

Research article

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Thinking like an electron: concepts pertinent to developing proficiency in organic reaction mechanisms

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Abstract: The difficulties students face with organic reaction mechanisms have been the subject of much research in chemical education however, no concept inventory has been reported in this area. The development of a concept inventory would be useful for the large-scale assessment of students' understanding of concepts pertinent to developing proficiency in reaction mechanisms. The first step in the design of such an inventory is identifying the pertinent concepts. In phase 1 of this study, open-ended interviews were carried out with organic chemistry instructors ($N = 11$) in order to ascertain their opinions on pertinent concepts for developing proficiency in reaction mechanisms. Phase 2 of the study consisted of a national survey of organic chemistry instructors ($N = 183$) to explore the general consensus regarding the concepts identified in phase 1. The results yielded 10 concepts identified by experts to be pertinent to reaction mechanisms. The general consensus among organic chemistry instructors is that the topic of reaction mechanisms is important to the study of organic chemistry, but students have difficulty understanding the meaning of the curved-arrow notation. Future work will include the design and development of a concept inventory based on these pertinent concepts.

Keywords: concepts for proficiency; organic chemistry education; organic reaction mechanisms.

Introduction

Organic chemistry is a required course not just for chemistry majors but also for various other majors (Seymour & Hewitt, 1997). Pre-health students are required to take organic chemistry to apply to medical, dental, and optometry schools; however organic chemistry is usually perceived as a “weed-out” class which separates out the students not qualified for medical school (Moran, 2013). Among the organic chemistry students, the course has a reputation of being a gatekeeper: difficult, complex, and with some material that students may perceive as being irrelevant (Grove, Cooper, & Cox, 2012).

An important topic in undergraduate organic chemistry is reaction mechanisms. The use of the curved-arrow notation or the electron-pushing formalism to convey electron flow during bond breaking and bond making is of great importance in the teaching and learning of organic chemistry (Grove, Cooper, & Rush, 2012).

The importance of reaction mechanisms in an organic chemistry class was emphasized in the qualitative study by Duis (2011). In this study organic chemistry instructors' opinions on concepts that are important, core, or foundational in organic chemistry were explored and the results indicated that 16 of the 18 participants

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identified reaction mechanisms as an important organic chemistry topic. It was further reported that 15 of the 18 participants stated that the topic of reaction mechanisms is difficult for organic chemistry students.

Bhattacharyya and Bodner (2005) have argued that the ability to use the curved-arrow notation in reaction mechanisms is a vital skill for organic chemists to possess. Bhattacharyya (2013) has shown that students use this curved-arrow notation as their primary tool to explain and/or predict reaction outcomes including the generation of side products, regioselectivity, and stereochemistry.

There are several qualitative studies showing that undergraduate students and even graduate students encounter difficulties when using the curved-arrow notation to propose reaction mechanisms; these difficulties include a failure to understand the basic purpose of the notation and how to utilize it effectively for problem-solving (Anderson & Bodner, 2008; Bhattacharyya, 2014; Bhattacharyya & Bodner, 2005; Ferguson & Bodner, 2008; Grove, Cooper, & Rush, 2012; Kraft, Strickland, & Bhattacharyya, 2010). Flynn and Ogilvie (2015) reported a “mechanisms-first” approach to teaching organic chemistry rather than the traditional functional-group approach. The existing organic chemistry curriculum was modified to introduce reaction mechanisms before students learned a single organic reaction. The aim of this curricular change was to ensure that students learn to interpret reactions based on patterns of reactivity which would assist them when they are faced with new reactions.

Studies have also shown that students are unable to attribute any meaning to the curved-arrows when utilized to depict reaction mechanisms (Bhattacharyya & Harris, 2018; Galloway, Stoyanovich, & Flynn, 2017). The results indicated that students struggled the most with describing the structural representations, and different students used a different language to describe the same reactions.

