On the phenomenon of variable activation energy for condensed phase reactions

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Various effects that liquid and solid media produce on the experimental activation energy of a reaction involving a single chemical step are discussed. The effects are experimentally observed as significant variations in the activation energy with temperature or extent of reaction. Since these phenomena are inconsistent with the concept of a constant activation energy, that of variable activation energy is considered as an alternative. The discussion covers the kinetics of such processes as electron transfer, liquid phase polymerization, desorption from solids, and solid state decomposition.

Introduction

A constant activation energy is usually the anticipated outcome of kinetic evaluations. This expectation appears to be supported by theoretical reasoning. The Arrhenius equation, eqn. (1),

$$k = A \exp(-E/RT) \quad (1)$$

where E is the activation energy (the heat of activation), A the preexponential factor, T the temperature, R the gas constant, materializes Arrhenius' hypothesis[1] that normal (*i.e.* inactive) molecules are in an endothermic equilibrium with active ones, which take part in the reaction. According to Arrhenius, E is the heat absorbed in the process of transformation of inactive molecules into active ones, or, in other words, the heat (or energy) of activation. Owing to its thermodynamic meaning, E was treated[1,2] as a constant that is independent of the pathway taken by a system from an initial to a final state. Van't Hoff[2] expected only a minor temperature dependence of the activation energy as a result of the temperature dependence of the heat capacity.

Later, collision theory[3,4] and activated-complex theory[5] introduced the idea of an energy barrier that has to be crossed over for a reaction to occur. From the standpoint of these theories, Arrhenius' activation energy is a parameter that is directly related to the height of the energy barrier. Unlike the Arrhenius theory, collision theory and activated-complex theory treat the activation energy as a truly kinetic (dynamic) parameter, which is associated with the reaction act itself. However, similar to Arrhenius theory, these theories treat the activation energy as an essentially constant parameter of a reaction system.[6] These theoretical considerations led to the formation of the concept of constant activation energy, which seems to be a very reasonable approximation for the gas phase where chemical transformations take place by a series of isolated binary collisions of molecules. However this concept also appears to dominate the interpretation of condensed (*i.e.* liquid and/or solid) phase kinetics which is unavoidably affected by the physical properties of the reaction medium.

Liquid phase reactions have demonstrated significant variations in activation energy since the time of the earliest kinetics measurements. The first systematic kinetic study was conducted in 1850 by Wilhelmy,[7] who measured the rate of the inversion of cane sugar in the presence of acids. It appears to be rather symbolic that for this incipient process Moelwyn-Hughes[8] found the activation energy to vary with temperature as in eqn. (2).

$$E = 193789 - 1019.53T + 1.52171T^2 \quad (2)$$

This dependence is plotted in Fig. 1 for the temperatures used in Moelwyn-Hughes' experiments. A more profound variation of the activation with temperature can be observed (Fig. 2) for data reported by van't Hoff[2] for the reaction between sodium chloracetate and sodium hydroxide. Obviously, detecting small systematic variations in E imposes high requirements on the accuracy of kinetic measurements, which usually are subject to significant random errors.[9] For instance, in Fig. 2 each rate constant was estimated as an average of 3–6 experiments[2] which assures the statistical soundness of the observed variation.

The temperature variation of the activation energy has always been a topic of considerable interest among kineticists. Hulett[10] published a short review, which appears to be the

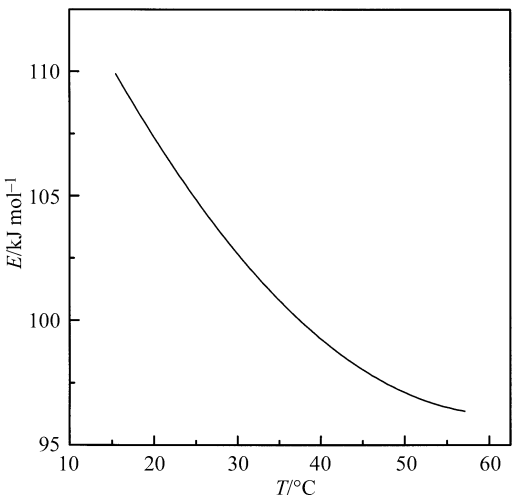

Fig. 1 Temperature variation of the activation energy for the inversion of cane sugar, as reported by Moelwyn-Hughes.[8]

