

## THE ROLE OF THEORY IN TEACHING ORGANIC CHEMISTRY

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**Abstract** - Recent advances in theoretical chemistry had a profound effect on organic chemistry. The empirical hit and miss practice is being replaced by planned approaches where theory and computational methods play an ever increasing role. This development is also felt in chemical education where textbooks on all levels are becoming more abstract and less concerned with experimental and descriptive chemistry. However theory is often introduced at a too early stage and tendencies toward simplifications sometimes lead to erroneous interpretations of theoretical principles. Samples of this can be found on all levels, from high-school chemistry to graduate courses which contributes to the lessening of the attractiveness of chemistry among students. To regain its appeal a proper balance between theoretical and practical organic chemistry has to be found. It is important to take into account the fact that only a small proportion of chemistry students will go into fundamental research.

Theory entered the field of organic chemistry rather late. In the first 150 years of its existence organic chemistry achieved a position of remarkable importance in modern life without any significant contribution from theory. Structures of many important natural products such as vitamins, hormones and alkaloids were determined before the nature of the covalent bond was properly understood. Numerous synthetic organic chemicals were prepared and big industrial plants were erected before anything was known about hybridization, molecular orbitals or molecular mechanics. Aromatic compounds were functionalized and thousands of tons of synthetic aromatics were prepared before Hückel formulated his famous  $4n+2$  rule. It is therefore not surprising that attempts to seek theoretical explanations for organic reactions were at first met with some scepticism. While theoretical organic chemistry dates back the early work of Sir Robert Robinson around 1920, it was the introduction of the concept of orbital symmetry by Woodward and Hoffmann in 1964 which changed the organic chemists attitude towards theory. The importance of Hückel's work which was until that time known only to a handful of physical chemists was suddenly realized. Gradually long awaited link between theoretical physics, quantum chemistry and organic chemistry was established. Much of the largely empirical hit and miss practice of organic chemists was replaced by planned approaches where theory in combination with computational methods became one of the standard tools of the practicing organic chemist.

The realization of the increasing importance of theory had also a significant impact in the field of chemical education. Chemistry textbooks on all levels became more theoretical, descriptions of chemical phenomena more abstract while examples and exercises demanded more mathematical thinking (1-3).

These changes in subject and form of teaching coincided with or immediately preceeded a decline in interest towards chemistry among high school graduated. The loss of appeal for chemistry raised questions is not an over-emphasis on theory one of the possible culprits. What are the significant differences between modern and "classical" organic chemistry which made the latter, some 20 or more years ago so attractive to students of chemistry.

Firstly, classical organic chemistry was a highly sophisticated art. The act of performing experiments in the laboratory, the making of new compounds gave the student the feeling of participating in new discoveries. Each new compound guaranteed the entry into Beilstein! Later, when the importance of physical organic chemistry was recognized, studies of reaction mechanisms added a new quality to organic chemistry. Unrestricted growth and support for this kind of research led to some excesses. Experimental results were always "explained" by some kind of mechanism and this became the standard pattern which provided the required sophistication to publications of this time. An illustrative example of this situation can be given by referring to the so called nonclassical ion controversy (4). Regardless what judgement history will cast on this subject the fact remains that this controversy revealed many deficiencies of current theories of physical organic chemistry. Not without reason theories were regarded as being "soft". Opinion was expressed that in organic chemistry theory can be adjusted to accommodate almost any result. Not even the meaning of the term theoretical organic chemistry was well defined. While some restricted this term to quantum chemistry and the set of theoretical procedures aimed to solve the Schrödinger equation, for others it had a much broader meaning covering the whole field of physical organic chemistry. By elevating simple mechanistic descriptions of organic reactions to the level of a theory created the false impression that in order to formulate a theory it will suffice to accumulate enough experimental data on a given reaction. It is therefore not surprising that to day in instructions to referees for a well known chemical journal the following sentence can be found: "It would be very helpful if you pay special attention to the Experimental Section, which in the opinion of many chemists is the only one of lasting importance".

