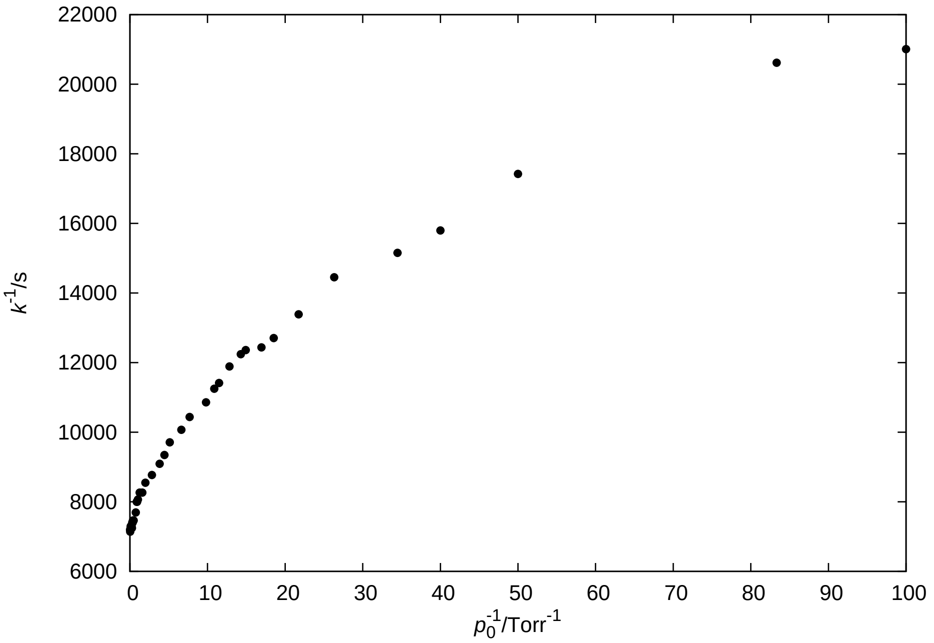

Figure 1: Reciprocal plot of the effective first-order rate constant vs initial pressure for the isomerization of 3-methylcyclobutene to *trans*-penta-1,3-diene (Frey and Marshall, *Trans. Faraday Soc.* **61**, 1715, 1965).

A plot of k^{-1} vs a_0^{-1} should therefore give a straight line. Figure 1 shows some typical data taken over a large range of initial pressures of the reactant, in this case 3-methylcyclobutene. The plot is clearly not linear over the whole range of initial pressures. While the Lindemann mechanism explains some features of the kinetics of unimolecular reactions, it's clearly missing something too.

2 RRK theory

In order for a molecule to undergo a particular reaction, it's not good enough for the molecule to have enough total energy. The energy has to be stored in the appropriate normal mode, i.e. the reactive mode discussed in the notes on transition-state theory. Implicit in the Lindemann mechanism is the idea that a collision either puts energy in that one specific mode, or it doesn't. There is no allowance made for internal redistribution of energy. In a sufficiently complex molecule, the probability of a collision putting enough energy in a specific one of the $3N-6$ normal modes must clearly be very small, and yet there is no particular trend toward lower unimolecular rate constants with increasing molecular size. Internal redistribution must therefore be important.

In the late 1920's, Rice and Ramsperger and, independently, Kassel, proposed two similar theories that extended the Lindemann treatment to include internal redistribution of energy. While the basic ideas of these two theories were very similar, there were some differences, and it is really Kassel's version which has survived. Nevertheless, the theory is generally known as RRK theory, in honor of these three scientists.

The starting point of RRK theory is a slight elaboration of the Lindemann mechanism:

$$\mathrm{A} + \mathrm{X} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{X},$$
$$\mathrm{A}^* \overset{k_{2a}}{\longrightarrow} \mathrm{A}^\ddagger \overset{k^\ddagger}{\rightarrow} \mathrm{P}.$$

Here, X can be any molecule in the system (reactant, product, inert gas, etc.) that can collisionally activate A. $\mathrm{A}^\ddagger$ is the transition state of the reaction. The idea behind writing the mechanism this way is that while A^* may have enough energy to reach the transition state, that energy may need to flow from several normal modes into the reactive normal mode in order for the transition state to be reached, and thus for the reaction to occur. This takes time, so it's treated as a rate process.

