J. Phys. Chem. A **2007,** *111,* 11809−11813 **11809**

Comparison of Two Types of Dispersive Kinetic Approaches in Relation to Time-Dependent Marcus Theory

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Received: May 8, 2007; In Final Form: August 31, 2007

Two different approaches presented in recent literature for the treatment of dispersive kinetics for a first-order (F1) conversion mechanism are compared from a physicochemical perspective. The author's approach is found to be successful in describing activation energy trends as a function of time that can be predicted from a simple extension of Marcus theory. Thus, the approach is considered to have a sound fundamental basis.

Introduction

Dispersive kinetics occur in chemical reactions and phase transformations for which the rate of internal rearrangements (e.g., molecular relaxation), responsible for causing continuous "system renewal", is similar to or slower than the rate of the overall conversion.[1] As dispersive kinetics can be observed in all phases of matter and (in part, consequently) at very different time-scales,[1−4] the study of systems exhibiting this type of behavior is very important.

The kinetic trends exhibited by dispersive systems are often exemplified by "stretched exponential" or "asymmetric, sigmoid" fractional conversion versus time ($x-t$) plots, obtained under isothermal conditions. As such curve shapes are usually difficult to fit with traditional (i.e., nondispersive) kinetic models, the use of a dispersive approach for treating the kinetics might be more appropriate.

Two independent approaches for the treatment of dispersive kinetics have been described in recent literature. While one approach is based on the idea of a Maxwell−Boltzmann (M−B) distribution of activation energies, the other utilizes the concept of fractal conversion time. Each approach defines a very different functional form for the time-dependent rate coefficient (note that in traditional kinetics, the rate coefficient is not time-dependent; thus, it is often called a rate constant). The purpose of this work is to provide a brief comparison of these treatments, as they relate to a first-order conversion mechanism, and to identify the approach that best fits with Marcus theory.

Results and Discussion

First-Order Dispersive Kinetic Models Based On A Maxwell−Boltzmann Distribution of Activation Energies. In recent publications,[2,3,5−9] the author has described an approach for the treatment of dispersive kinetic data based on the assumption of an activation energy distribution possessing the functional form of the Maxwell−Boltzmann (M−B) distribution. In the author's treatment, the M−B distribution of activation energies, $D(E_a)$, originates from molecular-level differences in the energies of either the reagent state or the activated state (AS)/product species involved in defining the rate-determining step, depending on whether the conversion is deceleratory or acceleratory in nature (note: for deceleratory $x-t$ sigmoids, the inflection point typically occurs earlier in the conversion than for acceleratory transients).[8] The dispersion (i.e., variation) in the activation energy has been attributed to differences in the molecular kinetic energies; these energies can be depicted by an inverted distribution that is superimposed on a hypothetical potential energy surface (PES) for the conversion. The resulting activation energy distributions, when plotted as a function of the extent of conversion, x, can be either concave-up (for deceleratory $x-t$ sigmoids) or concave-down (for acceleratory cases);[7] as a point of interest, this finding might explain some of the solid-state thermal analysis data trends[7] obtained for elementary processes using so-called isoconversional[10] or model-free methods. More recently, the dispersion in $D(E_a)$ has been shown to relate a stochastic change in the activation entropy associated with the reagent molecules as they transition over the activation energy barrier.[5]

In previous work,[3] $D(E_a)$ was converted to a distribution of molecular rate constants, $D(k)$, using the Eyring equation. Employing a simple assumption and performing some basic mathematical manipulations/simplifications,[3] $D(k)$ was shown to relate a time-dependent rate coefficient, $k(t)$, for the overall conversion. The general form of $k(t)$ might be adequately represented by the Gaussian function:

$$k(t) \approx \alpha e^{\beta t^2} \tag{1}$$

where α and β are constants (i.e., global rate parameters for the overall conversion), each with physically meaningful units in the time domain. In eq 1, the value of β is negative if the reaction is deceleratory and positive if it is acceleratory. Using the integrated, first-order (F1) reaction model expression:[7,11]

$$x = \exp - (t^{n}) \int_0^t k(t)\, dt \tag{2}$$

(where x represents the mole fraction of reagent material in the system at time t and the term, t^n, allows for various dimensionalities,[12] other than zero, to be considered, e.g., for conversions involving the solid-state) one can obtain the following dispersive kinetic models:[3,7]

$$x \approx e^{\alpha t(e^{-\beta t^2}-1)} \tag{3}$$

$$x \approx e^{-\alpha/t(e^{\beta t^2}-1)} \tag{4}$$

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10.1021/jp0735132 CCC: $37.00

