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ABSTRACT

Correctly predicting the products and having a qualitative understanding of their ratios is a fundamental skill fostered in organic chemistry. This skill can involve electron-pushing formalism (EPF) and reaction coordinate diagrams (RCDs). These representations can be important for evaluating whether product formation is driven by kinetic or thermodynamically favored rationale. For this research, students in organic chemistry were given a two-stage investigation. First, they were given an online multiple-choice assessment surrounding three distinct types of reactions for elucidating understanding of product formation: the Markovnikov addition of HBr to an alkene, an E2 elimination favoring the Zaitsev product, and an E2 elimination favoring the Hoffman product. This task was followed up with a semi-structured interview involving these same three reaction contexts to identify what resources were activated in their rationale for determining major and minor products, and how these resources were applied to create RCDs. Our findings indicate that these students focus predominately on resources associated with intermediate stability for the stepwise Markovnikov addition, with limited activation of resources regarding product stability. Conversely, resources focusing on product stability were activated more often with concerted eliminations. When provided with possible RCDs, activation of additional resources was observed. These data highlights the need for the integrated use of RCDs and creates the...
impetus for future studies on scaffolding these resources to encourage their activation during analyses of novel reactions.

**GRAPHICAL ABSTRACT**

![Graphical Abstract Image](image)

**KEYWORDS**
Second Year Undergraduate, Organic Chemistry, Problem Solving/Decision Making, Reactions, Chemical Education Research

**INTRODUCTION**
Acquiring mechanistic reasoning skills to explain how and why reactions occur is a central learning outcome in organic chemistry. The Morrison and Boyd\textsuperscript{1} electron pushing formalism (EPF) representations have been widely adopted in undergraduate organic chemistry since their textbook was first published in 1959,\textsuperscript{2,3} and EPFs are perhaps the most important representation in organic chemistry.\textsuperscript{4} EPFs illustrate the movement of electrons to explain the specific order in which bonds are broken and formed in a chemical reaction by depicting
the lowest energy and most kinetically favored pathway. Despite the goal of EPFs to promote understanding and the development of mechanistic reasoning skills, students often memorize EPF representations and attempt to regurgitate\textsuperscript{3, 5-7} these representations on formative and summative assessments. Students’ reliance on memorization of EPFs\textsuperscript{8-11} is further supported by findings reporting students are unsure of the physical meaning and interpretation of EPFs.\textsuperscript{3, 12} Students’ understanding of the physical meaning of EPFs is improved by incorporating kinetics and thermodynamics when discussing reaction mechanisms.\textsuperscript{13, 14} Kinetic and thermodynamic arguments can be coupled with EPFs using Reaction Coordinate Diagrams (RCDs), which are two-dimensional graphical representations of the energy changes as a function of structure. Coupling EPFs and RCDs provides a multi-dimensional representation depicting the sequence in which bonds are broken and formed and the relative energy changes of a structure over a reaction.

This research study expands on existing research on RCDs in general chemistry\textsuperscript{15-21} and was specifically guided by Popova’s research in organic chemistry.\textsuperscript{22-24} The general chemistry studies provided insight into how students interpret and analyze RCDs. Parobek et al.\textsuperscript{18} analyzed students’ conceptions of the x-axis on RCDs and associated challenges with making inferences about reaction rates. Parobek et al. emphasized the importance of using RCDs across the curriculum, such as while discussing organic mechanisms.\textsuperscript{18} Lamichhane et al.\textsuperscript{17} likewise identified students’ challenges with interpreting the x-axis. Atkinson\textsuperscript{25, 26} developed a Reaction Coordinate Diagram (RCD) Inventory that analyzed students’ understanding and confidence in interpreting RCDs. Atkinson reported an improvement in interpreting RCDs as students progress across the chemistry curriculum.\textsuperscript{25} Additionally, Atkinson reported a correlation between performance and student confidence.\textsuperscript{25}

Popova’s studies\textsuperscript{22-24} focused on organic chemistry students and organic-specific reactions. Organic chemistry students were asked to analyze RCDs to assess their understanding of the
starting and ending points of RCDs, the chemical interpretation of peak height and peak width, and the meaning of peaks and valleys in RCDs.\(^\text{24}\) The study provided insight into common challenges that organic chemistry students face when analyzing RCDs. Popova reported that students tend to focus predominately on the major product when analyzing RCDs and ignore nuanced details, which is a key finding because of the significance of the nuanced information in explaining kinetics and thermodynamics.\(^\text{23}\) This study extends on Popova’s studies by considering how students rationalize the major and minor products formed in different reaction contexts – specifically when the product distribution must be rationalized by a careful analysis of the kinetics and thermodynamics.

