‘Holy Grails’ of Chemistry

The Transition State in a Chemical Reaction

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In discussions of chemical reactions, particularly their rates, the concept of a ‘transition state’ appears frequently. In all undergraduate textbooks in chemistry, the notion of a transition state (henceforth abbreviated as TS) or an activated complex (synonymous) is used in describing the passage of a reaction from reactants to products. However, everyone understands and interprets the exact meaning of the term, TS, in one’s own way. In this article, I shall attempt to develop the concept and try to provide a working definition for the TS in a chemical reaction.

The Concept

To begin with, it is important to distinguish between an elementary reaction, which goes in one step, and a complex reaction which requires multiple elementary steps. In the absence of evidence of an intermediate (see *Box* 1) or when the kinetic equation corresponds to the stoichiometry of the reaction, it may be tentatively inferred that the reaction is elementary, though this inference may change as a result of more detailed investigation on the reaction.

Box 1. Intermediate

An intermediate is a transient species occurring in a composite reaction. It is a short-lived product of one elementary reaction and a reactant in another. It is, in principle, identifiable through an appropriate detection technique as long as the technique does not affect its formation or disappearance.

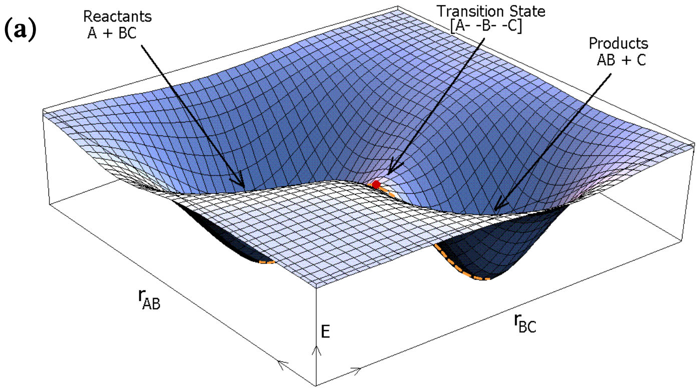
The TS of a chemical reaction is best illustrated by considering an example. Let us suppose that an atom A reacts with a diatomic molecule BC leading to another diatomic AB and an atom C, as products in a hypothetical reaction – a real example is H + DF ® HF + D. The path chosen for illustrative purposes is just one of several possibilities, such as AB + C, AC + B and A + B + C. Let us assume that the reactants and products are all in the gas phase at ambient temperature and pressure. This will also maintain historical correctness since the concept of a TS in a reaction was first suggested in the context of explaining the temperature variation of reaction rates of gas phase reactions. *Figure* 1 shows schematically how (potential) energy of the reactants A and BC changes as the reaction proceeds in the forward direction from the reactants into products. At the molecular level, the gaseous A and BC molecules collide with each other in the course of the reaction, perhaps get distorted, break old bonds and make new bonds and then start to separate. The energy rises to a maximum at intermediate A-B and B-C distances (under the implicit assumption that there is an energy barrier to this reaction, which is most often encountered in an atom-diatomic exchange reaction). At the molecular level, a repulsive interaction between A and BC as they approach each other during a collision, will lead to such a barrier. The horizontal axis in *Figure* 1c represents all these through the course of the reaction and is called the ‘reaction coordinate’.

The notion of a transition state is used in describing the passage of a reaction from reactants to products.

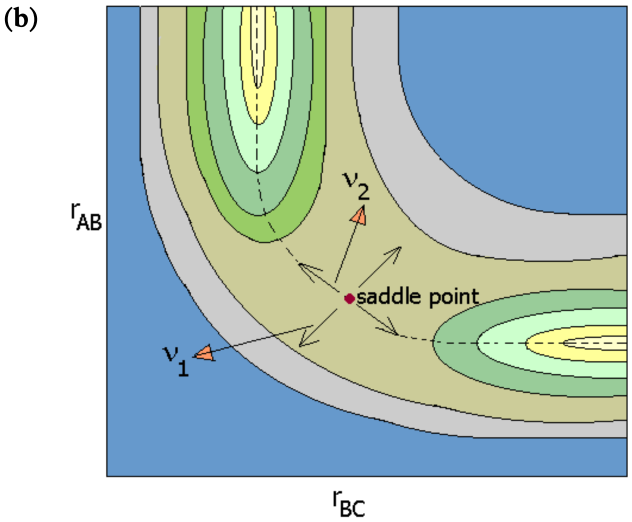
However, this definition of the reaction coordinate is elusive and creates no concrete impression about its nature and characteristics. For a clearer understanding we need to examine how such a potential energy diagram is generated for the reaction stated above. If we confine the A and BC collision to a collinear geometry wherein all the three atoms A, B, and C fall on a straight line, the potential energy of the A-B-C system will depend on two coordinates, namely the A-B and B-C bond distances. A diagram depicting the potential energy along one axis and the coordinates along other axes, known as the potential energy diagram, will be drawn later for this system. On the reactant side, the reaction path is along the A-B distance (where the change is taking place as the collision between A and BC progresses) while it is the BC distance for the products. In the intermediate region of the potential energy surface (See *Box* 2) or PES, the reaction path is described in terms of both of these two bond distances.