Equation 3 assumes a negative value of β (explicitly shown in the equation) and $n = 2$; it has been shown to be useful in modeling two-dimensional (2-D) nucleation/denucleation kinetics.[3] Equation 4 assumes (explicitly) a positive β value and $n = 0$; it has been shown to be useful for modeling polymorphic transformation $x-t$ transients that are nucleation rate-limited.[3] Of all of the dispersive variants of the classical kinetic models developed to date,[7] eq 3 and eq 4 have been used most extensively by the author in various applications.

It is important to highlight the fact that the approximations pertaining to eqs 3 and 4 stem from the fact that these models were actually derived using a time-dependent rate coefficient having the functional form:

$$k(t) = \pm\left[\frac{\alpha}{2\beta t^2}\,(\mathrm{e}^{\pm\beta t^2}-1)+\alpha(\mathrm{e}^{\pm\beta t^2})\right] \tag{5}$$

where β can be either positive or negative, as shown explicitly in the equation; the sign in front of the brackets on the right-hand side of the equation is opposite to that of β. Equation 5 is used in lieu of eq 1 since the direct integration of a Gaussian does not yield a simple analytical solution (the exact solution to eq 2). Using eq 1 would necessitate the use of the error function or imaginary error function, in eqs 3 and 4, respectively;[7] however, implementing these functions would likely make the models less attractive to many workers because they require numerical solution. While an investigation into the validity of this approximation will be presented later, it is reiterated here that eq 1 is, itself, only an approximation.[3] However, despite this fact, the usefulness of eqs 3 and 4 in modeling real-world dispersive kinetics, as mentioned above, supports the idea that these models have a solid physical foundation. For this reason, it is not necessarily critical here to ascertain the exact functionality of $k(t)$ but rather to note that its time-dependence is generally consistent with a Gaussian, for example, not an exponential, as defined in the closely related Gompertz equation.[9]

The activation energy for dispersive processes, like the rate coefficient, $k(t)$, is time-dependent. The author has shown that, using eq 1, the activation energy obeys the general relation:[8]

$$E_a(t) \approx E_a^0 \pm RT\beta t^2 \tag{6}$$

where E_a^0 is the potential energy (i.e., time-independent/classical Arrhenius) portion of the activation energy barrier, R is the gas constant, and T is the absolute temperature. Because of the sign differences possible for β (hence the ± in the above equation), $E_a(t)$ can either increase or decrease with time.[8] If β is negative (i.e., from eq 3), the activation energy increases with time and the process exhibits a rate deceleration. Conversely, if β is positive (i.e., from eq 4), $E_a(t)$ decreases with time and an acceleratory, sigmoid $x-t$ trend is typically observed.

Utilizing eq 6, the distribution functions for the activation energies corresponding to eqs 3 and 4 are:

$$f(E_a) \approx \exp(\alpha\sqrt{({E_a}^0-E_a)/\beta RT}\,[\mathrm{e}^{(E_a-E_a^0/RT)}-1]) \tag{7}$$

$$f(E_a) \approx \exp-(\alpha\sqrt{(E_a-E_a^0)/\beta RT}\,[\mathrm{e}^{(E_a-E_a^0/RT)}-1]) \tag{8}$$