The rate constant $k^\ddagger$ represents the very rapid process associated with the reactive mode. Given that $k^\ddagger$ is much larger than any normal rate constant, the formation of the transition state is rate limiting for the conversion of A^* to product (not unexpected, of course). Accordingly, the Lindemann mechanism $k_2 = k_{2a}$ from the RRK treatment. We can apply the steady-state approximation to the concentration of $\mathrm{A}^\ddagger$. We get

$$k_{2a} = k^\ddagger[\mathrm{A}^\ddagger]/[\mathrm{A}^*]. \tag{2}$$

Suppose that A^* has energy ε^*. We will consider the distribution of values of ε^* later. RRK theory assumes that energy moves rapidly between vibrational modes. That being the case, at any given time, the ratio $[\mathrm{A}^\ddagger]/[\mathrm{A}^*]$ is equal to the probability $p^\ddagger$ that the minimum energy required for the reaction to occur, $\varepsilon^\ddagger$, is localized in the correct normal mode in a molecule with total energy ε^*. The next assumptions we make are that the normal modes are harmonic and that they all have the same frequency. Then we can write $\varepsilon^* = n^* h\nu$ and $\varepsilon^\ddagger = n^\ddagger h\nu$. Our question about the probability of energy localization in the reactive mode becomes one about the probability that at least $n^\ddagger$ quanta are localized in the reactive mode out of a total of n^* quanta. Let the number of normal modes of the reactant be s. The number of different ways of putting n^* quanta in s normal modes is

$$W_{\text{total}} = \frac{(n^* + s - 1)!}{n^*!(s-1)!}.$$

If I want one particular mode to contain at least $n^\ddagger$ quanta, then we have $n^* - n^\ddagger$ quanta to place randomly in the s normal modes. There are

$$W^\ddagger = \frac{(n^* - n^\ddagger + s - 1)!}{(n^* - n^\ddagger)!(s-1)!}$$

different arrangements. The probability that at least $n^\ddagger$ quanta are in the reactive mode is therefore

$$p^\ddagger = \frac{W^\ddagger}{W_{\text{total}}} = \frac{(n^* - n^\ddagger + s - 1)!n^*!}{(n^* - n^\ddagger)!(n^* + s - 1)!}.$$

The number of quanta required to reach the transition state is large, and it is likely that there will be many more quanta of vibrational energy stored in the molecule than the minimum in order for there to be a reasonable probability that the reactive mode contains $n^\ddagger$ of them. Each of the terms in $p^\ddagger$ is therefore a factorial of a large number, to which we can apply Stirling's approximation. After doing this and cancelling some terms, we get

$$\ln p^\ddagger = (n^*-n^\ddagger+s-1)\ln(n^*-n^\ddagger+s-1)+n^*\ln n^*-(n^*-n^\ddagger)\ln(n^*-n^\ddagger)-(n^*+s-1)\ln(n^*+s-1).$$

Again, the number of quanta stored in an activated molecule is large. In particular, it should be much larger than s. If we take $s-1=x$ to be a small quantity, then both the first and last term of this equation are of the form $f(x)=(a+x)\ln(a+x)$. The first two terms of the Taylor series of this function are $f(x)\approx a\ln a + x(\ln a+1)$. If we apply this approximation to the first and last terms of $\ln p^\ddagger$ and cancel terms, we get

$$\ln p^\ddagger = (s-1)\ln(n^*-n^\ddagger)-(s-1)\ln n^*,$$

or

$$p^\ddagger = \left(\frac{n^*-n^\ddagger}{n^*}\right)^{s-1}.$$

Because of the assumption that all the normal modes have the same frequency, n^* and $n^\ddagger$ are proportional, respectively, to ε^* and $\varepsilon^\ddagger$, so we can also write

$$p^\ddagger = \left(\frac{\varepsilon^*-\varepsilon^\ddagger}{\varepsilon^*}\right)^{s-1}.$$

Since $p^\ddagger$ is the ratio of $[\mathrm{A}^\ddagger]$ to $[\mathrm{A}^*]$, equation 2 becomes

$$k_2 = k_{2a} = k^\ddagger\left(\frac{\varepsilon^*-\varepsilon^\ddagger}{\varepsilon^*}\right)^{s-1}.$$

This equation gives us the rate constant k_2 as a function of the total energy of the molecule ε^*. Of course, different amounts of energy will be gained in different collisions, so not every molecule has the same energy after collisional activation.

Our next task is to figure out the distribution of energies of the molecules caused by collisional activation. Here, we treat the normal modes as classical oscillators that can hold any amount of energy. The Boltzmann distribution in this case gives us the probability that the energy of a particular oscillator, say oscillator n, is between ε and $\varepsilon+d\varepsilon$ as

$$P(\varepsilon\le\varepsilon_n\le\varepsilon+d\varepsilon)=\frac{1}{kT}e^{-\varepsilon/(kT)}d\varepsilon.$$

The probability that the energy is greater than ε is found by

$$P(\varepsilon_n>\varepsilon)=\int_\varepsilon^\infty\frac{1}{kT}e^{-\varepsilon'/(kT)}d\varepsilon'=e^{-\varepsilon/(kT)}.$$

Now suppose that we have two oscillators with a total energy of at least ε. Say that one of them has an energy between ε_0 and $\varepsilon_0+d\varepsilon_0$. Then the other has an energy of at least $\varepsilon-\varepsilon_0$.