A recent study (Bodé, Deng, & Flynn, 2019) explored the causal mechanistic explanations that organic chemistry students provide when comparing two proposed reaction mechanisms. The results indicated that the majority of the students understood the need for providing causal arguments to support their claims but they did so irrespective of whether the claims were correct or incorrect. Therefore the conclusion that can be drawn is that students tend to struggle with using mechanistic thinking to make claims and explain them.

The difficulties that students face with reaction mechanisms seems to stem from a lack of understanding of fundamental concepts. Studies exploring student understanding of fundamental organic chemistry topics (Anzovino & Bretz, 2016; Cruz-Ramirez De Arrellano & Towns 2014), indicate that students possess gaps in their knowledge such as classifying substances as nucleophiles and/or bases and accurately describing the steps that take place and the intermediates that are formed during the course of the reaction. These studies demonstrate that students lack the fundamental skills needed to solve mechanistic questions.

While these qualitative studies are important to gain an understanding of how students view reaction mechanisms and the difficulties they face, no concept inventories have been developed to conduct large-scale assessment of students' understanding of concepts that are pertinent to developing proficiency in organic reaction mechanisms. ACID I (McClary & Bretz, 2012) is an inventory that was developed to test organic chemistry students' alternate conceptions of acids and bases but there are no inventories to test students' alternate conceptions of other organic chemistry concepts pertinent to reaction mechanisms. The development of such an inventory would help organic chemistry instructors gain insight into their students' understanding of pertinent concepts before they start the study of reaction mechanisms. Instructors can then decide if they need to review some of these concepts before teaching reaction mechanisms or modify their course content to incorporate some of these concepts. Additionally, the inventory may inform the general chemistry instructors on concepts taught in general chemistry that are further used in organic chemistry. To develop such an inventory, it is necessary to obtain information on the concepts that are pertinent to developing proficiency in organic reaction mechanisms.

The present study was divided into two phases. The first phase consisted of open-ended interviews with organic chemistry instructors to obtain their opinion on concepts that they consider are pertinent to developing proficiency in organic reaction mechanisms. The second phase consisted of a national survey to generalize the results obtained from the first phase. With this aim in mind the research questions that govern this study are:

- (1) What are the chemistry concepts perceived by experts to be pertinent to developing proficiency in organic reaction mechanisms?
- (2) Is there a consensus at the national level regarding the concepts perceived to be pertinent to developing proficiency in organic reaction mechanisms?

Methodology

Phase 1: Semi-structured, Open-ended interviews

Participants: Interviews were conducted with a purposeful sample (Creswell, 2013) of organic chemistry instructors. The main criterion for participation was that the instructors had to have had experience with teaching the organic chemistry course. An invitation was sent via email to instructors at universities in the Rocky Mountain region of the USA. The sample consisted of 11 organic chemistry instructors (five females and six males). Among the participants, 10 had doctorate degrees and one had a master's degree as their highest earned degrees in chemistry. Based on the Carnegie classification of universities, three participants were from an M1 university (masters colleges and universities – larger programs), six participants were from a D/PU university (doctoral/professional universities), and two participants were from an R1 university (doctoral universities – very high research activity). Among the 11 participants, eight participants had over 10 years of teaching experience and nine participants mentioned the use of the ACS standardized exams in their classes. Prior to data collection, Institutional Review Board approval was obtained through the University of Northern Colorado (1185245-1).

Data collection: The data were collected using semi-structured, open-ended interviews (Creswell, 2013) with organic chemistry instructors to gain their opinions on organic reaction mechanisms and the concepts involved in the process. All participants were asked to provide demographic information before the interview was conducted. The full protocol for the interviews along with demographic questions is provided in the Supplemental Information. All participants were assigned a code (OI# for organic chemistry instructor followed by a number) to maintain their anonymity. The interviews lasted approximately 30–45 min. The participants were asked to provide their opinions on the importance of organic reaction mechanisms, the concepts that are pertinent to developing proficiency in organic reaction mechanisms, and the difficulties students face with organic reaction mechanisms. Additionally, they were asked about their approach to teaching organic reaction mechanisms and problems that can be solved in organic chemistry with the electron-pushing formalism.