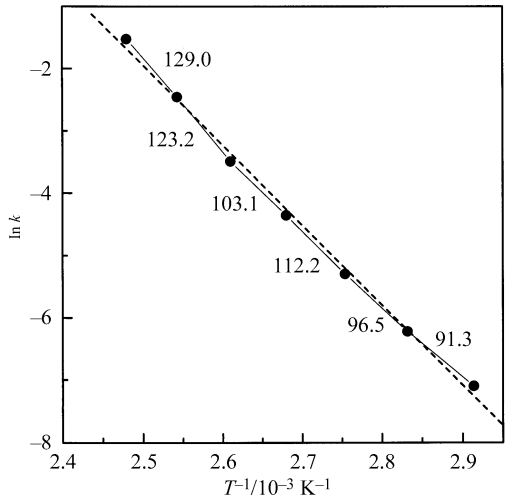

Fig. 2 Arrhenius plots for the reaction between sodium chloracetate and sodium hydroxide (circles). Numbers next to linear segments represent respective values of the activation energy in kJ mol^{-1}. The dashed line represents the least squares fit.

first attempt to systematize the effects causing deviations from the Arrhenius law. The major focus of his work was on quasi-thermodynamic (temperature dependence of the heat capacity of activation) and quantum-mechanical (tunneling) effects, whereas the effects of the reaction medium (dielectric properties and viscosity) were only briefly mentioned. A more recent review by Perlmutter-Hayman[11] comprehensively covers the quasi-thermodynamic effects and those caused by various multi-step mechanisms (concurrent, reversible, and consecutive reactions). Both reviews are primarily concerned with liquid and gas phase kinetics. The current paper discusses the effects of the reaction medium on the activation energy of liquid and solid phase reactions. The discussion is focused on the experimental activation energy, which is estimated from the temperature dependence of the reaction rate. By its nature, the experimental activation energy is an effective value, which may vary significantly over a small temperature region. These variations appear prevalently to be explained by simultaneous occurrence of two or more single-step reactions having their own constant activation energy.[4] Needless to say, this explanation does not contradict the concept of constant activation energy.

On the other hand, variation of certain physical properties of the reaction medium may cause the activation energy to vary significantly, even for reactions that involve a single chemical step. Such effects are obviously inconsistent with the concept of constant activation energy. This paper considers several effects, which are observed for fundamentally different processes such as electron transfer, liquid state polymerization, reactions of radicals in solids, solid–gas reactions, and are primarily known to the kinetic experts working in the respective fields. Usually, these effects are not discussed explicitly even in advanced kinetics texts, and, therefore, they largely escape the attention of the general chemical audience. I, therefore, hope that this paper will provide the "non-kineticist" with a helpful introduction to the phenomenon of variable activation energy.

Liquid phase

For reactions of ions and/or polar molecules the reaction rate depends on the dielectric properties of the solvent.[12] The effect is treated by both collision theory[8] and activated-complex theory.[5] For instance, the latter suggests that the rate constant of reaction between two ions is given by eqn. (3),

$$\ln k = \ln k_0 - \frac{z_A z_B e^2}{\varepsilon d_{AB} k_B T} \quad (3)$$

where e is the electronic charge, z_A and z_B are the numbers of charges on the ion, ε is the dielectric constant (relative permittivity) of the medium, d_{AB} the distance between the centers of the ions in the activated state and k_B the Boltzmann constant. The activation energy determined from the Arrhenius plot includes the dielectric constant [eqn. (3)], whose temperature variation causes a variation in the activation energy.[5]