The specific research questions, designed by guidelines presented by Bunce\(^\text{27}\), are:

**Research Question 1 (RQ1):** What resources are activated and productively applied when constructing RCDs across organic reactions with differing thermodynamic and kinetic favorability?

**Research Question 2 (RQ2):** How does prompting a selection of RCDs impact the mechanistic reasoning, resource activation, and representational competence during interviews with undergraduate students?

The research aims to identify pedagogical strategies for effectively incorporating more productive discussions of energetics in the organic chemistry curriculum.

**THEORETICAL FRAMEWORKS**

**Representational Competence**

EPFs and RCDs are visualizations used to communicate information about chemical phenomena. Representational competence (RC) is the theoretical framework referenced by Popova\(^\text{22-24}\) and Atkinson’s\(^\text{26}\) previous research on RCDs. From Kozma and Russell\(^\text{28}\), RC is defined as a “set of skills and practices that allow person to reflectively use a variety of representations or visualizations, singly and together, to think about, communicate, and act
on chemical phenomena.” To construct RCDs, students must demonstrate competence in understanding the information provided by RCDs and how this information is graphically conveyed. For example, a concerted reaction has only one energy maxima versus a stepwise reaction with more than one energy maxima. More detailed information is provided that illustrates the relationship between RC and the resources framework in Figures 3 and 4.

**Resources Framework**

The research was further guided by the resources framework developed by Hammer and Elby\(^ {29-31} \). Wittman,\(^ {32} \) Parobek et al.,\(^ {18} \) and Rodriguez\(^ {33} \) define a resource as “fine-grained knowledge” elements that are activated and contribute productively or unproductively in problem-solving. Modir et al.\(^ {34} \) further extended the definition of resource to “a manifold of knowledge pieces.” The manifold of knowledge pieces is context-dependent,\(^ {33} \) with resources being activated to differing extents based on the prompt or other cues, and resources activated will evolve with student experiences. The grain size of a resource varies widely based from fundamental phenomenological primitives (p-prims),\(^ {35-38} \) which are accepted facts used in explanations to complex theories.\(^ {38} \)

Research question 1 compares the resources activated when constructing RCDs for reactions having differing mechanisms and kinetic and thermodynamic favorability. Research question 2 compares and contrasts the resources activated as students construct RCDs before and after a set of perceptual cues. These multidimensional research questions are key because researchers and practitioners can use the findings to develop scaffolds to better instruct students in constructing RCDs and rationalizing them to organic mechanisms, ultimately leading to a deeper understanding of the logic behind chemical reactions. The resources framework aligns with scaffolding activities because the framework asserts that conceptual understanding is not stable but dynamic depending on the resources activated, which likewise depends on the context, such as the type of reaction.\(^ {39} \)
For organic chemistry, EPFs are used to explain the pathway reactions that follow, and RCDs are used to explain the energetics of these pathways. To successfully write EPFs and construct RCDs, resources must be activated and productively applied to different representations. Specifically, the activation of the resource, “the reaction is stepwise” can only be applied productively if students have RC with RCDs.

METHODS

Research Setting

The research was conducted at a private research-intensive R1 university in the Southern United States. The university uses a 1-2-1 model for chemistry in which students take General Chemistry I, then a year of organic chemistry, and complete General Chemistry II as the fourth course in the sequence. The institutional review board (IRB) approved the data collection using a Qualtrics multiple choice survey (IRB #2022-0203, IRB #2022-0270). The survey was implemented in two Organic Chemistry II courses: (1) Spring 2022 (N=46, at the end of the course) and (2.) Summer 2022 (N = 46, at the beginning of the course). The participants enrolled in Organic Chemistry were predominantly sophomores interested in pre-health and medical school. The demographics of the class were representative of the tabulated student population.\textsuperscript{40} Data were discarded for participants less than 18 years of age or who declined to have their data included in the study.

