AIP | The Journal of Chemical Physics

Kinetic study of the conversion of presolvated to solvated silver atoms in polycrystalline ice: Activation energy of water molecule rotation with Ddefect annihilation

A. S. W. Li and Larry Kevan

Citation: The Journal of Chemical Physics **75**, 5968 (1981); doi: 10.1063/1.442021
View online: http://dx.doi.org/10.1063/1.442021
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/75/12?ver=pdfcov
Published by the AIP Publishing

Kinetic study of the conversion of presolvated to solvated silver atoms in polycrystalline ice: Activation energy of water molecule rotation with *D*-defect annihilation

A. S. W. Li and Larry Kevan

Department of Chemistry, University of Houston, Houston, Texas 77004

(Received 13 July 1981; accepted 26 August 1981)

Silver atoms have served as powerful environmental probes of solvation in frozen solutions[1-17] and on zeolite interior surfaces.[18,19] The most detailed picture of solvation geometry has been obtained in polycrystalline ice.[15] Silver atoms generated by electron reduction of the ion at 4 K are initially produced in site WI with a solvation shell characteristic of Ag^+ composed of four waters with their molecular dipoles oriented toward the atom. This is a presolvated, nonequilibrium state for the solvated atom however. Atom solvation is induced thermally to give site WII in which one water has rotated about its OH bond to bring a proton 0.14 nm closer to the atom. Here we study the kinetics of this solvation site conversion and determine an activation energy for this process. This gives new information on the activation energy in crystalline ice for water molecule rotation.

Solutions of 0.5 M silver perchlorate and 0.5 M sodium fluoride were x-irradiated in 4 mm o.d. Spectrosil quartz sample tubes. The added NaF acts as a hole trap to increase the silver atom yield.[16] X-irradiation doses at 60 kV and 50 mA were typically 0.4 Mrad at a dose rate of 0.8 Mrad h^{-1} in liquid helium. The samples were transferred to a Helitran (Air Products and Chemicals, Inc.) flow Dewar preset to various temperatures in the cavity of a Varian E-9 electron spin resonance (ESR) spectrometer. The temperature was monitored by a 0.07 atomic percent iron in gold thermocouple and was controlled to ±0.1 K by a model 5301-S Artronix temperature controller.

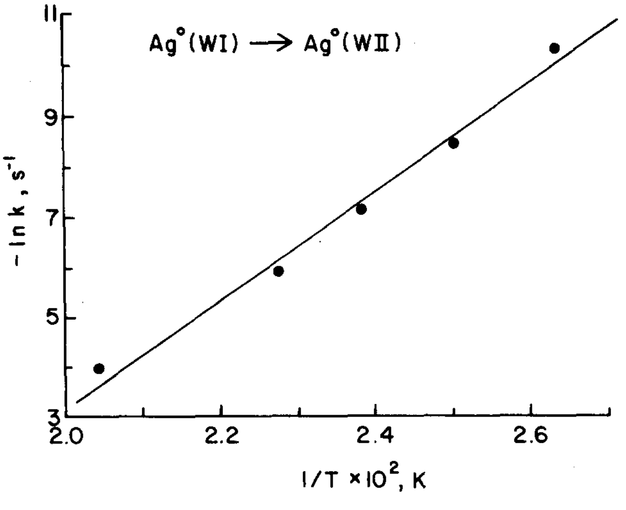

FIG. 1. Arrhenius plot of the conversion of silver atom from site WI to site WII in polycrystalline ice.

The high field lines of ^{109}Ag and ^{107}Ag were monitored by ESR. A sweep range of 100 G covered both sites WI and WII. Kinetics were run at 38, 40, 42, 44, and 49 K. At lower temperatures the site WI halflife was longer than 3 h and at higher temperatures it is too short for meaningful data on our observation time scale. The decays were approximately first order with a slight curvature on a log plot as is typical for decay kinetics in solids. Effective first order rate constants were determined from the initial slopes of the log intensity vs time plots and from the halflives. An Arrhenius plot of the halflife data is shown in Fig. 1. The Arrhenius relation is well obeyed and an activation energy of 0.09 ± 0.01 eV is determined.

