A DEEPER LOOK 12 The RRK model

The essential feature of the RRK model is that although a molecule might have enough energy to react, that energy is distributed over all the modes of motion of the molecule, and reaction will occur only when enough of that energy has migrated into a particular location (such as a particular bond) in the molecule.

Step 1 *Set up the model*

Suppose that a molecule consists of s identical harmonic oscillators, each of which has frequency v. In practice, of course, the vibrational modes of a molecule have different frequencies, but assuming that they are all the same is a reasonable first approximation. Next, suppose that the vibrations are excited to a total energy $E = nhv$: that is, there are n quanta in total

Step 2 *Calculate the number of ways in which the energy can be distributed over the oscillators*

Represent the n quanta as follows:

$$\square...\square\square\square$$

These quanta must be put in s containers (the s oscillators), which can be represented by inserting $s - 1$ walls, denoted by |. One such distribution is

$$\square\square|\square\square\square\square|\square\square||\square\square\square|\square\square\square\square\square\square\square\square|\square\square\square\square|||\square\square\square\square\square|\square\square\square\square...\square|\square\square$$

The total number of arrangements of the quanta and the walls (of which there are $n + s - 1$ in all) is $(n + s - 1)!$ where, as usual, $x! = x(x - 1)\cdots 1$. However the $n!$ arrangements of the n quanta are indistinguishable, as are the $(s - 1)!$ arrangements of the $s - 1$ walls. Therefore, to find the number N of ways in which the energy can be distributed, divide $(n + s - 1)!$ by $n!$ and by $(s - 1)!$ to give

$$N = \frac{(n+s-1)!}{n!(s-1)!}$$

Step 3 *Consider the effect of excitation of a critical oscillator that undergoes dissociation*

The distribution of the energy throughout the molecule means that it is too sparsely spread over all the modes for any particular bond to be sufficiently highly excited to undergo dissociation. Suppose that a bond will break only if it is excited to at least an energy $E^\star = n^\star hv$. Therefore, isolate one critical oscillator as the one that undergoes dissociation if it has *at least* $n^\star$ of the quanta, leaving up to $n - n^\star$ quanta to be accommodated in the remaining $s - 1$ oscillators (and therefore with $s - 2$ walls in the partition in place of the $s - 1$ walls used above). For example, consider 28 quanta distributed over 6 oscillators, with excitation by at least 6 quanta required for dissociation. Then all the following arrangements of quanta and walls will result in dissociation:

$$\square\square\square\square\square\square|\square\square\square\square\square|\square\square\square\square\square\square\square\square|\square\square\square\square||\square\square\square\square\square$$
$$\square\square\square\square\square\square\square|\square\square\square\square|\square\square\square\square\square\square\square\square|\square\square\square\square||\square\square\square\square\square$$
$$\square\square\square\square\square\square\square\square|\square\square\square|\square\square\square\square\square\square\square\square|\square\square\square\square||\square\square\square\square\square$$
$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

(The leftmost partition is the critical oscillator.) However, these arrangements are equivalent to

$$\square\square\square\square\square\square \qquad |\square\square\square\square\square|\square\square\square\square\square\square\square\square|\square\square\square\square||\square\square\square\square\square$$
$$\square\square\square\square\square\square \qquad \square|\square\square\square\square|\square\square\square\square\square\square\square\square|\square\square\square\square||\square\square\square\square\square$$
$$\square\square\square\square\square\square \qquad \square\square|\square\square\square|\square\square\square\square\square\square\square\square|\square\square\square\square||\square\square\square\square\square$$
$$\vdots \qquad\qquad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots$$

and the problem is that of permuting $28 - 6 = 22$ (in general, $n - n^\star$) quanta and 5 (in general, $s - 1$) walls, and therefore a total of 27 (in general, $n - n^\star + s - 1$ objects). Therefore, the calculation is exactly like the one above for N, except that you need to find the number of distinguishable permutations of $n - n^\star$ quanta in s containers (and therefore $s - 1$ walls). The number $N^\star$ is therefore obtained from the expression for N by replacing n by $n - n^\star$ and is

$$N^\star = \frac{(n - n^\star + s - 1)!}{(n - n^\star)!(s - 1)!}$$

Step 4 *Write an expression for the probability of dissociation of an oscillator*

It follows from the preceding discussion that the probability that one specific oscillator will have undergone sufficient excitation to dissociate is the ratio N^*/N, which is

$$P = \frac{N^*}{N} = \frac{n!\,(n-n^*+s-1)!}{(n-n^*)!\,(n+s-1)!}$$

This equation is still awkward to use, even when written out in terms of its factors:

$$P = \frac{n(n-1)(n-2)\cdots 1}{(n-n^*)(n-n^*-1)\cdots 1} \times \frac{(n-n^*+s-1)(n-n^*+s-2)\cdots 1}{(n+s-1)(n+s-2)\cdots 1}$$

Consider first the ratio of the terms in blue

$$\frac{(n-n^*+s-1)(n-n^*+s-2)\cdots 1}{(n-n^*)(n-n^*-1)\cdots 1}$$

The denominator cancels all terms in the numerator from $n-n^*$ down to 1, so the surviving part of this term is simply

$$(n-n^*+s-1)(n-n^*+s-2)\cdots(n-n^*+1)$$

Now consider the terms in black in the expression for P

$$\frac{n(n-1)(n-2)\cdots 1}{(n+s-1)(n+s-2)\cdots 1}$$

In this case, the numerator cancels all terms in the denominator from n down to 1, leaving

$$\frac{1}{(n+s-1)(n+s-2)\cdots(n+1)}$$

The expression for P therefore simplifies to

$$P = \frac{(n-n^*+s-1)(n-n^*+s-2)\cdots(n-n^*+1)}{(n+s-1)(n+s-2)\cdots(n+1)}$$

However, because $s-1$ is small (in the sense that $s-1 \ll n-n^*$), approximate this expression by

$$P = \frac{\overbrace{(n-n^*)(n-n^*)\cdots(n-n^*)}^{(s-1\text{ factors})}}{\underbrace{(n)(n)\cdots(n)}_{(s-1\text{ factors})}} = \left(\frac{n-n^*}{n}\right)^{s-1}$$

Because the energy of the excited molecule is $E = nh\nu$ and the critical energy is $E^* = n^*h\nu$, this expression may be written as

$$P = \left(1 - \frac{E^*}{E}\right)^{s-1}$$

Step 5 *Write an expression for the rate constant*

The unimolecular rate constant $k_b(E)$ for the decay of A^* to products may now be written as

$$k_b(E) = \overbrace{\left(1 - \frac{E^*}{E}\right)^{s-1}}^{P} k_b \quad \text{for } E \geq E^*$$

Unimolecular rate constant

where k_b is the rate constant used in the original Lindemann–Hinshelwood theory for the decomposition of the activated intermediate (Topic 17F). This is eqn 18A.11 of the text.