The interview protocol and prompts were approved by the IRB (IRB #2022-0366). Nine participants were recruited from Organic Chemistry I, a separate course from the ones surveyed, in the spring of 2022. There were two sections of Organic Chemistry I taught by different instructors, but the content and textbook\textsuperscript{41} were shared across both classes. All participants were first-year students, and as first years, they had not officially declared majors. Of the nine participants, seven identified as female, and two identified as male. The interviews were conducted in the 12\textsuperscript{th} and 13\textsuperscript{th} weeks of the semester. Addition, substitution,
and elimination reactions were taught and assessed in both sections before the interviews. Participants received a gift card as compensation.

**Data collection**

The Qualtrics survey was administered to two sections of Organic Chemistry II. During the spring of 2022, the survey was administered in a recitation section, and points were not awarded. During the summer of 2022, the survey was assigned as homework, and participation points were awarded.

The semi-structured, think-aloud interview format was tailored based on Popova’s study. Two researchers conducted the interviews using a semi-structured interview guide, and two trial interviews with volunteers were conducted before starting the research interviews. Participants were instructed to analyze the reaction and construct RCDs that best explain the product distribution. Students were provided an iPad and an Apple pencil and were asked to draw structures, transition states, EPF mechanisms, or other figures of importance while verbally outlining their thought processes. The iPad screen was recorded to capture drawings and audio. Zoom was used as a backup to capture the voice recording with the video capture turned off.

**Description of Survey Multiple Choice Items and Interview Prompts**

A multiple-choice Qualtrics assessment was developed using common reactions presented in Organic Chemistry I. The survey consisted of ten multiple-choice items – three of which will be discussed in this study. The three items are shown in Figures 1 and 2. The same questions were used for the interview prompts, but participants were instructed to construct RCDs and explain their reasoning during the interviews. Once participants finished constructing their RCDs, the multiple-choice options, as shown in Figures 1 and 2, were provided. Participants were allowed to change their answers to one of the options provided or...
keep their original RCD. Again, they were instructed to provide an explanation to support their decision.

The three items were designed to illustrate reaction scenarios in which the major and minor products have different kinetic pathways but are similar in terms of thermodynamic favorability (Figure 1, Problem 1), in which the major product is both the kinetic and thermodynamic product (Figure 2, Problem 2), and in which the major product is the kinetic product but not the thermodynamic product (Figure 2, Problem 3).

![Figure 1. The Markovnikov Addition of HBr to an asymmetric alkene. The major product is the more substituted tertiary alkene. The minor product is the less substituted secondary alkene. The reaction is stepwise with a carbocation intermediate (this rules the concerted mechanisms depicted by A and C in the options below). The formation of the carbocation is the rate-determining step. The tertiary carbocation is more stable, and from the Hammond Postulate, the formation of the tertiary carbocation will have a lower activation energy. Following the formation of the carbocation, the bromide nucleophile adds to yield the alkyl halide. The carbocation is present in both transition states in the reaction. The chemical bonds at the beginning of the reaction and the end of the reaction are the same. The change in entropy would be similar for the major and minor products. Therefore, both have similar thermodynamic favorability. From the rate-determining step, the differences in carbocation stability, and the thermodynamic similarity, the answer is (B). There is a small difference in the energies of the products based on steric strain in the chair conformation. The small difference was not considered for the answer.](image-url)
Figure 2. An E2 elimination with sodium methoxide is a concerted one-step mechanism. The thermodynamic product, the more substituted alkene, is produced in a greater yield in this reaction. The kinetic barrier is best rationalized by analyzing the transition state in which the C-C double bond is partially forming while the C-H and C-Br bonds are partially breaking. The formation of the C-C double bond at the more substituted site is electronically favored (stronger bonds) but sterically unfavored because the base is deprotonating at a more sterically hindered site. In this reaction, the electronic effects outweigh the steric effects – the base is less bulky, and the more substituted alkene will have a lower activation and final energy. Therefore, the more substituted alkene will be favored both kinetically and thermodynamically. The answer is I for problem 2. For problem 3, the bulkiness of the base increases, which accounts for the difference in product composition. Product C is the less substituted alkene and is less thermodynamically favored than product B. The thermodynamic favorability does not change – the activation energies change, and hence kinetic favorability changes. The bulkier base increases the steric effect at the more substituted site, which causes the activation energy of product B to increase, making product C more kinetically favored because of the reduced steric strain. The answer is (A) for problem 3.