Data analysis: The interviews were transcribed verbatim except for stammering phrases such as 'uh' and 'um' which were removed for clarity. An inductive approach to thematic analysis was used where codes and themes were created from the data (Riessman, 2008). The validity and reliability of the data obtained were established by member check and inter-rater reliability (Creswell, 2013). The transcripts were sent back to the participants as a form of member-check for them to make sure the information was accurate. They were also asked to add details to help clarify their ideas. The transcripts were evaluated by four other researchers with experience in chemical education as a form of inter-rater reliability to check the reliability of the identified themes giving a percentage agreement of 95%.

Phase 2: national survey

Participants: A national survey was administered to organic chemistry instructors across the USA. An email list of organic chemistry instructors at different universities across the USA was compiled using the research group indices database from the organic chemistry division of the American Chemical Society (ACS) (Organic Synthetic Faculty, 2020; OrganiclinksPUI, 2018). A total of 1500 organic chemistry instructors were invited to participate and 183 completed the survey for a response rate of 12.2%. Of the participants who completed the survey, 127 were male, 181 had earned doctorate degrees in chemistry, 158 had over five years of organic chemistry teaching experience, 111 were from primarily undergraduate institutions (PUI), and 91 used the ACS

standardized exams in their class. Prior to data collection, Institutional Review Board approval was obtained through the University of Northern Colorado (1245324-1).

Survey instrument: The survey was created on Qualtrics and consisted of five sections including a consent form, a screening question, questions on concepts, questions on the participants' opinions regarding reaction mechanisms, and demographic questions. The participants were asked to give their consent on the first page of the survey and if they have taught or are currently teaching an undergraduate organic chemistry course. If they failed to give their consent or answered "no" to the question on teaching an undergraduate organic chemistry course, they were directed to the end of the survey. The concepts identified by experts from Phase 1 were included on the national survey, and additionally a space was provided for comments or addition of new concepts. Participants were asked to classify the concepts in terms of their relevance to developing proficiency in organic reaction mechanisms using a scale of important (critical for proficiency in organic reaction mechanisms), foundational (moderately critical for proficiency in organic reaction mechanisms) and not important (not critical for proficiency in organic reaction mechanisms). The participants were asked for their opinions regarding the importance of organic reaction mechanisms, their approach to teaching organic reaction mechanisms, and the barriers that students face when learning reaction mechanisms. Demographic information was also collected from the participants. Example questions from the national survey as well as demographic questions are shown in the Supplemental Information.

Data collection: An initial email with a link to the Qualtrics survey was sent to the participants. The survey was open for one month with a reminder email being sent two weeks after the initial email was sent. All participants were given a code (NS# for national survey followed by a number) in order to maintain their anonymity.

Data analysis: The data were analyzed in Qualtrics. The percentage of responses for each concept was analyzed. The concepts that were identified as important were retained. The concepts that were identified as foundational were further analyzed by examining the comments of the participants regarding the concepts.

Results and discussion

Phase 1: semi-structured, open-ended interviews

Importance of reaction mechanisms: Ten (91%) participants indicated that organic reaction mechanisms are important to the success of students in their organic chemistry courses. One of the organic chemistry instructors (OI 003) mentioned that organic reaction mechanisms are important only at the beginning of the course, and students seem to use it as a tool for predicting the product of reactions only initially:

"What I find frequently is that once the students can understand the process of the movement of electrons they are more easily able to say okay this is very repetitive across different reaction styles. That's when they can rely less on completing a mechanism in order to predict the product of a reaction." OI 003

Nine (82%) participants said that understanding intermediates in reactions, reaction rates, and acid-base chemistry are the types of problems one can solve using the arrow-pushing formalism. Five (46%) participants mentioned that every problem in organic chemistry can be solved using the arrow-pushing formalism. These results confirmed and emphasized the importance of organic reaction mechanisms in the study of organic chemistry.

