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Implications of Berthelot's Description of Associative Reactions

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Abstract

Berthelot's equation, $k_{\infty}(T) = A_{\infty} \exp\{-Dk_B T\}$, provides a good description of the high-pressure rate coefficient for associative reactions such as $CH_3 + CH_3$, $CH_3 + OH$, and $CH_3 + H$. The parameter D may be used to characterize an effective temperature-dependent barrier, $\Delta E_{eff} = Dk_B^2 T^2$, which is due to the internal energy, i.e. rotational and vibrational energy, or the centrifugal barrier of the associating species. The parameter A_{∞} may be identified as the rate coefficient for association when the species approach one another with zero translational and internal energy. A microcanonical rate expression is given which may be used to directly compare experimental results with theoretical calculations. In addition, this approach suggests that the Arrhenius expression for the high-pressure rate coefficient for dissociation should contain both the change of enthalpy of the reaction and this effective barrier.

I. INTRODUCTION

Recently, we noted that the high-pressure rate coefficient for methyl-methyl recombination[1] may be described by Berthelot's equation, $k_{\infty}(T) = A_{\infty} \exp\{-Dk_B T\}$, rather than the modified Arrhenius expression, $k_{\infty}(T) = A_{\infty} T^m \exp\{-\Delta E/k_B T\}$. This observation is consistent with theoretical calculations[2] and has been found[3] to also hold for $CH_3 + OH \rightarrow CH_3OH$

and $H + CH_3 \rightarrow CH_4$. All of these associative reactions proceed on a potential-energy surface which is barrierless. To be as useful as the Arrhenius expression is for reactions which proceed over a barrier, physical significance must be attached to the parameters A_∞ and D in Berthelot's equation. Here, Laplace transforms are used to calculate the microcanonical rate constant. The parameter D may be used to characterize an effective barrier which is a function of temperature, $\Delta E_{eff} = Dk_B^2 T^2$. This barrier is due to the energy within the associating species. Molecules which approach one another with a translational energy which is below the height of this barrier will not form a complex and therefore, may not be stabilized. The parameter A_∞ is identified as the rate coefficient for association when the species approach one another with zero internal and translational energy. These results have implications for a description of associative reactions. The microcanonical rate constant may be used to compare directly experimental observations with theoretical calculations. In addition, a microcanonical rate coefficient for dissociation has also been derived.

II. DERIVATION

The general equation for a temperature-dependent rate coefficient, $k(T)$, in terms of an energy-dependent reactive cross section[4] is given by

$$k(T) = \left[\frac{8}{\pi \mu (k_B T)^3} \right]^{1/2} \int_0^\infty \epsilon_t \sigma(\epsilon_t) \exp(-\epsilon_t/k_B T) d\epsilon_t$$

where the reduced mass of the reacting species is μ , Boltzmann's constant is k_B , the translational energy in the center-of-mass reference frame is ϵ_t , and the reactive cross section as a function of this energy is $\sigma(\epsilon_t)$. The temperature-dependent rate coefficient is the Laplace

transform[5] of $\varepsilon_t \sigma(\varepsilon_t)$. From a table of Laplace transforms one notices that if

$$\varepsilon_t \sigma(\varepsilon_t) = \frac{A}{\sqrt{\pi D}} \sin 2\sqrt{D\varepsilon_t}$$

then

$$k(T) = A\sqrt{\frac{8}{\pi\mu}} \exp(-Dk_B T).$$

The prefactor $A\sqrt{8/\pi\mu}$ may be identified as A_∞ in Berthelot's equation. Therefore, the reactive cross section is given by

$$\sigma(\varepsilon_t) = A_\infty \sqrt{\frac{\mu}{8\varepsilon_t}} \frac{1}{\sqrt{D\varepsilon_t}} \sin 2\sqrt{D\varepsilon_t}$$

and the microcanonical rate constant, $k(\varepsilon_t)$, is

$$k(\varepsilon_t) = \frac{A_\infty}{2} \frac{1}{\sqrt{D\varepsilon_t}} \sin 2\sqrt{D\varepsilon_t}.$$

For completeness, the prefactor in the above equation may be converted to the inverse of the translational partition function and, thereby, obtain a density of states, $\rho(\varepsilon_t)$, which is given by

$$\rho(\varepsilon_t) = \frac{4\sqrt{2}\pi\mu^{3/2}}{h^3} \sqrt{\varepsilon_t}$$

where h is Plank's constant. Note, this is the density of states per unit volume which is consistent with the dimensionality of the translational partition function.