Data analysis
The resources framework and RC were used to guide the data collection. Figures 3 and 4 illustrates an expert resource map and RCD for the Markovnikov Addition and Zaitsev Elimination in which the resources are denoted in circles. Using a methodology similar to Braun and Graulich\textsuperscript{38}, the specific information for constructing RCD, which could extracted from a given resource, was identified. The four pieces of information include (1.) structure, (2.) the type of reaction, (3.) kinetic, and (4.) thermodynamic. The extracted information provides key insight into the energetic information used to construct the RCD. The block arrow denotes how students transitioned between a resource and the graphical RCD. This transition between the representational competence (RC) aspect is associated with the analyses.

The qualitative interview data were transcribed verbatim and analyzed individually by three research team members. Each researcher reviewed and coded the transcripts to identify the specific resources activated as students constructed the RCDs de novo and the resources activated when the multiple-choice items were provided. Resources were coded based on explicit statements from students – if it was not explicitly stated, the resource was coded as not activated. The three researchers analyzed the constructed RCDs from the resources activated to evaluate whether the resources were productively applied into an RCD feature. Four codes emerged from the discussions: (1.) activated and productively applied, (2.) activated and not productively applied, (3.) not activated, and (4.) activated once the multiple-choice options were provided. Activated and productively applied denotes scenarios where the resource was activated and represented accurately in the RCD. This is linked to the selection of the resources and RC frameworks. Activation of the resource represents part of the challenge, with the second requiring accurate representation in an RCD. Activated and not productively applied denotes scenarios in which resources were activated but not productively applied in constructing the RCD. The researchers met and discussed each coding scheme until reaching an agreement on the final codes reported in the manuscript.
The researchers used a consensus coding approach. The three coders met and discussed all the codes for each scenario until a consensus was met.\textsuperscript{43}

Sample codes are included in the supplemental section.

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The carboxation formation is the rate determining step or the step with the highest activation energy denoted with *. Once formed the carboxation lies at a lower energy denoted as X.

Thermodynamic comparison of bond stabilities. An sp\textsuperscript{3} C-Br bond has similar energy regardless of alkyl substitution. Therefore, similar thermodynamic favorability. The curves converge as shown at Z.
Figure 3. A sample resource map for the Markovnikov Addition. The extract represents the information that could be attained from the given resource. The block arrow translates the resources to the graphical representation (RC).
Figure 4. A sample resource map for the Zaitsev Elimination. The extract represents the information that could be attained from the given resource. The block arrow translates the resources the the graphical representation (RC).

RESULTS AND DISCUSSION

A comparison of the problems by cohorts is provided in Figure 5. The survey data provided insight into student success based on the type of problem and the resources needed to identify the correct RCD successfully.

![Figure 5. A summary of the performance on the assessment items by cohort. The z-score from the two-population proportion comparison. The proportions that were statistically different using a 95% level of confidence are indicated with a *.

The survey was used to gain insight into student performance before the interviews. Three reactions were analyzed, which required differing use of resources. The z-scores for two population proportions were calculated to compare student success on each problem within the spring and summer cohorts. The proportion of correct responses for the Zaitsev elimination was statistically higher using a 95% level of confidence in both the spring and summer cohorts. There was no statistical difference between the Markovnikov and Hofmann
proportion correct for either cohort. The association between the extent of substitution and stability is a heuristic introduced for students to gauge the reactivity and stability of alkenes. Using the heuristic, students can rationalize both greater kinetic and thermodynamic favorability of the Zaitsev product.

Unlike the Zaitsev elimination, in which analyses of alkene substitution can afford the correct conclusion, there is not a lone heuristic for the Markovnikov addition and Hofmann elimination. The Markovnikov reaction is kinetically favored, but the products have roughly the same thermodynamic favorability. With the Hofmann elimination, the less substituted alkene, the less thermodynamically favored product, is formed as the major product. Thermodynamic resources that analyze product stability and kinetic resources that analyze intermediates or transition states are important to account for the observed kinetics and thermodynamics.