Approach to teaching the course: When asked whether they used the functional group approach or mechanisms based approach when teaching their course, five (46%) of the participants indicated they use a combination of both, and four (36%) of the participants mentioned teaching by using the functional group approach because traditionally in textbooks the organization of the chapters is based on functional groups.

These four participants stated that ideally they would like to use more of a mechanistic approach to teaching their classes which further reiterates the importance of mechanisms in organic chemistry.

When asked how they introduce the topic of reaction mechanisms to their students, seven (64%) of the participants indicated using acid-base chemistry. These participants indicated that their students are exposed to the arrow-pushing formalism when they are introduced to acid-base chemistry but the first time they see a complete mechanism is when they cover electrophilic addition reactions of alkenes or substitution reactions of alkyl halides. This suggests that a fundamental understanding of the arrow-pushing formalism is important for understanding other topics covered in the organic chemistry course.

Concepts pertinent to developing proficiency in reaction mechanisms: Of the total participants, seven (64%) mentioned that resonance and induction effects are pertinent while six (54%) of the participants stated that electron density and polarity, acids and bases, and electrophiles and nucleophiles are pertinent to developing proficiency in reaction mechanisms. The full list of concepts identified, the number of participants who identified these concepts and the ranking based on percentage agreement are shown in Table 1.

Atomic structure, electronic configuration, Lewis structures, molecular geometry, and bonding are concepts covered in general chemistry and typically reviewed in the beginning of a first-semester organic chemistry course. Acids and bases, electron density and polarity, and hybridization are also covered in general chemistry but they are typically reviewed in detail in the first-semester organic chemistry class and their applicability to organic chemistry is introduced. Resonance and inductive effects, electrophiles and nucleophiles, and stability of intermediates are covered usually within the first month of a first-semester organic chemistry course.

Difficulties students face: Of the participants, six (54%) mentioned that one of the main barriers to understanding reaction mechanisms that students face is the difficulty in understanding how the tool works and what the arrows actually represent. One of the participants (OI 011) explained how students in general are unable to give proper meaning to the curved-arrows:

"I guess to some extent just arrow pushing backwards. A lot of the time people don't quite understand that arrows are electrons only, nothing else ever. And so you see arrows coming off of plus charges drifting around the molecule and arrows backwards for a step that would otherwise be valid." OI 011

Lack of understanding of fundamental general chemistry principles like Lewis structures and acid-base chemistry was identified as another reason why students struggle with reaction mechanisms by five (46%) of the faculty interviewed. This is one of the participant's (OI 004) opinion:

"One big issue that people have is they don't actually pay attention to how many lone pairs there are on hetero atoms. They don't think about the lone pairs unless they are really explicit and so that's one issue. Another issue is they don't actually understand

Table 1: Concepts identified as pertinent to developing proficiency in organic reaction mechanisms.

Concepts identified	Number of participants (N = 11)	Percentage agreement (%)
Resonance & inductive effects	7	64
Acids & bases	6	54
Electrophiles & nucleophiles	6	54
Electron density & polarity	6	54
Atomic structure	5	46
Electronic configuration	5	46
Lewis structures	5	46
Hybridization	5	46
Molecular geometry	5	46
Stability of intermediates	4	36
Bonding	2	18

really where the electrons are located. So they will kind of draw random arrows and you need to have the arrow pointing exactly who you are going to bond up to and they tend to be vague and sloppy on that. And that indicates to me that they don't really understand where the electrons are really located and that whole idea of breaking bonds and forming bonds it's not inculcated in their brain. They are just trying to memorize mechanisms as just like little lines on a little drawing type of thing you know." OI 004

This participant talked about students resorting to rote memorization of reaction mechanisms. Five other participants also mentioned that students seem to struggle with variations in reaction patterns and resort to rote memorization.