The kinetics of electron transfer reactions is largely determined by the medium (solvent). According to Marcus theory,[13] the rate constant is given by eqn. (4),

$$k = A \exp(-\Delta G^{\ddagger}/k_B T) \quad (4)$$

where the free energy of activation, $\Delta G^{\ddagger}$, is a function of the equilibrium free energy gap, ΔG°, and the reorganization energy, λ, which is the sum of the intramolecular vibrational reorganization energy, λ_v and the solvent reorganization energy, λ_s. The latter is usually estimated by representing the medium as a dielectric continuum.[13] For highly polar solvents, this treatment predicts λ_s to increase moderately with the temperature, whereas experimental measurements demonstrate a significant decrease.[14] The negative temperature dependence is adequately described by molecular theory,[14] which also correctly predicts the experimentally measured decrease in ΔG°. Molecular theory has been developed to describe electron transfer reactions in weakly polar[15] and non-polar[16] media. For weakly polar media, Matyushov[15] has found that the temperature dependence of the translational portion of λ_s may give rise to strongly non-linear Arrhenius dependencies (Fig. 3). A similar effect has been predicted by Matyushov and Schmid[16] for non-polar media. Experimental studies by Read *et al.*[17] have demonstrated a significant increase in the free energy of activation for charge separation in both weakly polar and non-polar media.

An important advancement in understanding of condensed phase kinetics is given by Chandler and co-workers.[18] For reaction systems that involve large polyatomic molecules or large clusters containing solvent, co-operative motion among condensed phase molecules gives rise to multiple saddle points

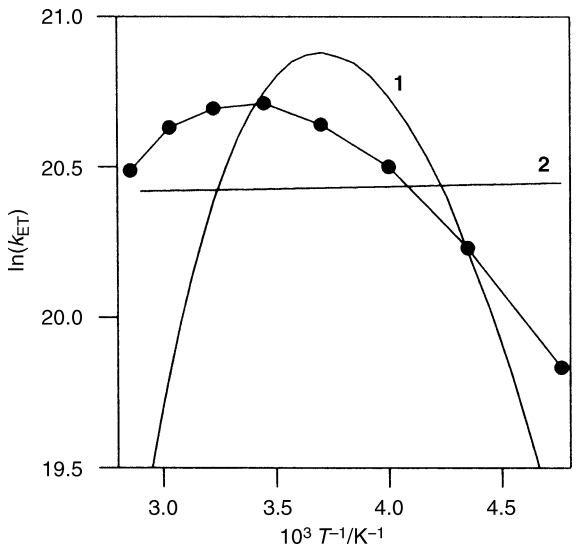

Fig. 3 Temperature variation of the electron transfer rate constant in butyl acetate measured experimentally (circles) and calculated by the molecular (1) and dielectric continuum (2) theories. Curve 2 has been shifted downward by 8 units of $\ln(k_{ET})$. Reprinted from ref. 15, copyright 1996, with permission from Elsevier Science.

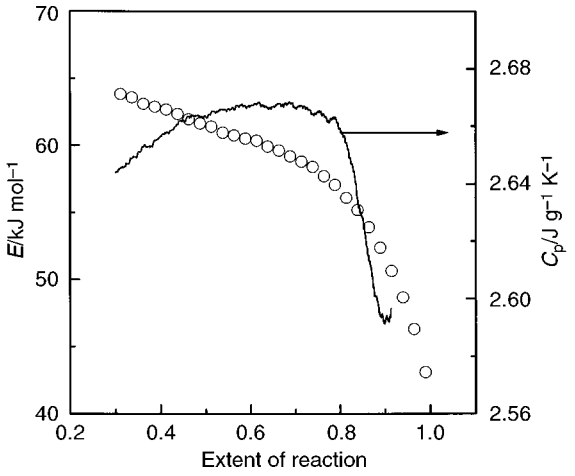

Fig. 4 Activation energy (circles) for epoxy-amine copolymerization.[31] The decrease in the complex heat capacity (C_p) indicates (solid line) vitrification of the reaction system.

on the potential energy surface.[18] In this situation, the reaction kinetics are determined by an ensemble of numerous transition states of different energy. The transition path sampling method is proposed[18] to locate and sample an ensemble of transition states.

Depending on its mechanical properties, the reaction medium may impose transport limitations on the reaction rate. Neither collision theory nor activated-complex theory directly accounts for the mechanical properties of the medium. The effect is treated by Kramers' theory,[19] which introduces the viscosity of the medium as a crucial kinetic factor. In the case of a large viscosity, the theory suggests that the rate constant is given by eqn. (5),

$$k = k_{ac}\,\kappa(\eta) \tag{5}$$

where k_{ac} is the activated-complex theory rate constant, $\kappa(\eta)$ is a term that accounts for the effect of the generalized viscosity on the reaction rate. Schroeder and Troe[20] have extensively tested the effect over the entire range of applicability of Kramers' theory. Generally, they observed that k on η dependencies are strongly non-linear and, in certain cases, may even be bell-shaped.[20] This obviously suggests the effective activation energy to be a function of viscosity as well as of temperature, because the latter is a factor affecting viscosity.