respectively. Equations 7 and 8 indicate that the activation energy distribution might be complex in certain cases, depending on the relative magnitudes of E_a^0 and E_a. However, this observation should be considered in light of Maksimov's use of both real and imaginary components in the partition function and, correspondingly, in the free energy of activation to describe nucleation kinetics;[13] along similar lines, the author believes that many nucleation/denucleation rate-limited processes are dispersive (particularly those involving smaller critical nuclei that cannot be adequately described by the classical nucleation theory (e.g., see ref 14) because of the limited applicability of classical thermodynamic relations on the microscopic level; note that use of the M−B distribution implies the possibility of energy quantization in the overall activation energy barrier). As an aside, the well-known works by the Nobel-laureate Zewail[15] over the last two decades have demonstrated that it is possible to observe (on the femtosecond scale) both classical saddle point transition states as well as (conversely) a small dip in the PES in the vicinity of the activated state. Transition state theory (TST)[16−18] typically assumes only the latter case because any activated complex located at a saddle point would necessarily require a (low energy) imaginary vibrational frequency to dissociate it[19].

First-Order Dispersive Kinetic Model Based On Fractal Time. Plonka[1,4,20−22] has described/reviewed extensively the dispersive kinetics literature that introduces the concept of fractal time via the use of the Kohlrausch−Williams−Watts (KWW) relaxation function, $\Phi(t)$:

$$\Phi(t) = \mathrm{e}^{(-t/\tau)^n} \tag{9}$$

where n and τ are constants; τ is a so-called time constant and $0 < n \leq 1$ (note: for $n = 1$, a time-independent, classical, rate constant is obtained, as one can consider τ to be inversely related to k). Equation 9 can be thought of as a superposition of first-order exponential decays with a probability density defined by a function, $g(\tau)$; it is this superposition that gives the overall appearance of a stretched exponential.

Equation 9 has been used analogously[20] to eq 1/eq 5 to derive dispersive kinetic model variants[7] of the classical[12] first-order (F1) and second-order (F2) models. Like the author's F1-based dispersive models presented earlier (eqs 3 and 4) only the F1 dispersive variant, based on eq 9, will be discussed here (note: the author's dispersive models for other conversion mechanisms are provided elsewhere[7]).

Defining a time-dependent rate coefficient having the form:[20]

$$k(t) = Bt^{n-1} \tag{10}$$

where B and n are constants ($0 < n \leq 1$; $B \equiv n/\tau^n$), the Arrhenius equation can be used together with eq 10 to obtain an expression for the time-dependent activation energy, $E_a(t)$, of the process:[15]

$$E_a(t) = E_a^0 + (1-n)RT\ln\left(\frac{t}{\tau}\right) \tag{11}$$

For a classical F1 mechanism, the dispersive variant describing the overall conversion is given by:[20]

$$x = \mathrm{e}^{-(t/\tau)^n} \tag{12}$$

and the activation energy distribution function, $f(E_a)$, can be written as:[20]

$$f(E_a) = \mathrm{e}^{\{-e^{[n(E_a-E_a^0)/(1-n)RT]}\}} \tag{13}$$

Note that eq 12 is often referred to as the Johnson−Mehl−Avrami−Erofe'ev (JMAE) equation,[23−27] for specific values[7,12] of n; it finds wide application in solid-state kinetics involving nucleation and growth. Unfortunately, the values of n (a unitless parameter) obtained through curve-fitting of experimental data are not always aligned with existing theory. Nonetheless, given the differences in the definitions of $k(t)$ between eq 1/eq 5 and eq 10, that yield very different corresponding dispersive kinetic models (i.e., eqs 3 and 4 versus eq 12) and ultimately give rise to the differences that can be observed between the author's eq 7 and eq 8, relative to eq 13, it might be useful to try to evaluate the accuracy of the two approaches. As both sets of F1 dispersive kinetic models have already been shown to be useful in the modeling of various experimental $x-t$ transients, a comparison of the two approaches on a more fundamental level might be prudent.