The survey data provided insight into students’ abilities to correctly identify RCDs, with the data specifically providing insight into the proportion correct and the number of resources that must be activated, and greater RC is needed for the productive application of the resources. For example, for the Markovnikov addition, RC depicts stepwise reactions with intermediates, elementary steps having differing activation energies, and the relationship between the energies of the major and minor products. Likewise, for the Hofmann elimination, the productive application required RC to depict kinetic versus thermodynamic favorability. The survey data is a precursor to the interview data, which explores more closely the specific resources activated for each problem and whether these resources are used productively.
Connecting Problem-Solving Resources to RCDs for the Markovnikov Addition, Zaitsev Elimination, and Hofmann Elimination

The next three sections will analyze the interview data for each of the three reactions to identify the problem-solving resources used to construct the RCDs to explain reaction regioselectivity. **Markovnikov Addition** RCDs were constructed for the Markovnikov addition by the nine interviewees, and the interview codes are summarized in Figure 6. From the qualitative data, two themes were identified to describe problem-solving strategies, specifically the activation and productive use of resources.
Figure 6: The resources used while students constructed the RCDs for the Markovnikov Addition Reaction. These resources were identified before the RCDs were provided. 1 – 9 are the student constructed RCDs.
Theme 1: Carbocation Resources Activated but Not Resources Related to Relative Stabilities

Carbocation formation was activated and productively applied across several interviews, which is not surprising. Only P7 drew a concerted diagram after noting the formation of a carbocation. For the interviewees, the addition of HBr to an alkene is the first reaction they learned in organic chemistry, and the formation of the carbocation is drilled through similar examples. Additionally, the textbook for the course illustrates the RCD emphasizes carbocation stability and identifies the formation of carbocations as the rate determining step. Additionally, at the time of the interviews, the participants were learning or had recently learned substitution and elimination reactions, which provides an additional review of carbocations.

Although carbocation resources were activated in several interviews, from Figure 6, the resources comparing the carbocation stability were generally either not activated or activated and unproductively applied. For mechanistic reasoning, carbocation formation is important; However, comparing two pathways and accounting for the differences is the more important learning outcome that extends beyond rote memory. For assessments, EPFs focus on explaining how a specific product is formed from a given reactant or identifying the major product formed given specific reaction conditions. Therefore, similar to Popova’s finding, the focus on the minor product was a challenging task for students during the interview. The resources activated and productively applied focused on the analysis of the major product and not the comparison of the two products.

Theme 2: Resources Comparing Stabilities of the Products were Activated to a Minimal Extent

There was a limited focus between the differences in bond stabilities between the secondary and tertiary alkyl halide. Oneinterviewee analyzed the bonds to rationalize qualitatively whether the reaction is exergonic or endergonic: P1: And so going from alkene to,
cause you're breaking a C-C bond, or at least pi C-C and you are forming a C-Br and a C-H. So trying to think whether this can be exergonic or endergonic. Is that so there's definitely going to be, you know, the delta G, the transition state? Interviewer: Okay. P1: And then. I'm just gonna assume this exergonic.

Additionally, the extent of alkyl substitution was used by P3. P3: I'm thinking the most substituted one would be lower energy [the tertiary product]. For alkenes, the extent of alkyl substitution is correlated with stability. That is a productive resource when considering alkene stability and reactivity. However, it is not productive in terms of comparing the stability of alkyl halides.

When discussing alkene addition reactions, there is a strong focus on the formation of the carbocation to account for the account. In fact, some textbooks only mention the formation of the carbocation as a resource and depict the truncated RCD (ending at the intermediate) to explain the outcome of the chemical reactions. The limited use of resources and limited representation provides an incomplete picture.

**Zaitsev Elimination**

As with the Qualtrics survey, interview participants performed better on the Zaitsev elimination problem than the Markovnikov addition and Hofmann elimination. Figure 7 summarizes the interview codes and RCDs constructed by the nine interviewees.
Figure 7: The resources used while students constructed the RCDs for the Zaitsev E2 eliminations. These resources were identified before the RCDs were provided. 1 – 9 are the student constructed RCDs.
Theme 1: The Extent of Alkyl Substitution is a Favored Heuristic

The extent of alkyl substitution is often used to explain alkene stability. Therefore, it is not surprising that seven of the nine participants identified the major product as being more substituted and more stable.

