

THE CHANGE IN ENTROPY OF ACTIVATION DUE TO SOLVATION/HYDRATION OF IONS: PROTON VERSUS CARBOCATION - A ONE HOUR GRADUATE CLASSROOM LECTURE

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Abstract. The significance of change in entropy of activation for two different reactions where in one involves the liberation of a proton and the other a carbocation is described based on the fact that the hydration of a proton involves a loss in entropy due to freezing of translational, rotational or vibrational degrees of freedom of solvent molecules.

Keywords: entropy, proton, carbocation, solvation, hydration.

The symbol S is for entropy, gives an idea of the extent of randomness or disorder in a system. The difference between the entropy of the transition state and the sum of the entropies of the reactants is called *activation entropy* $\Delta S^\ddagger$. Recalling the Eyring equation:

$$k = \frac{k_B T}{h} \exp[-\Delta H^\ddagger / RT] \exp[\Delta S^\ddagger / R] \quad (1)$$

Where k is the specific reaction rate, k_B is Boltzmann's constant, h – Planck's constant, T is Kelvin temperature, R is the gas constant, and $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are the

activation enthalpy and entropy, respectively. Eq. (1) has the above form if the so called *transmission coefficient* is zero. On the other hand, the usual Arrhenius equation is

$$k = A \exp(E_a / RT) \quad (2)$$

The comparison of both equations shows that the *enthalpy of activation* cannot be recognized as the *energy of activation*. The relationship between these quantities can be obtained through the slope of the straight line $\ln k$ vs. $1/T$:

$$d \ln k / dT = \frac{1}{T} + \frac{\Delta H^\ddagger}{RT} \quad (3)$$

$$d(1/T) / dT = -1/T^2 \quad (4)$$

$$\frac{d \ln k}{d(1/T)} = \frac{d \ln k}{dT} \frac{dT}{d(1/T)} = \frac{-(\Delta H^\ddagger + RT)}{R} \quad (5)$$

Hence, it is readily obtained that

$$E_a = \Delta H^\ddagger + RT \quad (6)$$

Therefore,

$$A = e \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (7)$$

If one knows the Arrhenius pre-exponential factor A , then the *entropy of activation* could be calculated using $\Delta H^\ddagger$ and k for a given temperature. If $\Delta S^\ddagger = 0$ (i.e. the standard molar entropy of the activated complex is equal to that of the reactant), then

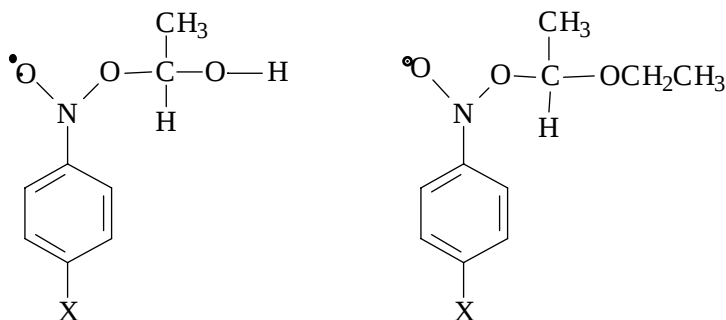
$$A_0 = e k_B T / h \quad (8)$$

The quantity on right-hand side of Eq. (8) is known as “*universal factor*” [1]. For example at 293 K the value of A_0 comes out to be $1.65 \cdot 10^{13} \text{ s}^{-1}$, i.e. $\ln A_0$ is equal to 13.2.

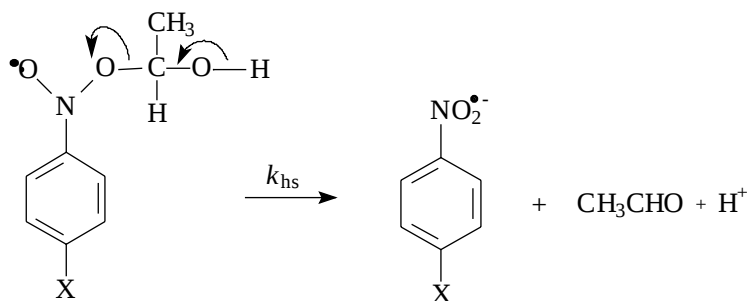
Therefore, if logarithm of A from an Arrhenius plot for a given reaction is < 13.2 , this corresponds to a negative value for $\Delta S^\ddagger$ (unfavorable). Therefore the transition state in the region of activated complex has a more ordered or more rigid structure than the reactants in the ground state. This is generally the case if on going from the ground state to the transition state, degrees of freedom of translation, rotation or vibration is “*frozen*”. If logarithm of A is > 13.2 , this corresponds to a positive value for

