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Using Quantum Chemistry to Achieve Sustainable Processes - How the Behavior of Electrons Determines Reactions

Chemical research is often based on trial and error. In the laboratory, things often go differently than expected: the reaction stalls or yields too little product. Knowledge of the chemical properties of the substances involved is then no longer sufficient. Instead, chemists would like to "look deeper" into the reaction, to the subatomic level. This is also possible - using high-tech analytics. And quantum chemistry is also increasingly in demand, which reveals critical moments in the catalytic process simply by calculating, for example, the behavior of electrons. At the LIKAT in Rostock, Dr. habil. Olga Bokareva is leading this topics. A current example is a novel Diels-Alder reaction.

Increasing computing power and ever better algorithms have made the modeling of chemical reactions indispensable in research. "Particularly where chemistry is breaking new ground, for example to replace fossil raw materials with the by-products of civilization. Or to expand the range of applications of classic and proven processes and use them for sustainable processes," says Olga Bokareva, head of a junior research group at the Leibniz Institute for Catalysis.

Diels-Alder reloaded: more effective with electricity

The chemist cites the Diels-Alder reaction as a current example. This has had a firm place in organic chemistry for three quarters of a century, particularly in the synthesis of medicinal substances and other complex molecules. Its discoverers were awarded the Nobel Prize for it in 1950.

Several laboratories are currently trying to make the Diels-Alder reaction usable for far more complex syntheses than before. At LIKAT, this was achieved by electrochemical means. Dr. Bokareva explains: "Electrodes in the reaction solution create a current flow that drives the process and makes it much more effective than the classic Diels-Alder reaction."

LIKAT Director Prof. Dr. Robert Franke collaborated with colleagues from Japan and together they submitted a paper. Their experiments had shown that the electrochemical Diels-Alder reaction works wonderfully with certain starting materials, but not at all with others. The authors made assumptions about the causes. However, the journal asked for a detailed mechanistic explanation using quantum chemical methods.

This is where the expertise of Dr. Bokareva and her team came into play. A doctoral student, Yanan Han, took on the work as part of her dissertation.

Comparable to Google Maps

In order to understand the reaction mechanism, the team used quantum chemistry to calculate the energy of the molecules along the reaction path. To do this, it is sufficient to know the starting material and product as well as some information about the reaction conditions, such as the temperature. Dr. Bokareva compares this approach to Google Maps: "You know your location and destination and want to avoid traffic jams, which could be an undesirable intermediate in the reaction. The program calculates the best route."



Fig.1 : Dr. habil. Olga Bokareva. Photo: private

Such quantum chemical calculations do not provide exact values, but approximations, explains Dr. Bokareva. The current state of individual molecules is the difference between their energy states. The reason for this lies in the quantum nature of electrons, which are described by wave functions.

The mathematical basis for such calculations was developed around a hundred years ago, such as the Schrödinger equations, which Olga Bokareva and her team use together with numerical methods.

Electron clouds determine the reaction

Today, the results can be represented graphically, for example as orbitals, which are the locations of the electrons in the atom. On the screen, they appear as colored shapes reminiscent of floating balloons. "We often talk about electron clouds when we mean the diffuse space in which electrons reside," says Olga Bokareva. Such representations would help not only to analyze reaction processes, but also to understand them intuitively. "Quantum chemistry is not only challenging, it is also beautiful."

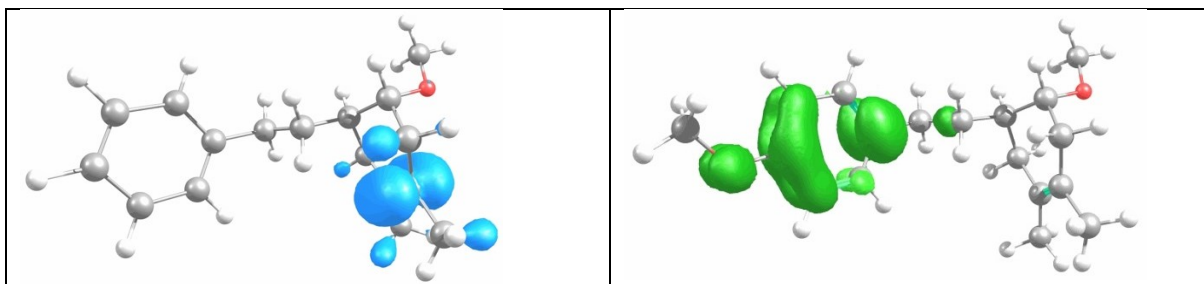


Fig. 2 Electron clouds of two substrates in comparison. Graphics: O. Bokareva

What did the calculations show about the novel Diels-Alder reaction? "We were able to identify an intermediate product that is formed at a critical moment in the process," says Dr. Bokareva. In order for the reaction to continue, this intermediate needs an additional electron. The system must allow this electron transfer in terms of energy, and the researchers were able to demonstrate specific prerequisites for this in the behavior of the electron clouds. In the case of the problematic substrates, these prerequisites were missing and the reaction broke down.

The reason for the disruption has therefore been found, the evidence has now been published together with the partners from Japan and has recently appeared online. According to Dr. Bokareva, the work offers approaches for making the previously unsuccessful substrates usable for electrochemical Diels-Alder synthesis. For example, by changing the electronic structure of these compounds or the electrochemical reaction conditions.

No longer a male domain

It may sound astonishing that this gain in knowledge is possible through theoretical work. For Olga Bokareva, it is a matter of course to clarify puzzling experimental findings and make hidden mechanisms visible through pure calculation and "genuine teamwork". This fulfills her more than working in the laboratory, which was many years ago.

Olga Bokareva received her doctorate and habilitated - both times in the fields of theory and quantum chemistry, which for a long time were strongly male-dominated. This is another reason why she is proud that four of her doctoral students are women. Her group is constantly growing and is working on current issues at the interface between theory and application.

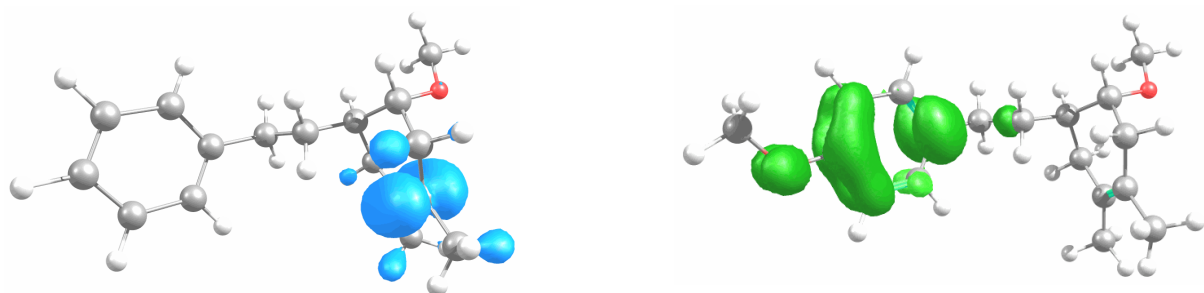


Fig. 3: Electron clouds of two substrates in comparison - they influence how the reaction takes place. Modified illustration from: <https://doi.org/10.1039/D4CY01192A>

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Contact:

Dr. habil. Olga Bokareva
Olgaa.bokareva@catalysis.de