Our teaching has been often inadequate and unprecise. A pertinent example where macroscopic and microscopic quantities were indiscriminately mixed can be found in the presentation of the so called energy profile of reaction. Here we can find diagrams such as shown in Fig. 1.

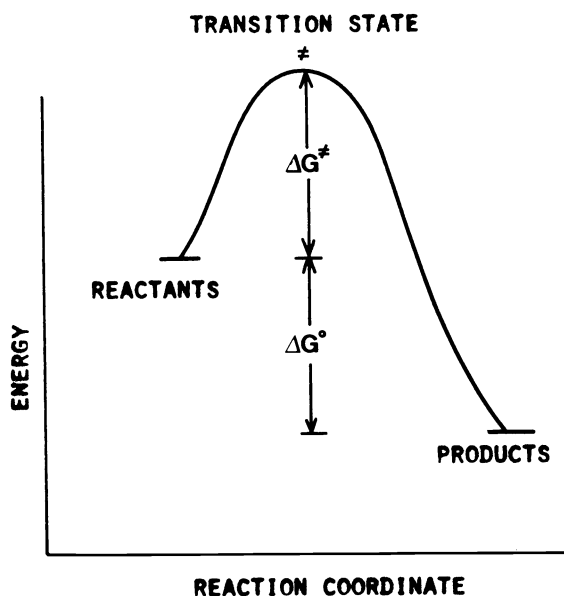


Fig.1

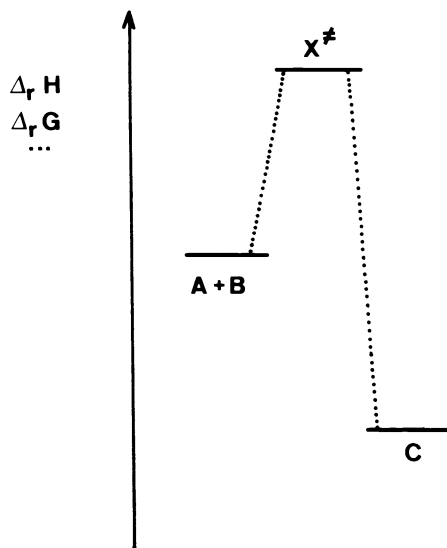


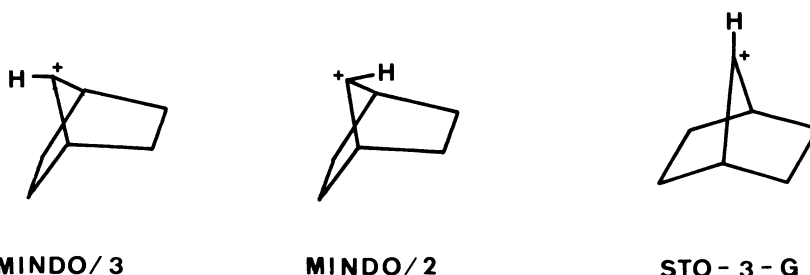
Fig. 2

Is it correct to indicate on the ordinate quantities such as activation energy, enthalpy, or Gibbs (free) energy? In case of a diatomic molecule we have the Morse curve where the reaction coordinate is the internuclear distance, i.e. a geometric parameter. The energy is the electronic energy of two interacting atoms. The same pertains for the bimolecular reaction presented in Fig. 1. The reaction coordinate represents one normal mode of vibration which leads to the decomposition of the activated complex. The quantities used in this description are associated with this particular ensemble of two molecules and we are dealing with microscopic quantities. These must not be mixed with macroscopic quantities such as activation energy, enthalpy or free energy. If a presentation of these quantities is needed, one dimensional diagrams should be used - here the reaction coordinate has no meaning (Fig. 2) (5).

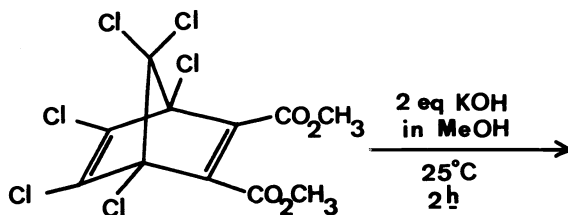
We also often fail to distinguish between experimental and observable facts which are used in developing theories and the theories themselves. How many students will answer to the question why is methane tetrahedral by saying it is because the carbon atom is  $sp^3$  hybridized.