Although the above description is mathematically correct, the oscillatory behavior of the cross section and microcanonical rate constant is not physical. To obtain a physically significant description, van't Hoff's equation[6] is written in modern notation as

$$k_\infty(T) = A_\infty T^m \exp \left[- \left(\Delta E + Dk_B^2 T^2 \right) / k_B T \right].$$

Here, the height of the barrier to the reaction is ΔE and the sign preceding the parameter D has been changed to be consistent with our experimental observations. Also, for simplicity Boltzmann's constant has been explicitly included. For convenience, let

$$E' = \Delta E + Dk_B^2 T^2.$$

Again, from a table of Laplace transforms one notes that if

$$\varepsilon_t \sigma(\varepsilon_t) = A \frac{(\varepsilon_t - E')^{\nu-1}}{\Gamma(\nu)} u(\varepsilon_t - E'),$$

where the unit step function is $u(\varepsilon_t - E')$, the gamma function is $\Gamma(\nu)$, and $\nu > 0$, then

$$k_\infty(T) = A \sqrt{\frac{8}{\pi\mu}} (k_B T)^{\nu-3/2} \exp[-E'/k_B T].$$

If we identify $A\sqrt{8/\pi\mu}$ as the prefactor A_∞ and $\nu-3/2$ as m , we obtain van't Hoff's complete equation. If we set $\nu = 3/2$ and $\Delta E = 0$ we, again, obtain Berthelot's equation. In particular, Berthelot's equation is also the Laplace transform of

$$\varepsilon_t \sigma(\varepsilon_t) = A \frac{(\varepsilon_t - Dk_B^2 T^2)^{1/2}}{\Gamma(3/2)} u(\varepsilon_t - Dk_B^2 T^2).$$

Following the same line of reasoning as above, a temperature-dependent microcanonical rate constant may be written

$$k(\varepsilon_t, T) = A_\infty \left(1 - \frac{Dk_B^2 T^2}{\varepsilon_t}\right)^{1/2} u(\varepsilon_t - Dk_B^2 T^2)$$

where $\Gamma(3/2) = \frac{1}{2}\sqrt{\pi}$ has been used to simplify the expression. The density of states function will be the same as above.

At first, it may appear incongruous to have a microcanonical rate constant which depends upon temperature. This may be rationalized if the temperature in the above expression is

assumed to be a measure of the internal energy of the associating species, i.e. the energy contained in the rotational and vibrational modes of the species. Under equilibrium conditions this temperature will be equal to the bath temperature. However, one may envision beam experiments where the internal energy is low and the translational energy high as well as experiments with species which have large amounts of internal energy while approaching one another at low translational energies. Under these conditions one would replace temperature in the above equation with the internal temperature, T_{int} , of the species. If the energy distribution within the species could not be described by a temperature, the expression for the microcanonical rate would be more complex.

To assign physical significance to the parameters A_∞ and D the dependence of the microcanonical rate constant on translational energy and "internal" temperature must be considered. First, consider the limit of low internal energy, $T_{int} \rightarrow 0$. Then,

$$k(\varepsilon_t, T_{int} \rightarrow 0) = A_\infty.$$

In the high-energy limit, $\varepsilon_t \rightarrow \infty$,

$$k(\varepsilon_t \rightarrow \infty, T_{int}) = A_\infty.$$

Therefore, the prefactor A_∞ is a measure of the rate of association of the species when they approach one another with zero translational and internal energy and is the upper bound of the rate for all values of internal energy. The parameter D characterizes a temperature-dependent barrier

$$\Delta E_{eff} = Dk_B^2 T_{int}^2$$

which is due to the internal energy of the species. Since this is a barrier, species which

approach one another with translational energies below this critical energy will not be able to overcome the barrier and, therefore, will not form complexes.

These ideas may be extended to the dissociative process. To accomplish this we simply retain the ΔE term in van't Hoff's equation. Therefore,

$$k_{diss}(\varepsilon_t, T) = A_\infty \left(1 - \frac{\Delta E + Dk_B^2 T^2}{\varepsilon_t} \right)^{1/2} u(\varepsilon_t - (\Delta E + Dk_B^2 T^2)).$$

Here, we see that in dissociation there is also an additional barrier. To be consistent with the above derivation this additional barrier must be due to energy in the nondissociative modes of the molecule. Simply stated, energy in modes other than the dissociative mode hinders dissociation and, therefore, may be expressed as an additional barrier to dissociation.