Comparison of the Two Dispersive Kinetic Approaches Using Marcus Theory. From the standpoint of comparing the two types of dispersive kinetic approaches presented here, it might be useful to employ the Marcus theory[28] to provide a physicochemical basis for the comparison, considering a simple, F1-type, chemical reaction mechanism (e.g., one that involves proton/electron transfer). Along these lines, the author has recently proposed a time-dependent Marcus theory (TDMT), for application to dispersive kinetics.[29] On the basis of that earlier work, it was concluded that the variation in the activation energy of dispersive processes might be linked to a time-dependent reorganization energy, $\lambda(t)$. With consideration of the schematic in Figure 1, the author's expression for $E_a(t)$, based on TDMT, can be written as:

$$E_a(t) = \frac{\lambda(t)}{4}\left[1 + \frac{\Delta G_r}{\lambda(t)}\right]^2 \qquad (14)$$

where ΔG_r is the standard Gibbs free energy of reaction. In Figure 1, both the reagent and the product Lennard-Jones potentials can be well-approximated by simple parabolas.[28] The work needed to move the reactants and products from their equilibrium positions on the reaction coordinate to an intermediate point where the two curves intersect defines the activation energy needed to form the (short-lived) transition state, TS, species (note: in Figure 1, the term TS is replaced by a more general one, the activated state, AS, which might be more useful for describing dispersive solid-state phase transformations, e.g., where the higher energy levels pertaining to the rate-determining step are those of the product nuclei[3,8]).

If one correlates the change in $\lambda(t)$ to a variation in the time-dependent energy component of the overall activation energy barrier,[8,29] for various molecules undergoing conversion, different molecules can be considered to convert with different specific reaction rates (i.e., rate coefficients). For this reason, dispersion in the activation energy of the process can be observed, as was discussed earlier. With the aid of Figure 1, this dispersion might be interpreted as molecular-level variations in the rate at which the AS is formed.

While the abscissa in the schematic is traditionally labeled the reaction coordinate, Figure 1 actually depicts the potential energy (E_{PE}) profiles of two independent, simple harmonic oscillators (SHOs) as a function of their displacement. It is common knowledge that $E_{\mathrm{PE}} = (1/2)\xi d^2$, where ξ is the force constant (related to the bond strength) and d is the atomic displacement of the oscillator. However, for a given SHO, E_{PE} and the kinetic energy, E_{KE}, continuously interconvert, out of phase with each other in time (note: the total energy is fixed and independent of motion). Thus, one can describe the system in Figure 1 equally well in terms of either kinetic energies or potential energies, as a function of d; over a region of d where E_{PE} is a concave-up parabola (as shown in the figure), E_{KE} for that same SHO will be concave-down, that is, complementary in shape (not shown).[30] If one considers that displacement is related to time via the function $\cos(\omega t)$, where ω is the angular frequency, the energies trend is a function of $\cos^2(\omega t)$ or $\sin^2(\omega t)$. The parabolic energy profiles shown in the figure (E_{PE}) can be shown to be well-approximated by these squared trigonometric functions, since, as pointed out by a reviewer, both the sine-squared and the parabolic functions are monotonically increasing (through the first turning point for the trigonometric function) and they are directly proportional at lower displacements (that are of primary interest in this work because they are far from the bond dissociation energies). For this reason, the horizontal axis in Figure 1 might also be considered the conversion time; this idea is depicted in the abscissa label of the schematic. Note that regarding the author's parabolic approximation for the dependence of $E_a(t)$ on the conversion time (discussed more later), it should not be seen as problematic that, according to eq 6, the energy profile can be either concave-up or concave-down since that same behavior can be observed for the classical case of the SHO energy dependence on displacement, as mentioned above (i.e., depending on whether the energy under consideration is potential or kinetic, respectively).

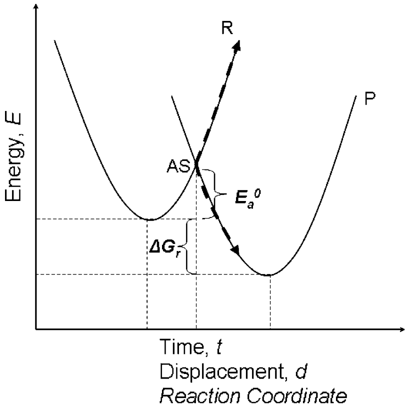

Figure 1. Schematic (potential) energy versus reaction coordinate diagram for a hypothetical first-order (F1) reaction, of the variety studied by Marcus. **R** denotes the reagent energy parabola, **P** is the product energy parabola. All other terms are defined in the text. The thin broken lines show the coordinates of the equilibrium positions of **R**, **P**, and **AS**. The thick broken lines depict trends in the activation energy versus time profiles of various dispersive processes; the activation energy can either increase or decrease with time over the course of conversion, as a function of t^2 (see text for details).