In defining stability, the interviewees immediately focused on thermodynamic stability by explicitly focusing on the differences in the energies of the products in constructing the RCD. The relationship between stability and transition state was mentioned: P7: I think product C is going to have both the higher transition and ... final product state. However, a detailed representation for the transition state was never provided. Additionally, students never provided a thorough argument for stability (electronics) versus sterics to account for why the activation energy of the major product is lower than the activation energy of the minor product. Similar to the Markovnikov addition, students appeared to apply a heuristic that the major product is both kinetically and thermodynamically favored.

Theme 2: Representational Competence (RC) May Limit Productive Use of Resources

The third emerging theme is linked to applying the appropriate resources, but they were not applied productively. Participants 2 and 4 defined the reaction as E2 and concerted, but they constructed stepwise RCDs. This observation reiterates the significance between the resources and representational competence frameworks. Constructing RCDs requires activating key resources with productive applications in competently transitioning between different representations.
Theme 3: Complete Analysis of Elimination Reaction Includes Activating Resources Surrounding Base Structure and Strength

The fourth theme was observed with participant 5, who selected an E1 stepwise pathway because of the tertiary alkyl halide. Tertiary alkyl halides do undergo E1 eliminations but in the presence of weak bases. The problem provided used a strong base, which promoted E2 elimination. In learning substitution and elimination reactions, analyzing the alkyl halide structure is generally the first step in the problem-solving strategy; therefore, it is not surprising that this is the first resource that is activated.

Hofmann Elimination

Figure 8 outlines the interview codes and RCDs constructed during the interviews. Analyzing the interview data for the Hofmann elimination revealed two opposing themes.
<table>
<thead>
<tr>
<th>Hofmann Elimination</th>
<th>Elimination Reaction</th>
<th>No Intermediate Formed</th>
<th>Concerted Mechanism</th>
<th>E2 Mechanism</th>
<th>Major Product is Kinetically Favored</th>
<th>Minor Product is Thermodynamically Favored</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>Elimination Reaction</td>
<td>No Intermediate Formed</td>
<td>Concerted Mechanism</td>
<td>E2 Mechanism</td>
<td>Major Product is Kinetically Favored</td>
<td>Minor Product is Thermodynamically Favored</td>
</tr>
<tr>
<td>P2</td>
<td>Elimination Reaction</td>
<td>No Intermediate Formed</td>
<td>Concerted Mechanism</td>
<td>E2 Mechanism</td>
<td>Major Product is Kinetically Favored</td>
<td>Minor Product is Thermodynamically Favored</td>
</tr>
<tr>
<td>P3</td>
<td>Elimination Reaction</td>
<td>No Intermediate Formed</td>
<td>Concerted Mechanism</td>
<td>E2 Mechanism</td>
<td>Major Product is Kinetically Favored</td>
<td>Minor Product is Thermodynamically Favored</td>
</tr>
<tr>
<td>P4</td>
<td>Elimination Reaction</td>
<td>No Intermediate Formed</td>
<td>Concerted Mechanism</td>
<td>E2 Mechanism</td>
<td>Major Product is Kinetically Favored</td>
<td>Minor Product is Thermodynamically Favored</td>
</tr>
<tr>
<td>P5</td>
<td>Elimination Reaction</td>
<td>No Intermediate Formed</td>
<td>Concerted Mechanism</td>
<td>E2 Mechanism</td>
<td>Major Product is Kinetically Favored</td>
<td>Minor Product is Thermodynamically Favored</td>
</tr>
<tr>
<td>P6</td>
<td>Elimination Reaction</td>
<td>No Intermediate Formed</td>
<td>Concerted Mechanism</td>
<td>E2 Mechanism</td>
<td>Major Product is Kinetically Favored</td>
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<td>No Intermediate Formed</td>
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<td>E2 Mechanism</td>
<td>Major Product is Kinetically Favored</td>
<td>Minor Product is Thermodynamically Favored</td>
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<td>Elimination Reaction</td>
<td>No Intermediate Formed</td>
<td>Concerted Mechanism</td>
<td>E2 Mechanism</td>
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<td>Elimination Reaction</td>
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<td>E2 Mechanism</td>
<td>Major Product is Kinetically Favored</td>
<td>Minor Product is Thermodynamically Favored</td>
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</table>