The term reaction coordinate is, therefore, these bond distances which describe the progress of the reaction along the reaction path. We now define the reaction path as the line of minimal energy from reactants to products. The location of the barrier is termed as the saddle point (see *Figure* 1). The potential energy

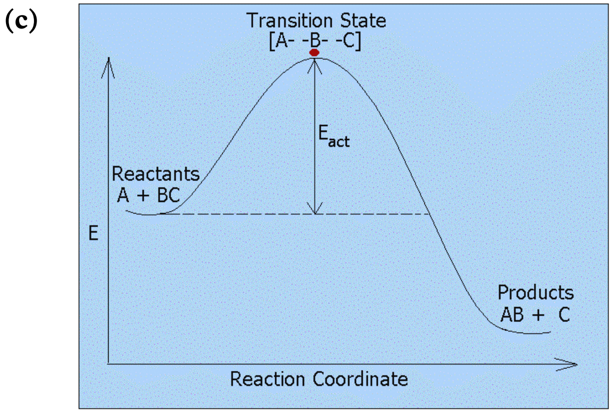
Figure 1.



A schematic 3-D PES for the collinear A + BC → AB + C reaction. The orange dashed line shows the reaction path and the saddle point is marked by the red dot.



A schematic 2-D contour map for the same reaction A + BC → AB + C where energy axis is omitted. The dashed line shows the reaction path. ν_1 corresponds to the symmetric stretch and ν_2, the asymmetric stretch of [A--B--C]. The saddlepoint is also marked.



A schematic 1-D energy profile for the same reaction A + BC → AB + C. The highest energy point on this curve is the saddlepoint marked in red. E_{act} is the activation energy.

increases as we deviate sideways from the reaction path (which is not clear in a 1-D (*Figure* 1c) and, perhaps, also in a 2-D (*Figure* 1b) diagrams. The PES near the barrier in a 3-D diagram looks like a saddle (the Oxford dictionary meaning of the word saddle is 'ridge of high land between two peaks'). The saddle point is a stationary point on the minimum energy path. At that point, the PES is not only parabolic downward (this is easy to realize in the 1-D plot of *Figure* 1c) along the reaction path in both the forward and reverse directions but is also parabolic upward (this is easy to see in a 3-D plot like in *Figure* 1a) in all other directions. Therefore, the passage from the reactants to products during a chemical reaction is like travelling from the reactant valley to the product valley through a mountain pass situated between two mountains. The saddle point is the highest point on that path. It is also possible to have wells, depressions and ridges along the path. In fact, mountain climbers and hikers would be particularly quick in analyzing potential energy (hyper) surfaces and contours (2-D representation of such surfaces) since they are familiar with the topographical terms used in this context such as pass, saddlepoint, valley, well, ridge, etc.

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At the saddle point the derivative of the potential energy with respect to each Cartesian coordinate is zero, i.e., $\partial V/\partial q_i = 0$. Since the PES curves downward (negative curvature) at the

Box 2. Potential Energy Surface

An N-atom system, in general, has $3N$ total degrees of freedom of which 3 each are translational and rotational degrees. Therefore, the potential energy of the system will depend on $3N$-6 independent (vibrational) coordinates or variables. It is natural to use internal coordinates such as bond stretches and bond angles to depict the potential mathematically or otherwise. If we bring in more constraints by defining a fixed geometry for collision etc., the number of variables can be reduced further. In a triatomic system like in the above reaction, the potential surface can be depicted as shown in Figure 1a by a 3-D surface in real space using two independent variable bond lengths AB and BC plus the potential energy. However, the potential energy will not appear explicitly in any of the discussion here and, therefore, it is easy to hide the potential energy dimension of *Figure* 1a in a topographical map called the potential contour map as shown in *Figure* 1b. These two-coordinate potential energy contour maps are widely used today to investigate the progress of a chemical reaction.

