

A critical review of some underlying concepts involving both Arrhenius equation and the transition state theory

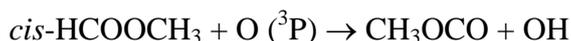
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Abstract: In this review, we highlight some parameters and fundamental concepts which are usually not fully discussed concerned to the Arrhenius Law and the transition state (TST) [1]. Most of papers and textbooks consider as a rule of thumb the pre-exponential A and the activation energy E_A as independent of the temperature in the classical Arrhenius equation. However, theoretical and experimentally a non-Arrhenius behavior should be the rule rather than an exception. Measurements of rate coefficients over wide temperature range confirm this effect. The transition state theory is based on a logarithm expression derivative of the classical Arrhenius and represents a culmination of an unified model of four keystones of chemical physics, i.e. quantum mechanical potential energy surface, kinetic theory, thermodynamics, and statistical-mechanics. This theory has an unquestionable success in a variety of applications in the predictions of rate constants and support the interpretation of experiments. However there are some drawbacks of the basic concepts of this model which should be highlighted. One important fact are the structures and the potential force field of the stationary states which are calculated out of the equilibrium geometry and used as input in the calculations of partition functions of the variational transition state theory. Also, the possibility of choice of Cartesian or Curvilinear internal coordinates, for the definition of the framework of reactants, transition state and products show a variance of values of certain complex properties as the coefficients of rate constants. Anharmonic effects on the modes with low values in flexible molecules is another important factor which should be considered in calculations of partition functions specially in the range of medium to high temperatures [1]. Thus, anharmonicity and the multi-structural character of flexible molecules are essential concepts not usually mentioned in the literature but which are essential in the affordable model of kinetics and thermochemistry. One of the starting examples we compare the deviation from the Arrhenius law on the model of the transition state theory (TST) for the elementary reaction [2],





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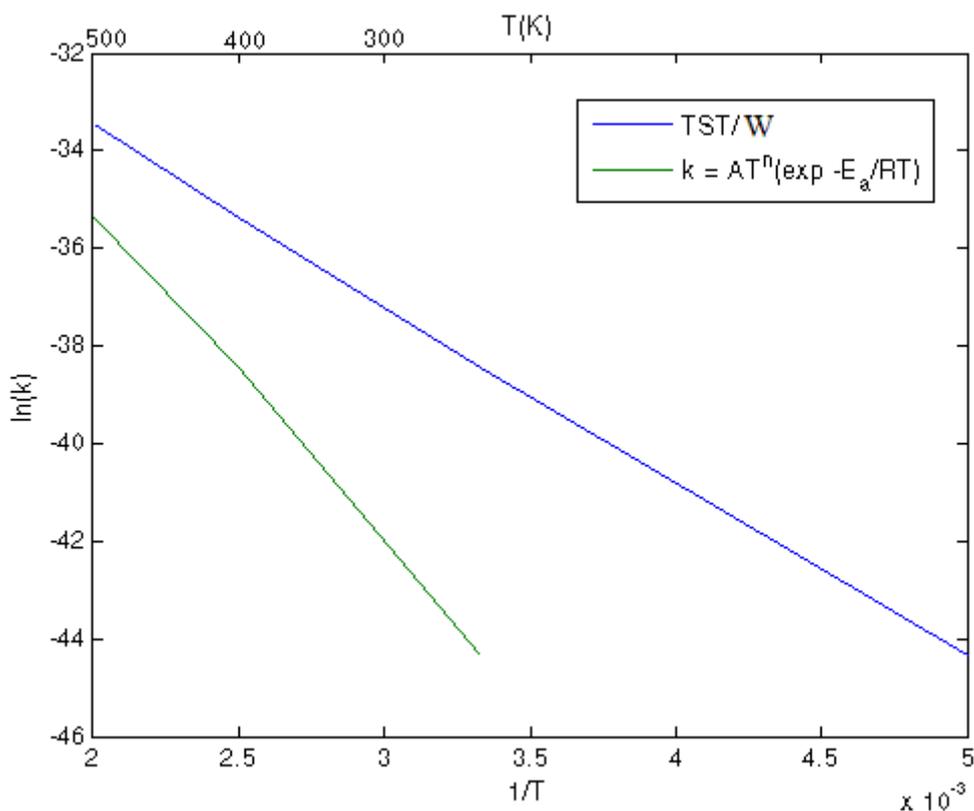
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whose rate of reaction is calculated by the adjustment given by the relation

$$k = AT^n \exp(-E_a/RT) \quad (1)$$

where A , n and R are constants E_a is the activation energy and T is the temperature as in the Arrhenius Law, and by the simple model of TST/W rate constants based on the Wigner-unidimensional tunneling corrections. Clearly we can check the deviation between the two methods in the plot below for the Arrhenius Law. We also compare the conventional linear Arrhenius law and TST results with the model of deformed transition TST [3] model which gives some heuristic insights on the critical chemical dynamics parameters controlling the reactivity.



Key-words: Arrhenius law; Transition state theory; Chemical kinetics

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References:

- [1] A. Fernández-Ramos, J. A. Miller, S. J. Klippenstein, D. G. Truhlar, Chem. Rev. 2006, 106, 4518.
- [2] Horiuti, J. B., Chem Soc Jpn 1938,13,210.
- [3] V. H. Carvalho-Silva, V. Aquilante, H. C. B de Oliveira, K. C. Mundim, J. Comput. Chem. 2017, 38, 178.