Although activated-complex theory does not account for the diffusion effect of a viscous medium on the reaction rate, the effect can be accounted for by using the so-called law of the addition of kinetic resistances.[21] The idea appears originally to have been developed by Fischbeck[22] to describe the overall rate of gas–solid reactions. By defining the reaction rate as a ratio of the "driving force" to the "reaction resistance", Fischbeck[22] suggests that the overall reaction rate is determined by the total resistance which is the sum of the reaction and diffusion resistances, W_r and W_d respectively, eqn. (6).

$$W = W_r + W_d \tag{6}$$

In this model the resistances are, in fact, the characteristic times of respective processes. For liquid state kinetics, a similar idea was later put forward by Rabinowitch,[23] who proposed that the effective characteristic time of a process should be defined as the sum of the characteristic time of a chemical reaction and the characteristic time for reactants to diffuse in the reaction medium. In the Rabinowitch model the characteristic times are replaced with the reciprocal rate constants, eqn. (7),

$$k_{ef}^{-1} = k^{-1} + k_d^{-1} \tag{7}$$

where k_{ef}, k and k_d respectively are the effective, reaction and diffusion rate constants. Because diffusion occurs as a succession of molecular jumps between the neighboring equilibrium positions, the characteristic time of the jump (k_d^{-1}) can be approximated by Debye's relaxation time,[24] eqn. (8),

$$\tau = (4\pi a^3\eta/k_B T) \tag{8}$$

where a is the molecular radius. Eyring's theory of viscosity[25] gives rise to an Arrhenius type of temperature dependence, eqn. (9),

$$\eta = \eta_0 \exp(E_\eta/RT) \tag{9}$$

where E_η is the activation energy of the viscous flow and η_0 the pre-exponential factor. Substitution of eqn. (9) into eqn. (8) allows one to introduce the diffusion rate constant in the form of eqn. (10)

$$k_d = C \exp\left(\ln T - \frac{E_\eta}{RT}\right) \tag{10}$$

where C is the pre-exponential factor. From eqn. (10) one easily finds a link between the activation energies of diffusion and viscous flow, eqn. (11).

$$E_d = -R\left(\frac{\mathrm{d}\ln k_d}{\mathrm{d}T^{-1}}\right) = E_\eta + RT \tag{11}$$

If RT is much smaller than E_η, E_d is practically equal to E_η, which has been experimentally established in a number of studies.[25] Substitution of the Arrhenius equation for k and eqn. (10) for k_d in eqn. (7) allows the effective activation energy to be derived,[26] eqn. (12),

$$E_{ef} = -R\left(\frac{\mathrm{d}\ln k_{ef}}{\mathrm{d}T^{-1}}\right) = \frac{(E_\eta + RT)k + Ek_d}{k + k_d} \tag{12}$$

where E is the activation energy of a chemical step. Since both k and k_d vary with temperature, the effective activation energy in eqn. (12) will also vary with temperature taking values between E and E_η. Naturally, if the relaxation time is significantly larger than the characteristic time of a chemical reaction (*i.e.* $k \gg k_d$), the effective activation energy determined from the Arrhenius plot will be approximately equal to that of the viscous flow. Vyazovkin and Sbirrazzuoli[26] have experimentally obtained this result by comparing activation energies respectively derived from kinetic and rheological data. According to Moelwyn-Hughes,[8] the temperature variation of the viscosity causes the variation in the activation energy of the inversion of cane sugar (Fig. 1). Strongly non-linear Arrhenius dependencies have been reported by Vauthey and Phillips[27] in their study of the effect of viscosity on the rate of back electron transfer.