saddle point along the reaction path, the corresponding force constant is negative. The force constant (*k*) is related to vibrational frequency (n_{vib}) by $n_{\mathrm{vib}} = \sqrt{k/\mu}\,/2p$ (where *m* is the reduced mass), which implies that the frequency is imaginary. Therefore, there will be at least one vibrational frequency among the 3*N*-6 frequencies that becomes imaginary at the TS (the location of the TS is the same as that of the saddle point or the barrier maximum on the reaction path). This frequency corresponds to infinitesimal motion along the reaction path. The TS is, therefore defined as a state of dynamical instability, motion to one side is qualitatively different from the motion to the other side. A little push towards the right leads to products whereas, a shove to the left leads to reactants.

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In the example above of A + BC ® AB + C, the asymmetric or antisymmetric vibrational stretch represents the passage of the system from reactants to products (the potential energy contour diagram of *Figure* 1b shows this clearly). In such a case the reaction coordinate in the TS is said to correspond to the asymmetric vibration. In fact, stretching vibrations are usually the important ones connected to the reaction coordinate – the most common exception being *cis-trans* isomerization where the reaction coordinate is the twist-angle. Generally for many reactions, it is possible to identify a particular vibrational mode (which is usually a normal mode (See *Box* 3) obtained from the internal coordinates using standard methods described in any physical chemistry textbook) as the reaction coordinate and to reduce the dimensionality of the problem to one.

In order to calculate rate constants applying the TS theory, properties of the TS are first analysed using an appropriate PES. In the example taken here, the TS, should have four vibrational frequencies among which three should be real and one imaginary. This imaginary frequency corresponds to the passage over the barrier. Using this information together with properties of reactants, the rate constant is calculated by applying the TS theory. For an approximate estimate of rate constants, the precise choice of reaction coordinate is not of great importance;

Box 3. Normal Mode

It is convenient to use internal coordinates such as bond stretches and angle bends to describe the PES of a poly-atomic molecule. For example, for a bent triatomic molecule like H_2O, one choice of three internal coordinates could be the two O-H distances (r_1 and r_2) and the angle bend (q) (*Figure* 2). This choice is perfectly valid and the potential energy can be adequately described in terms of these three coordinates. However, it has a serious disadvantage. For example, when one O-H vibration is excited (that is, when r_1 varies), the motion of the oxygen atom sets the other O-H bond in motion (leads to a change of r_2) and the energy of excitation flows back and forth between the two bonds. Instead the description is much simpler if we take the symmetric stretch of the two O-H bonds simultaneously and call it the symmetric stretch mode of vibration (q_1). Another mode is the antisymmetric stretch (q_2) in which one O-H bond is stretched and the other compressed. These two modes are stable in the sense that if one is excited the other is not disturbed. These two are called the two normal stretching modes of water. The other normal mode will be the in-plane symmetric bending motion (q_3). In the normal mode description of the vibration in polyatomic molecules, any mode may be excited without leading to excitation of the others.

vibrational frequencies of molecules do not vary significantly, particularly for stretching vibrations, and the rate constant does not depend strongly on which frequency becomes imaginary at the TS. For accurate calculation of rate constants, however, the choice of reaction coordinate is very important and can only be made on the basis of a reliable PES.

It is easy to locate (define) the TS uniquely in 1-D since the criterion is purely energetic. In more than one dimension, entropy is also a consideration and the best choice of TS is not necessarily the region of highest energy along the reaction coordinate. I shall skip a discussion on this issue due to the limited scope of this article.

Concluding Remarks

Description of TS in a chemical reaction along with clear definitions of some terms used frequently by the practitioners of chemistry have been provided in this article. In the 1980's and 90's experiments have been carried out where direct observation of the TS in a chemical reaction has been made. The current dream is to design experiments to probe the TS and gain complete control of the reaction path. A detailed understanding of the rich landscape of the PES obtainable from such experiments will be the topic of a future article.

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Suggested Reading

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[2] J I Steinfeld, J S Francisco and W L Hase, *Chemical Kinetics and Dynamics*, (Second International Ed.), Prentice Hall, 1999.

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