Phase 2: national survey

The results from Phase 1 were limited to the 11 participants from universities in the Rocky Mountain region of the USA. In order to generalize the results and gather information on what the consensus is at the national level regarding the concepts perceived to be pertinent to developing proficiency in reaction mechanisms, a national survey was conducted. Participants were asked to classify the identified concepts as important, foundational, or not important to obtain information on the relative importance of these concepts towards developing proficiency in organic reaction mechanisms. This information could assist in the design and development of items for the concept inventory. The 183 participants in this phase of the study were asked the same questions as those used in Phase 1 of the study.

Importance of reaction mechanisms: Of the participants, 87% stated that reaction mechanisms are important for their students' success. One participant's (NS 047) comment suggests that students could move forward with a limited familiarity of reaction mechanisms but it could affect their long-term understanding:

"Students can be moderately successful in organic chemistry 1 but they will struggle in organic chemistry 2 without a good understanding of mechanisms." NS 047

These results are consistent with the results from Phase 1 of the study where 91% of the participants indicated that reaction mechanisms are important for their students' success in organic chemistry.

Approach to teaching the course: As was the case in Phase 1 of the study, the participants were divided on their opinion of a functional group based approach versus a mechanisms based approach to teaching organic chemistry. Among the participants, 51% mentioned that they use a combination of both and 33% of the participants indicated they use a mechanisms based approach. The general consensus seems to be one where instructors prefer to use a combination of both methods as suggested by one participant's (NS 127) comment:

"Try to relate to mechanisms even when using a functional group approach. Functional group approach helps later in synthesis problems." NS 127

When the participants were asked how they introduce the topic of mechanisms, 74% indicated using acid-base chemistry which is comparable to the 64% of participants in Phase 1 who provided the same answer. These results indicate that most organic chemistry instructors use acid-base chemistry as the foundation for building an understanding of reaction mechanisms.

Concepts pertinent to developing proficiency in reaction mechanisms: Of the 11 concepts derived from Phase 1 of the study, nine were identified as important for developing proficiency in organic reaction mechanisms by more than 60% of the national survey participants. A larger percentage of participants stated that these concepts were important (critical) rather than foundational (moderately critical). For the concept of atomic structure, only 24% of the participants mentioned that it is important, 66% stated that it is foundational, and 10% stated that it is not important. Similarly, for the concept of electronic configuration 34% of the participants indicated that it is important, 58% stated that it is foundational, and 9% stated that it is not important. Since the

number of participants identifying that the two concepts were not important was less than 10% and due to the fact that we defined foundational as moderately critical, the comments made by the participants who determined these two concepts to be foundational, were further analyzed. It was found that 81% of these participants considered the concept of valence electrons to be more important to reaction mechanisms than the broad concepts of atomic structure and electronic configuration. The concept of valence electrons is related to both atomic structure and electronic configuration. Due to these results the two concepts of atomic structure and electronic configuration were combined under the concept of valence electrons instead. These results indicate that there is a general consensus at the national level regarding the concepts that are pertinent to developing proficiency in organic reaction mechanisms. A complete list of concepts and participants' opinions are presented in Table 2.

Participants in Phase 2 were asked to provide other concepts they considered important for developing proficiency in reaction mechanisms. The topics that were provided are ones that are usually covered under the major concepts identified such as understanding pK_a which is related to acid-base chemistry and formal charge, electron dot diagrams, and octet rule which are all related to Lewis structures. This information is useful while developing questions for the concept inventory since specific areas of each concept can be addressed.

Difficulties students face: Participants in Phase 2 of the study were asked to give their opinion on difficulties students face with understanding reaction mechanisms. The most common difficulties stated were lack in understanding of electron flow, failure in understanding the basics of bonding and valency, remembering fundamentals from general chemistry, and identifying electrophiles and nucleophiles. A consequence of these difficulties is that students resort to rote memorization. These results are consistent with those obtained in Phase 1.

Limitations

In Phase 2 of the study 60.8% of the participants were from a primarily undergraduate institution (PUI) with only 18.2% from an R1 school and even less from other institution types; was dictated by the number of participants who chose to complete the online survey. The final list of concepts represents the opinion of 183 participants out of the 1500 that were invited to take part in the national survey giving a response rate of 12.2%.