We have learned to live with the inadequacies and limitations of current theories of organic chemistry but what should we tell our students. When discussing the merits of various theoretical methods used in calculating stabilities or geometries of transient species we can easily run into controversial situations. We all teach our students that the Diels-Alder reaction is a concerted symmetry allowed process. What should be said of Dewar's MINDO calculations which favor a stepwise reaction (6). Or, let us take the example of the 7-norbornyl cation. Theory, depending on the level of sophistication gives widely different results for the most stable geometry (7).

#### CALCULATED MOST STABLE GEOMETRIES OF THE 7-NORBORNYL CATION



Students should be made aware of the limiting predictive power of theoretical organic chemistry and it should be repeatedly pointed out that it is the experiment which in the end can only give unequivocal answers. What predictions can be made of the outcome of the following simple and straightforward reaction (8)?



In our age of computers challenging statements can be made about stabilities and reactivities of as yet unknown compounds (9), but to prepare them in another story. Here one has to proceed very carefully balancing the required effort with the relevance of the results. It is unfortunate that the facilities of the computer have been often used as a substitute for experiments thus creating the impression that chemistry can be done without chemicals! It is questionable how many of the numerous calculations and theoretical explanations of present time will survive this century. We cannot foresee how organic texts will look ten years from now, but some predictions can be made. We may expect a trend towards "hardening" of the presently quite soft theories of physical organic chemistry. Probably less time will be needed to see frontline research results incorporated in university curricula. The subject will become more demanding for both the teacher and the student. We see even to day how difficult it is to sort out relevant topics and to make a choice between alternative and sometimes contradictory explanations.

As teachers we must not forget that only a few of our chemistry students will enter the field of basic research. A majority will end up doing applied research or routine analyses. For them it is doubtful of what value would be a detailed knowledge of how to perform extended Hückel MO calcula-

tions or how to apply the frontier orbital method to reactions of organo-metallic compounds. On the undergraduate level these are very useful intellectual exercises but the emphasis in teaching should still be given to the good old classical descriptive chemistry with its numerous tools and tricks which have to be learned the hard way. This has to be primarily done in laboratory courses of greater duration than it is practiced to-day. The undergraduates should also get the basic knowledge of theory but this has to be done in a selective manner. By indicating some of the attractive and successful achievements of theory their interest should be stimulated. A nice example for an agreement between theory and experiment are the calculations of stabilities of "unstable" molecules such as vinyl alcohol and hydrogen isocyanide and their detection or predictable detection in intrastellar space (10).

What is really important is to teach the students how to apply the scientific method in solving problems both theoretical and practical but in doing this we should not treat all our students as future scientists. Those few who have the gift and the motivation to become scientists will appreciate our selective and discriminative approach towards theory which by no means should become its own purpose. It is the Ph.D. student who has to learn what is the scope and limitation of present theories, and he has to be told the whole truth. The appeal of chemistry does not lie in its mathematical formalism - those who seek information in numbers only go into mathematics but seldom into chemistry. Only by combining reliable experimental results with general theoretical principles organic chemistry can be upgraded to the level where it belongs. In addition students should be introduced to the philosophy of how theories are developed, a field where most physical scientists are quite deficient. By choosing appropriate examples links between theory and observable phenomena should be established keeping always in mind the fact that theories are not absolute truths but rather our inventions developed in order to account for the observable facts. They are based on models but these models are subject to changes as new facts are discovered.

#### REFERENCES AND NOTES

1. It is usually thought that it was the famous textbook by Cram and Hammond (2) which marked the departure from the classical way of teaching organic chemistry. However, arrows and "polka dots" representing electrons and changes in electron density as well as descriptions of reaction mechanisms can be found much earlier but apparently these texts were overlooked or ignored by organic chemists of that time (3).
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