The probability of the latter is $e^{-(\varepsilon-\varepsilon_0)/(kT)}$. The probability of the former is $\frac{1}{kT}e^{-\varepsilon_0/(kT)}d\varepsilon_0$. The probability that both are simultaneously true is the product of these two probabilities. To get the probability that two oscillators have an energy greater than ε, we integrate this product over all possible values of ε_0 and add the probability that the first oscillator has energy greater than ε (since our integral assumes that it has energy less than or equal to this total):

$$P_2(\sum \varepsilon_i > \varepsilon) \equiv P_{2>} = \int_0^{\varepsilon} e^{-(\varepsilon-\varepsilon_0)/(kT)} \frac{1}{kT} e^{-\varepsilon_0/(kT)} d\varepsilon_0 + e^{-\varepsilon/(kT)} = \left(\frac{\varepsilon}{kT} + 1\right) e^{-\varepsilon/(kT)}.$$

If $P_2(\varepsilon)$ is the probability density for the sum of the energies of the two oscillators, then

$$P_{2>} = \int_{\varepsilon}^{\infty} P_2(\varepsilon')d\varepsilon'.$$

By the fundamental theorem of calculus, we have

$$P_2(\varepsilon) = \frac{dP_{2>}}{d\varepsilon} = \frac{\varepsilon}{(kT)^2} e^{-\varepsilon/(kT)}$$

since $\lim_{\varepsilon\to\infty} P_2(\varepsilon) = 0$. We can repeat this trick, using the probabilities that two oscillators have energy ε_0 and that a third has an energy greater than $\varepsilon - \varepsilon_0$, then repeat it again, and again, … The details are a bit grungy, but the final result is simple: The probability that s oscillators have an energy between ε and $\varepsilon + d\varepsilon$ is

$$P_s(\varepsilon)d\varepsilon = \frac{1}{(s-1)!}\left(\frac{\varepsilon}{kT}\right)^{s-1} \frac{1}{kT} e^{-\varepsilon/(kT)} d\varepsilon.$$

Now let's rewrite equation 1 a little:

$$k = \frac{(k_1/k_{-1})k_2 a_0}{a_0 + k_2/k_{-1}}. \tag{3}$$

k_1/k_{-1} is the equilibrium constant for the first reaction in the Lindemann mechanism, i.e. $k_1/k_{-1} = [\mathrm{A}^*]/[\mathrm{A}]$. If we interpret A^* as being an energized version of A with energy between ε^* and $\varepsilon^* + d\varepsilon^*$, then k_1/k_{-1} is the probability that, through random collisions, a molecule of A will have an energy in this range. $P_s(\varepsilon^*)$ is therefore the probability density we set out to calculate.

If we substitute $P_s(\varepsilon^*)d\varepsilon^*$ for k_1/k_{-1} along with our final expression for $k_2(\varepsilon^*)$ into equation 3, we get the effective rate constant corresponding only to molecules with energy in the range ε^* to $\varepsilon^* + d\varepsilon^*$. In order to get the rate constant for molecules of any energy greater than the minimum, $\varepsilon^\ddagger$, we have to integrate this expression over all values of ε:

$$k = \int_{\varepsilon^\ddagger}^{\infty} \frac{\frac{1}{(s-1)!}\left(\frac{\varepsilon^*}{kT}\right)^{s-1} \frac{1}{kT} e^{-\varepsilon^*/(kT)} k^\ddagger \left(\frac{\varepsilon^* - \varepsilon^\ddagger}{\varepsilon^*}\right)^{s-1} a_0}{a_0 + k^\ddagger \left(\frac{\varepsilon^* - \varepsilon^\ddagger}{\varepsilon^*}\right)^{s-1} / k_{-1}} d\varepsilon^*.$$

This integral can't be evaluated analytically. It can be evaluated numerically for given values of the constants. Reasonable agreement with experiment is obtained if we take s to be about half of the total number of vibrational modes of the molecule. The justification for this adjustment is that only some modes couple efficiently to the reactive mode in a typical molecule. Note however the word "about" in the above passage. This is a completely *ad hoc* adjustment, and there is no good way to tell ahead of time exactly how many modes we should include in the calculation. Another problem is the rate constant $k^{\ddagger}$. It is tempting to set this constant to (e.g.) the value found by the vibrational mode approach to the reactive mode in transition-state theory, namely $k^{\ddagger} = kT/h$. Unfortunately, this makes the preexponential factor much too small for many unimolecular reactions. Still, this theory pointed the way forward.

3 RRKM theory

RRKM theory was developed by Canadian Nobel prize winner R. A. Marcus based on RRK theory. RRKM theory merges transition-state theory with RRK theory: As in RRK theory, equation 3 is used to obtain an equation for the rate constant, and k_1/k_{-1} is replaced by a probability distribution $P_s(\varepsilon^*)d\varepsilon^*$. However, the correct probability distribution is used, considering both the fact that the vibrational modes have different frequencies, and that rotational modes are coupled to the vibrational modes. Another difference is that transition state theory is used to obtain an expression for $k_2(\varepsilon^*)$ instead of the statistical argument used in RRK theory. Calculations have shown RRKM theory to be very accurate.