Table 2: List of concepts and participants' percentage agreement from the national survey.

Concepts	Important	Foundational	Not important
Resonance & inductive effects	86%	14%	<1%
Acids & bases	79%	21%	<1%
Electrophiles & nucleophiles	92%	8%	<1%
Electron density & polarity	81%	18%	<1%
Atomic structure	24%	66%	10%
Electronic configuration	34%	58%	9%
Lewis structures	87%	13%	<1%
Hybridization	68%	31%	1%
Molecular geometry	64%	35%	1%
Stability of intermediates	84%	16%	<1%
Bonding	82%	17%	1%

Note: Important was defined as critical for developing proficiency in reaction mechanisms. Foundational was defined as moderately critical for developing proficiency in reaction mechanisms.

Not important was defined as not critical for developing proficiency in reaction mechanisms.

Although this response rate might seem low, it is comparable to the response rates reported for national surveys conducted in other studies (Bhattacharyya, 2013; Emenike et al., 2013).

Conclusions and future work

The purpose of this multi-step study was to gather the opinions of organic chemistry instructors regarding concepts that are considered pertinent to developing proficiency in organic reaction mechanisms. The results from Phase 1 of this study indicated that there were 11 concepts perceived by experts to be pertinent. Among the 11 concepts identified in this phase five concepts, electronic configuration, Lewis structures, polarity, acid-base chemistry, and electrophiles and nucleophiles, were found to be similar to those previously reported (Bhattacharyya, 2013). In addition to these concepts six new concepts were identified in this study; these include resonance and inductive effects, atomic structure, hybridization, molecular geometry, stability of intermediates, and bonding. The results of phase 1 were compared to the results obtained at the national level (phase 2), and it was found that the general consensus is very similar. The concepts of atomic structure and electronic configuration were combined under the concept of valence electrons based on the comments of the participants in the national survey to yield a final list of 10 concepts that were retained. The concepts that are considered pertinent to developing proficiency in organic reaction mechanisms in increasing order of importance are valence electrons, electron density and polarity, molecular geometry, hybridization, acids and bases, bonding, stability of intermediates, resonance and inductive effects, Lewis structures, and electrophiles and nucleophiles.

The results generated from this study indicate a general consensus among organic chemistry instructors regarding the importance of reaction mechanisms for gaining a comprehensive understanding of organic chemistry. From the instructors' perspective, students seem to have the greatest difficulty with understanding what the arrows in the curved-arrow notation mean, and consequently the students resort to rote memorization. A conclusion that can be drawn from these results is that the struggle with reaction mechanisms can be attributed to a lack of understanding of fundamental general chemistry and organic chemistry concepts which is consistent with the literature (Anzovino & Bretz, 2016; Bhattacharyya, 2013; Bhattacharyya & Bodner, 2005). This general consensus at the national level regarding the lack of fundamental general chemistry and organic chemistry understanding is troublesome and demands an intervention. One possible intervention could be better communication about content coverage between general chemistry and organic chemistry instructors to facilitate students' transition into an organic chemistry class. Organic chemistry instructors could also focus more on an in-depth general chemistry review at the beginning of their class which would help students refresh their memory on these fundamental general chemistry concepts needed for organic chemistry. Additionally, these results indicate that before we can explore student thinking and thought processes that lead to this difficulty with reaction mechanisms, it is important to make sure we are providing them with the necessary tools needed to develop mechanistic thinking. It may be difficult for students to use mechanistic thinking to solve higher order problems if they are struggling with fundamental chemistry concepts.

The development of a concept inventory for the large-scale assessment of students' understanding of these pertinent concepts would be useful for organic chemistry instructors to assess their students and address these alternate conceptions before introducing reaction mechanisms. The next phase of this research will be the design, development, and psychometric analysis of the inventory based on our findings and reported literature.

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