To summarize, the distribution of speeds at which different molecules achieve the AS creates dispersion in the activation energy barrier, ultimately resulting in a distribution of activation energies, that is, $f(E_a)$. It was shown earlier how $f(E_a)$ and $E_a(t)$ might be related. On the basis of the above discussion, one can consider that, for small displacements, the time-dependence of the oscillator energies in Figure 1 can be approximated as being parabolic. Thus, the remaining goals of this work are twofold: first, to see whether eq 6 or eq 11 does a better job of explaining the $E_a(t)$ versus t trends that can be inferred from Figure 1, and second, to utilize the more appropriate of those two equations to derive a new, physicochemically significant expression for $\lambda(t)$, with the aid of eq 14.

By considering eqs 6 and 11, it is clear that the former equation explains the $E_a(t)$ versus t trends highlighted in Figure 1 best, because of the fact that it has a t^2 dependence. On the other hand, in the author's experience, a logarithmic function, as per eq 11, cannot be used to satisfactorily approximate the time-dependence of the SHO energies (either periodic or when approximated as being parabolic) over any range of displacements.

According to eq 6, one can see that by starting at E_a^0 at $t = 0$ (i.e., the classical Arrhenius/Eyring definition of the activation energy potential), the time-dependent activation energy barrier for dispersive processes can either increase with time (for deceleratory processes, those that have a negative β value, according to the model given by eq 3) or decrease with time (for acceleratory conversions, those that have a positive β value, according to the model given by eq 4) as depicted by the two thick, broken lines in the graphic. For deceleratory dispersive processes, the dispersion in the activation energy has been shown elsewhere[8] to be attributable to potential energy differences associated with the reagent population (e.g., crystals used in a denucleation rate-limited thermal decomposition), that cause an increase in E_a with conversion time. Conversely, for dispersive kinetics exhibiting accelertory sigmoid $x-t$ trends, it can be seen from Figure 1 that the decrease in the activation energy is attributable mainly to potential energy variations in the product species (e.g., nuclei, in nucleation rate-limited processes); a finding that is also supported by the author's previous works.[3,8] Note that the latter effect is distinct from the so-called Marcus inverted region which, for very exothermic reactions, relates an increase in the activation energy/decrease in reaction rate with increasing thermodynamic driving force.[28]

An alternative description of the $E_a(t)$ versus t trends depicted in Figure 1 involves a discussion of the kinetic, rather than potential, energies. In deceleratory conversions (e.g., homogeneous reactions), the reagent molecules with the highest kinetic energies are first to undergo conversion. Conversely, in acceleratory conversions, such as nucleation, it is the slowest molecules that are most likely to first form critical nuclei. Thus, in dispersive kinetics, it is possible to describe activation energy trends in terms of both kinetic and potential energies. The link between these two descriptions might be the rate parameter, β, which provides a fundamental connection between the molecular-level kinetic energies and the time-dependent change in the overall activation entropy[5] of the conversion.

In eq 6, β can be considered to be a shape factor that serves to describe the parabolas shown in the figure (the derivation of eq 14 assumes that the shapes of the two parabolas are identical). In previous work, β was discussed to be instrumental in describing the shape of the activation energy distribution for dispersive processes.[7,8] Additionally, as mentioned above, this parameter can describe the stochastic change in the activation entropy as molecules transition over the activation energy barrier, during the course of conversion. As an aside, it has been shown that the second fit parameter in the author's dispersive models, α, relates both E_a^0 and the frequency factor found in classical Arrhenius kinetic treatments.[8]

Equating eq 6 and eq 14, we found it possible to derive the following relation (utilizing the quadratic formula):

$$\lambda(t) = -\Delta G_r + 2(E_a^0 - RT\beta t^2) \pm 2\sqrt{(E_a^0 - RT\beta t^2)(E_a^0 - RT\beta t^2 - \Delta G_r)} \quad (15)$$