![Energy Reaction Coordinate Diagram](https://doi.org/10.26434/chemrxiv-2024-n6v02) ORCID: https://orcid.org/0000-0001-7169-9777 Content not peer-reviewed by ChemRxiv. License: CC BY 4.0
Figure 8: The resources used while students constructed the RCDs for the Hofmann E2 eliminations. These resources were identified as students constructed the RCDs. 1 – 9 are the student-constructed RCDs. The Hofmann elimination was completed after students had constructed a RCD for the Zaitsev elimination and were provided with multiple-choice options.

Theme 1: Conflicting Conclusions but Major and Minor Product Labels are the Most Important Resources

The major product is favored both kinetically and thermodynamically. This conclusion contradicts the one drawn in the previous problem on the Zaitsev elimination, particularly given that the starting material and products are the same. Therefore, the heuristic using the extent of alkyl substitution to gauge stability should apply. However, while some addressed this resource, the predominant resource that gained the most attention was the major and minor product labels, which guided the construction of the RCD. This finding reiterates the importance of metacognition during problem-solving. During the interview, students were not coached to rethink their solutions.

The heuristic that the major product is kinetically and thermodynamically favored is a theme that appeared during each of the interview prompts, and is one that needs to be carefully addressed. With Zaitsev and Hofmann elimination, instructors and textbooks focus on the structure of the alkene as a guiding point. A key resource is the Zaitsev product being more substituted alkene and more stable. Therefore, this is a resource that students can memorize. Using transition state resources to compare the interplay of electronics and steric to account for kinetic control does not change the identity of the Zaitsev and Hofmann product. To determine the product outcome, students can associate the strong base, E2, bulky base, and Hofmann product resources. Similarly, they can associate the strong base, E2, non-bulky base, and Zaitsev product resources. Therefore, the use of mechanistic reasoning to rationalize the outcome is effectively absent without applying the transition state resources and using RC to compare transition states.

Theme 2: Steric Hindrance Impacts the Transition State Energies
The second theme is the realization of kinetic control from the steric hindrance of the bulky tert-butoxide base. For example, **P9**: *Okay, so this is highly branched, as far as the base, which means that it will tend more toward disobeying Zaitsev’s rule. So, I would say. I think it would have maybe a higher energy. I’m not sure. Okay. So go with like B here and C here, because I think this one might have a higher transition state....B might have a higher [transition] energy state. Because the base is highly branched or the Yeah, the base is highly branched. So in order to reach the beta hydrogen, it would be more difficult.* The student did not elaborate on electronic factors but did note that the base would lead the products to disobey Zaitsev’s rule. Detailed transition states were not constructed. As resources, transition states were only verbally described and not elaborately represented. The correct RCDs were constructed using steric resources, but no one accounted for the role of electronic resources in determining the overall transition state energies. In fact, while used extensively as a resource to predict thermodynamic stability, no one used the extent of substitution as a resource for gauging transition state stability for either the Zaitsev or Hofmann elimination problems.

**RESOURCES ACTIVATION AND PRODUCTIVE USE WHEN GIVEN REACTION COORDINATE DIAGRAMS**

The second research question was designed to explore how resource activation and productive use evolved when students were provided with a set of RCDs. Figure 8 illustrates the trajectory of the participants across the three interviews. Namely, the information summarizes whether students correctly constructed the RCD, changed their answers when provided with the multiple-choice prompts, and whether additional resources were activated. Figures 5 – 7 summarize the specific resources activated when the multiple-choice items were provided. Three themes provided insight into how scaffolding assignments could be designed in future iterations.
Figure 9: A summary of the trajectory of the participants across all three interviews. The highlighted cells are associated with the observation of a specific action item listed in the columns. If an incorrect option was selected from the MC options, the specific option selected is denoted in parentheses.