The negative temperature dependence of associative reactions is not universally accepted.[7] Therefore, it is instructive to investigate the implications for a rate coefficient which increases with temperature. For a simple discussion, one only has to change the sign of the parameter D . Therefore, the internal energy of the associating species would effectively reduce the already none existing barrier to association. This behavior would correspond to situations where some internal modes enhance association. These situations can not be ruled out. An alternate approach is to note that if

$$\varepsilon_t \sigma(\varepsilon_t) = \frac{A}{\sqrt{\pi D}} \sinh 2\sqrt{D\varepsilon_t}$$

then

$$k(T) = A \sqrt{\frac{8}{\pi \mu}} \exp(+Dk_B T).$$

Therefore,

$$k(\varepsilon_t) = \frac{A_\infty}{2} \frac{1}{\sqrt{D\varepsilon_t}} \sinh 2\sqrt{D\varepsilon_t}.$$

Here, in the low energy limit of $\varepsilon_t \rightarrow 0$, $k(\varepsilon_t) = A_\infty$ and in the high energy limit the microcanonical rate constant diverges. This divergence implies that as the translational energy increases the probability of forming a complex and stabilizing it increases. This appears to go against physical intuition. One would think that at very high translational energies only the high inner repulsive barrier will be significant. At these energies, the species may exchange internal energy but it will be very difficult to form a complex and stabilize it. Therefore, this alternate model is not physical.

III. NUMERICAL EXAMPLE

To illustrate the above ideas the microcanonical rate constant for methyl-methyl recombination has been calculated. For convenience, it is written

$$k_{assoc}(\varepsilon_t, T_{int}) = A_\infty \left(1 - \frac{Dk_B T_{int}^2}{\varepsilon_t/k_B} \right)^{1/2} u \left(\frac{\varepsilon_t}{k_B} - Dk_B T_{int}^2 \right)$$

Therefore, the translational energy may be given in degrees Kelvin. For this example the parameters calculated from Oref's formulation of the pressure dependence of the recombination rate coefficient[1] are used: $A_\infty = 8.78 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $Dk_B = 1.38 \times 10^{-3} \text{ K}^{-1}$. These parameters were obtained by fitting experimentally measured pressure-dependent rate coefficients which covered the temperature range from 296 to 1800 K. In figure 1, the translational-energy dependent microcanonical rate constant is shown for three different value of internal energy, $T_{int} = 30, 300, \text{ and } 1000 \text{ K}$. For each of these the effective barrier heights are 1.25, 125, and 1383 K, respectively.

IV. DISCUSSION

The derivation presented above provides a physical interpretation of the parameters obtained when the temperature-dependent behavior of the high-pressure limit of associative reactions can be described by Berthelot's equation. The derivation is semi-classical; translational motion is treated classically and the details of the interaction of the associating species is introduced by a single effective parameter. Thermal rate coefficients simply do not contain any direct information about the structure of the reacting species. Therefore, we have been forced to contain all of this information in a single term, $Dk_B^2 T_{int}^2$. The microcanonical rate constant obtained from this derivation depends both on the internal energy of the associating species and their translational energy. This rate constant may be considered an alternate description of the experimental data since it is related to the temperature-dependent rate coefficient through the Laplace transform. Therefore, it can then be used to compare experimental results to theoretical calculations such as the flexible transition state calculations[8] of Wardlaw and Wagner and it may be used as a starting point in master equation calculations[9] of behavior in the falloff region.

Although it is not possible to assign a unique source to the effective barrier it is important to point out that the amplitude of this barrier may be correlated with an average centrifugal barrier. Another question one may ask is, what is the relationship of this effective barrier to the transition state in flexible transition state calculations? It is hoped that this work will motivate additional questions, detailed calculations of the effective barrier, and additional comparisons with experimental data.

This article represents an attempt to answer a question posed by Michael J. Pilling

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Figure Captions

Figure 1. Microcanonical rate constant as a function of translational energy, ε_t/k_B , for the association of methyl with methyl to form ethane. Internal energies given by $T_{int} = 30$, 300, and 1000 K are shown. See the text for parameters.