Equation 15 can be expressed equivalently as:

$$\lambda(t) = -\Delta G_r + 2(E_a^0 - RT\beta t^2) \pm \sqrt{[\Delta G_r - 2(E_a^0 - RT\beta t^2)]^2 - \Delta G_r^{\,2}} \quad (16)$$

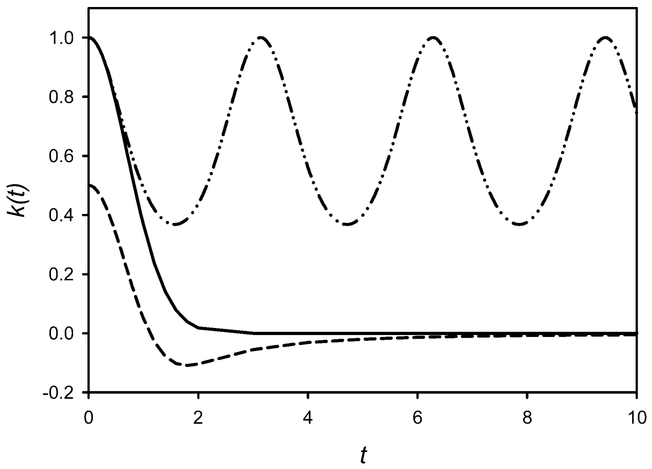

Figure 2. Plot of the functions: $k(t) = e^{-\sin^2(t)}$ (dashed-dotted line, top), $k(t) = e^{-t^2}$ (solid line, middle), and $k(t) = (2t^2)^{-1}(e^{-t^2} - 1) + e^{-t^2}$ (dashed line, bottom) as a function of t, over the interval $0 \le t \le 10$.

Both eq 15 and eq 16 yield appropriate units for energy (note: β has units of time^{-2}). However, as for eqs 7 and 8, there exists the possibility for $\lambda(t)$ to be complex. Nonetheless, on the basis of its ability to accurately relate TDMT, for smaller SHO displacements, the author's dispersive kinetic approach is believed to possess an advantage over the other treatment described in this work.

On the Nature of the Time-Dependence of the Rate Coefficient in Dispersive Kinetics. Utilizing TDMT to describe the behavior of the time-dependent portion of the activation energy, disregarding the author's parabolic approximation, eq 1, one can derive the following expression for $k(t)$:

$$k(t) = \alpha e^{-\beta \sin^2(\omega t)} \quad (17)$$

where ω is the angular frequency; the constant, β, has units of energy, rather than time^{-2}. Note that eq 17 relates specifically to deceleratory dispersive conversions, but a complementary expression can be derived to describe acceleratory processes (not discussed in this section).

From the plots shown in Figure 2 (where it is assumed that $\alpha = \beta = \omega = 1$, for simplicity), it can be seen that eq 5 serves as a good compromise between eq 1 and eq 17, for short, t.

It should be highlighted that the direct integration of eq 17 is problematic, even more so than eq 1. Thus, a simple kinetic model based on eq 17 does not seem feasible. Furthermore, it is not realistic to expect that all (deceleratory) dispersive reactions are oscillatory; rather, $k(t)$ should tend toward zero as $t \to \infty$ for most systems, consistent with eqs 1 and 5. Only on the atomic/bond level, that is, on the femtosecond time-scale for gas-phase reactions, can one routinely observe such oscillations. However, these oscillations typically appear damped in cases like that of NaI (which survives for more than one oscillation following excitation). The oscillations can significantly affect the shapes of experimentally obtained $x-t$ transients.[31] As a complementary view to representing a manifestation of both covalent and ionic bonding character, these oscillations can be considered to be a natural outcome of TDMT.

Conclusion

This work demonstrates that the use of a Maxwell–Boltzmann activation energy distribution to define a time-dependent rate coefficient having an approximately Gaussian functional form can yield dispersive kinetic models that, in addition to successfully modeling conversion kinetics in various real-world systems, can relate a time-dependent activation energy that varies (approximately) as a function of t^2. Using a simple extension of Marcus theory, this time-dependence of the activation energy variation was able to be supported for lower SHO displacements and shorter values of t. Finally, a new, physicochemically relevant description of the time-dependence of the reorganization energy was developed.

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