Temperature is not the only factor that affects the mechanical properties of the reaction medium. Dramatic changes can be caused by the chemical reaction itself. Reactions of liquid phase polymerization provide an excellent example of this phenomenon. If polymerization occurs below the glass transition temperature of the respective polymer, the mixture of polymer and monomer transforms to an immobile glass at a certain extent of polymerization.[28] As described by Flory,[28] the monomer molecules become frozen in their positions in the glassy state which causes the virtual cessation of polymerization. Stutz *et al.*[29] have studied the kinetics of epoxy-amine copolymerization in the glass transition region and found that the process has very low activation energies, of the order of a few kilojoules per mole. This means that vitrification of the mixture of polymer and monomer should cause a decrease of the effective activation with increasing extent of polymerization. This effect can be conveniently observed by using isoconversional methods that allow the activation energy to be evaluated as a function of the extent of reaction. All these methods take their origin in the basic equation, eqn. (13),

$$E_\alpha = -R[\mathrm{d}\ln(\mathrm{d}\alpha/\mathrm{d}t)_\alpha/\mathrm{d}T^{-1}] \tag{13}$$

where α is the extent of conversion, $d\alpha/dt$ is the reaction rate, and the subscript α denotes values related to a given extent of reaction. The major contribution to development of these methods, and especially to their application to reactions of polymers, has been made by Flynn.[30] Vyazovkin and Sbirrazzuoli[31] have applied the isoconversional method to rate data on epoxy-amine copolymerization and observed the above-mentioned decrease in the activation energy that is caused by vitrification of the reaction system (Fig. 4).

Solid phase

Reactions of solids tend to occur as multiple steps that may give rise to strong dependencies of the activation energy on temperature and/or extent of conversion.[32,33] Most of these dependencies can be explained by a change in the reaction mechanism and, therefore, are not considered here. Instead, attention is again focussed on the effects caused by the reaction medium.

As noted above, Fishbeck[22] proposed that the overall rate of a solid–gas reaction is determined by the rate of a chemical step as well as of diffusion of a gas in the solid medium [eqn. (6) and (7)]. From eqn. (7) one easily obtains the effective activation energy, eqn. (14).

$$E_{ef} = -R\left(\frac{d \ln k_{ef}}{dT^{-1}}\right) = \frac{E_D k_R + E_R k_D}{k_R + k_D} \qquad (14)$$

In a similar fashion to eqn. (12), (14) gives rise to the temperature dependence of the effective activation energy. In addition to imposing diffusion limitations on the reaction rate, the effect of the solid medium is also revealed in an alteration of the diffusion rate that ultimately causes the activation energy to vary. Such an effect was described by Jost,[34] who demonstrated that thermal expansion may cause a variation in the activation energy of diffusion.

However, the most intriguing effects are those that are uniquely characteristic of the solid medium. Owing to the highly restricted molecular motion, a solid medium allows a reactant to exist in states of significantly different free energy that are non-uniformly distributed throughout the medium. For this reason, the same reaction step may occur with different activation energies depending on the spatial location of the reaction center. This fact was taken into account by Constable[35] to describe the catalytic activity of a non-uniform solid surface. He hypothesized that the surface has a number of various reaction centers that can be characterized by specific activation energies. The catalytic activity of the surface is then determined by a distribution of activation energies, $F(E)$, over the reaction centers. By assuming that the activation energy takes values between E_{min} and E_{max}, Constable arrived at eqn. (15) for the reaction rate,

$$v = \int_{E_{min}}^{E_{max}} S\sigma_E^{-1} F(E) \exp\left(\frac{-E}{RT}\right) dE \qquad (15)$$

where S is the surface area and σ_E the mean life of a molecule on the center characterized by the activation energy E. The idea of an activation energy distribution was later employed by Roginskii[36] to develop a comprehensive theory of adsorption and catalysis on non-uniform surfaces. Temperature-programmed desorption studies are commonly used to determine such distributions, which provide important clues for clarifying the mechanism of the interaction between adsorbed species and a solid surface. Fig. 5 shows the activation energy distributions found experimentally by Hunger *et al.*[37] for desorption of water from different zeolites. The presence of several peaks in the distribution suggests the existence of different adsorption centers. Seebauer[38] has presented a comprehensive kinetic method of obtaining continuous activation energy distributions from temperature programmed desorption spectra.