$\Delta S^\ddagger$ (favorable). A positive change in entropy of activation indicates that the system has become more disordered. Degrees of freedom are “*liberated*” on going from the ground state to the transition state. The reaction is fast. Although the determination of the activation parameters must be performed accurately, it should not pretend an excessive accuracy. The values of the activation energy and activation enthalpy are rounded to one decimal place. The value of activation entropy is basically written in whole numbers. Values of entropies $\Delta S^\ddagger < \pm 10$ are written to one decimal place of accuracy. The value of logarithm of A shall be expressed with an accuracy of two decimal places. A precise determination of the activation enthalpy (and the other activation parameters) requires at least three rate constants obtained at different reaction temperatures. The temperature intervals should be at least 5°C. If the data points in the plot of $\ln(k/T)$ or $\ln(kh/k_B T)$ vs. $1/T$ using Eyring equation do not lie exactly on a straight line, a linear regression analysis providing the ‘line of best fit’ will not increase the accuracy. If the plotted points deviate significantly from the straight line, the rate constant should be determined at a further reaction temperature, since each of the three data points can be “wrong”. Basically, it recommends increasing the accuracy of the measured values by improvement of the measuring method (accurate thermostating of the reaction mixture).

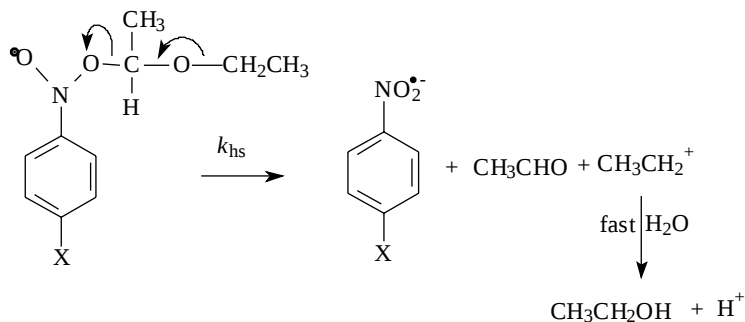
Here it is desired to discuss about the *activation entropy*, $\Delta S^\ddagger$, in two cases where in one case a proton, and in other, a carbocation, are produced during the heterolysis of two types of nitroxyl adducts. The two types of nitroxyl adducts are those formed by addition of α -hydroxy alkyl and α -alkoxy alkyl radicals to nitrobenzenes [2]:



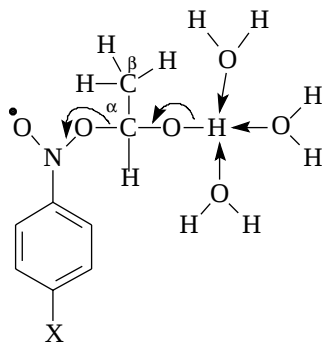
At this point a question may be anticipated from the readers of this article, that why only the proton versus a carbocation is selected to explain the situation when there are several types of reactions exist in literature. Here the contrast between the changes in activation entropy for the heterolysis of the above two adducts is a quite outstanding facet and the student may conceive it very easily. The activation entropies [2] are measured for the above two adducts with several substituents (X's) in the para position of the benzene ring.



and



In the above two heterolysis reactions one involves the production of H^+ and the other a carbocation. Values of -12 to $-20 \text{ cal.mol}^{-1}\text{K}^{-1}$ indicate extensive reorganization of the solvent (water) shell in the transition state as a result of production of the incipient ions specifically, the proton which would be hydrated to a large extent. In fact the entropy change on hydration of a proton by four water molecules to yield hydronium ion $\text{H}(\text{H}_2\text{O})_4^+$ is $-24 \text{ cal.mol}^{-1}\text{K}^{-1}$ [3]. The fact that the experimental values are less negative than this value is suggested to be due to the positive contribution that results from the increase in number of molecules in going from the adduct to the radical anion, the oxo compound, and the H^+ . That it is the hydration of the proton that leads to negative $\Delta S^\ddagger$ values can be unequivocally shown by replacing the proton by an alkyl group i.e. the second heterolysis reaction given above. In this case, the positive ion formed in the transition state is a carbocation and not a proton, which becomes less hydrated than the proton. For these systems, the experimentally observed $\Delta S^\ddagger$ values are *positive* ($\sim 15 \text{ cal.mol}^{-1}\text{K}^{-1}$ (Jagannadham & Steenken, unpublished material)). The same situation exists with the heterolysis of the nitroxide formed by addition of α -alkoxy alkyl radicals to tetranitromethane; $\Delta S^\ddagger$ values are again *positive* [4], since the positive ion formed in the transition state is a carbocation and again not a proton. The hydration of the proton produced during the heterolysis can be depicted as the following:



And this is further supported by the study of the solvent isotope effect [2] on k_{hs}

and which $\left(\frac{k_{\text{H}_2\text{O}}}{k_{\text{D}_2\text{O}}} \right)$ was found to be 2.2 for the adduct I.

Therefore this is generally the case if on going from the ground state to the transition state, degrees of freedom of translation, rotation or vibration are “frozen” which leads to the negative $\Delta S^\ddagger$ values.

This article is dedicated to my mentor Prof. Dr. Steen Steenken (Rtd), Max-Planck-Institut für Radiation Chemistry, Muelheim a.d. Ruhr, Germany.

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