Electron–spin echo and electron–spin resonance studies have established the geometrical difference between Ag^0 in sites WI and WII in ice.[15] In site WI Ag^0 is surrounded by 8 protons at 0.31 nm while in site WII Ag^0 is surrounded by 7 protons at 0.31 nm and 1 proton at 0.17 nm. This site conversion can be described as a rotation of one of four water molecules about its OH bond in the first solvation shell of Ag^0. Thus the measured activation energy of 0.09 eV for the site conversion can be identified with such a water molecule rotation in ice. This energy is significantly lower than the 0.24 activation energy associated with the diffusion of orientational defects in ice[20] which can also be envisioned as due to water molecule rotation about an OH bond.

We have recently suggested that *D*-defect formation is probably adjacent to cations like Ag^+ in polycrystalline ice.[5] A *D*-defect is two protons between two oxygens in the ice lattice. When Ag^+ is converted to Ag^0 the first solvation shell water molecule rotation that occurs to solvate the atom then also involves the annihilation of a *D* defect. This is expected to lower the activation energy for the molecular rotation compared to defect diffusion in bulk ice.

This research was supported by the Department of Energy.

[1] R. A. Zhitnikov, N. V. Kolesnikov, and V. I. Kosyakov, Sov. Phys.–JETP **17**, 815 (1963).

[2] L. Shields, J. Chem. Phys. **44**, 1685 (1966).

[3] B. L. Bales and L. Kevan, Chem. Phys. Lett. **3**, 484 (1969).

[4] D. R. Brown and M. C. R. Symons, J. Chem. Soc. Faraday Trans. I **73**, 1490 (1977).

[5] T. Ichikawa, A. S. W. Li, and L. Kevan, J. Chem. Phys. **75**, 2472 (1981).

[6] L. Shields, J. Chem. Soc., Faraday Trans I **62**, 1042 (1966).

0021-9606/81/245968-02$01.00

[7] J. Michalik and L. Kevan, J. Magn. Reson. 31, 259 (1978).
[8] R. A. Zhitnikov and D. P. Peregud, Sov. Phys.-Solid State (Engl. Transl.) 12, 1583 (1971).
[9] A. S. W. Li and L. Kevan, J. Phys. Chem. 84, 2862 (1980).
[10] T. Ichikawa, L. Kevan, and P. A. Narayana, J. Phys. Chem. 83, 3378 (1979).
[11] A. S. W. Li and L. Kevan, J. Phys. Chem. 85, 2557 (1981).
[12] C. K. Alesbury and M. C. R. Symons, J. Chem. Soc. Faraday Trans. I 76, 244 (1980).
[13] L. Kevan, H. Hase, and K. Kawabata, J. Chem. Phys. 66, 3834 (1977).
[14] L. Kevan, J. Chem. Phys. 69, 3444 (1978).
[15] T. Ichikawa, L. Kevan, and P. A. Narayana, J. Chem. Phys. 71, 3792 (1979).
[16] B. L. Bales and L. Kevan, J. Phys. Chem. 74, 1098 (1970).
[17] B. L. Bales and L. Kevan, J. Chem. 55, 1327 (1971).
[18] M. Narayana, A. S. W. Li, and L. Kevan, J. Phys. Chem. 85, 132 (1981).
[19] A. Abou-Käis, J. C. Vedrine, and C. Naccache, J. Chem. Soc. Faraday Trans. II 74, 959 (1978).
[20] N. H. Fletcher, *The Chemical Physics of Ice* (Cambridge University, Cambridge, England, 1970), pp. 153–156.