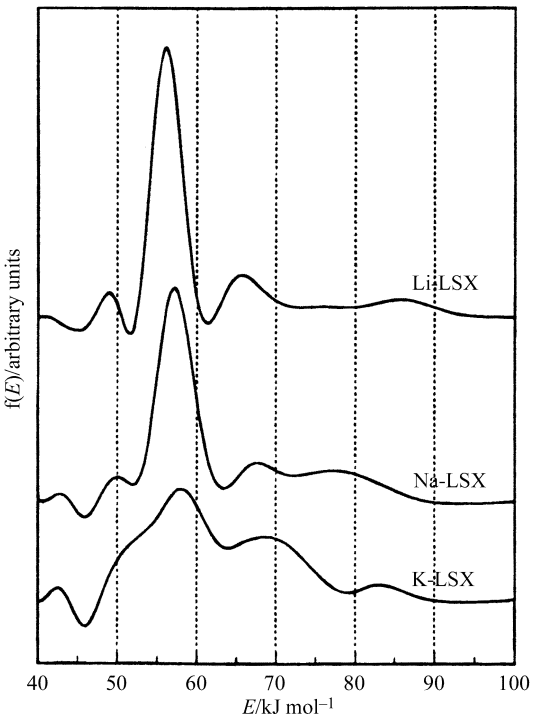

Fig. 5 Activation energy distributions for desorption of water on LSX zeolites with different cations. Reprinted with permission from ref. 37. Copyright 1999, American Chemical Society.

Vand[39] and Primak[40] have demonstrated that the kinetics of annealing are characterized by a distribution of the activation energy. Halpern[41] has recently discussed the significance of the temperature-dependent distributions of activation energies for the processes of dielectric relaxation and ionic conductivity.

The idea of a distribution of the activation energies has been successfully developed by Lebedev,[42] Emanuel and Buchachenko[43] and Davydov *et al.*[44] to describe the kinetics of chemical reactions in the solid phase. A reacting solid is represented by a set of kinetic ensembles comprising species having the same rate constant or activation energy. This approach has been advantageous in describing the solid-state reaction kinetics of macroradical species. Extensive electron spin resonance studies suggest[43] that such species often form kinetic ensembles having a rather wide distribution in the activation energies (*e.g.* $E_{max}/E_{min} = 2$–4). Evaluation of the effective activation energy, using the isoconversional method [eqn. (13)], reveals a variation in the activation energy with the extent of conversion that is used to estimate the parameters of the distribution. The temperature variations of the activation energy have also been reported.[43,44]

Activation energy distributions have also found broad application in the kinetics analysis of processes involving complex solid materials. Burnham and Braun[45] have recently published an excellent review of kinetic models which employ various distributions of the activation energy to characterize such processes. With regard to the kinetic applications of activation energy distributions, one should also mention work by Liebovitch and Tóth,[46] who developed a mathematical apparatus that relates such distributions with the temporal variations of the effective rate constant. These variations suggest that the experimental activation energy changes with the extent of reaction.

Conclusion

The reaction medium may induce significant variations in the experimental activation energy even if a reaction involves a

single chemical step. The effects considered are conventionally of two types. The first type comprises effects in which the free energy barrier of a chemical step is at least partially determined by the physical properties of the medium. This is the case for a liquid medium (solvent), whose dielectric properties affect the free energy barrier of electron transfer reactions, and for a solid medium that allows a reactant to exist in states of significantly different free energy. The second type includes the effects that do not change the free energy barrier of a chemical step but affect the experimental activation energy by imposing diffusion limitations on the rate of the chemical step. Although the resulting reaction still consists of a single chemical step, it also involves a transport step. The latter does not change the identity of the reaction products, but the rate of their formation. As a result, one may observe a variation in the experimental activation energy while the total reaction appears to occur as a single chemical step.

While these two types of effect are fundamentally different, they are quite similar from a phenomenological point of view. Both types of effect are experimentally observed as a variation in the experimental activation energy for a process that involves a single chemical step. Since this phenomenon is obviously inconsistent with the concept of constant activation energy, it seems reasonable to introduce a concept of variable activation energy. This is not only more practical, but also universal because it permits a constant activation energy as a special case of a variable activation energy.

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