Diffusion theory of reaction rates for multiple potential barriers

Marc Mangel

Department of Mathematics, University of California, Davis, California 95616

(Received 29 May 1981; accepted 21 August 1981)

According to the diffusion theory of reaction rates (proposed by H. Kramers in 1940[1]) as molecules move in physical space, they execute a random walk in a field of force in reaction coordinate space. The original paper of Kramers spawned many others (see, e.g., Refs. 2–14). In these papers, the diffusion process occurs in a field of force in which the potential barrier has a single peak separating reactant and product states. There are applications of present interest, however, in which the reactant proceeds to the product by means of many intermediate states, so that there are many potential barriers to overcome. Some examples are weak ionic conductivity in periodic lattices,[14–16] the migration of ligands in biomolecules,[17–20] the photocycle of bacteriorhodopsin;[21–23] and membrane transport.[24–26] In these cases, the method proposed by Kramers for the calculation of the rate constant is difficult to apply, and breaks down if the barrier heights are not large enough. Instead of using the method of Kramers, we shall use the method developed in Ref. 2 (for one-dimensional reaction coordinate potentials) in which the rate constant is calculated exactly and the results of Kramers are obtained as a certain limit (that of high barriers).

When reaction rates in solution are studied experimentally, two parameters that can be adjusted are the temperature and viscosity of the solution. Consequently, the dependence of reaction rate on temperature and viscosity will be studied in this paper so that the theory can be used when analyzing rate data. In the classic setting for analyzing rate data, the rate constant is given by $k=A\,e^{-Q/k_BT}$, where k is the rate constant, Q the barrier height, k_B is Boltzmann's constant, and T is temperature. Thus, a plot of $\log k$ against $1/k_BT$ has slope $-Q$ and intercept $\log A$. In this paper, we show that the simple interpretation changes for potentials with many barriers.

In the Einstein–Smoluchowski limit of the diffusion theory,[2] the reaction coordinate $X(t)$ is assumed to satisfy the stochastic differential equation

$$dX=\frac{F(X)}{\eta}\,dt+\sqrt{\frac{2k_BT}{\eta}}\,dW\ . \tag{2.1}$$

In this equation, η is proportional to the viscosity, k_B is Boltzmann's constant, T is absolute temperature, and $W(t)$ is Brownian motion.[27] The force $F(x)$ is derived from the potential $V(x)$, so that $F(x)=-V'(x)$. The potential is assumed to have a local minimum at $x_R=0$, corresponding to the reactant state, and at x_P corresponding to the product state, and n interior barriers. Thus, there are $2n-1$ interior stationary points x_j, labeled so that local maxima have odd indices and local minima have even indices. The potential is assumed to increase monotonically for $x<x_R$ and $x>x_P$.

If $\hat{T}(x)$ is the mean time to reach the x_P state, starting at the value $X(0)=x$, then according to the diffusion theory of reactions $\hat{T}(x)$ is exactly given by[2]

$$\hat{T}(x)=\frac{\eta}{\beta}\int_x^{x_P}\exp[V(s)/\beta]\int_{-\infty}^{s}\exp[-V(y)/\beta]\,dy\,ds, \tag{2.2}$$

here $\beta\equiv k_BT$.

Equation (2.2) is exact. The rate constant is defined as the reciprocal of the average of $\hat{T}(x)$ against the initial density for $X(0)$. Regardless of the form of this distribution or the number of barriers, from Eq. (2.2) we see that the rate constant is proportional to η^{-1}.

Thus we conclude that a simple extension of the Kramers model to the case of n barriers does not explain recent experiments[20,23] in which the rate constant was found to have a $\eta^{-\kappa}$ dependence, with $0<\kappa<1$. Equation (2.2) holds for barriers of arbitrary height. The formula that Kramers derived[1] is valid for barriers that are large so that we now study the large barrier limit of $\hat{T}(x_R)$.

To do this, let Q_j be the height of the jth barrier and let Q be the minimum value of Q_j, $j=1,\ldots,n$.

In the large barrier approximation, we assume that

J. Chem. Phys. 75(12), 15 Dec. 1981 0021-9606/81/245969-03$01.00