Theme 1: Resource Activation Decreased with Multiple-Choice Options as Interviews Progressed

The number of unobserved resources activated by the multiple-choice items decreased as the interview progressed, with the most being activated by the initial set of multiple-choice items in the Markovnikov addition. We have three hypotheses for the decrease in resource activation. The first hypothesis is the multiple-choice RCDs in the Markovnikov addition promoted the activation of key resources in future problems. The similarities in the Zaitsev and Hofmann eliminations and the fact that the same multiple-choice RCDs were provided for both may account for the decrease in the number of additional resources activated for the Hofmann elimination. Finally, only concerted multiple choice RCD options were provided for
the Zaitsev. Therefore, from the similarities of the reactions, students may have predicted
that the Hofmann elimination occurs via an E2 concerted mechanism.

**Theme 2: RCDs May Prompt Students to Re-evaluate Resources Surrounding the Reaction Mechanism**

Mechanistic details for the Markovnikov addition, including carbocation formation, carbocation stabilities, and specific energetics, were activated from the provided RCDs. For example, P1 (Markovnikov Addition): *And so, the first reactive intermediate would be a carbocation. Oh yeah. And then it would be a nucleophilic attack. So, I know the hump represents the reactive intermediate, so I mean first of all forming the carbocation would be the rate determining step, so yeah, I change my answer. If I am going to say minor and then major, I’m gonna say B.* P1 observed both concerted and stepwise RCDs, which activated the carbocation, the stepwise mechanism, and rate determining step resources, and they productively applied these resources to identify the correct RCD. Likewise, a similar response was observed for P7 (Markovnikov Addition): *I just remembered that I think HBr addition to an alkene is not a concerted reaction that has a carbocation intermediate... So because the difference between the minor and major product would be in the cation formation step and the more stable carbocation would be the lower energy.* Although most prevalent with the Markovnikov addition, similar observations were noted for the Zaitsev elimination. When provided with the four options, P5 (Zaitsev Elimination): “Okay, um, so I guess it was E2.” The RCDs were concerted, which allowed P5 to rule out the E1 as a possible mechanism.

**Theme 3: The Benefit of RCDs on RC Varies**

In comparing the RCDs constructed by P3 in Figures 5, 6, and 7, they benefited from the provided RCDs. Initially, their constructed RCD only compared product energies without considering reactions, intermediates, or transition states. However, their RCDs in Figures 6 and 7 compared the energies, included sketches of the transition states and depicted the concerted mechanism. Therefore, they may have been initially uncertain of what information
to include and how to proceed. The multiple-choice RCD options gave insight into what information should be represented using an RCD.

The RCDs constructed by P4 were almost identical; however, different resources, such as stepwise versus concerted mechanisms, were activated in the individual interview prompts. Therefore, while key resources were activated, productive use was hindered by RC—in both the Zaitsev and Hofmann, they constructed a stepwise RCD, yet selected a concerted multiple-choice option. They never noted the disconnect in their representations and the multiple-choice options. Finally, students were not asked to identify the axes, but for the x-axis, reaction rate, reaction progress, time, and extent of reaction were observed, consistent with existing findings by Parobek\textsuperscript{18} and Popova\textsuperscript{22, 24} regarding challenges students have with interpreting the meaning of the x-axis.

**CONCLUSION**

We analyzed how resource activation and application to constructing RCDs varied depending on the reaction context. For the stepwise Markovnikov addition reactions, students activated resources related to the formation of the carbocation, the rate-determining step, and the stepwise nature of the reaction. Fewer resources were activated focusing on the structures and differences in stabilities of the major and minor products. The opposite was observed with the concerted elimination reactions in which resources focusing on the structure of the product stability were activated to a greater extent than resources focusing on transition state energies. The strategies observed stem from the strategies used successfully in lectures. On exams, the major products can be successfully predicted by considering the most substituted carbocation for Markovnikov additions or the impact on alkene substitution as the bulkiness of the base increases in an E2 elimination.

Students did statistically better on the Zaitsev multiple-choice elimination item, in which the major product was kinetically and thermodynamically favored. The activation of
the resource, the more substituted alkene is more stable, will allow for a correct conclusion. The Markovnikov addition and Hofmann elimination require more resources. An idea that needs further probing is how students conceptualize representing reactions with differing kinetic and thermodynamic favorability.

When assessing RCDs as possible scaffolds, we observed the activation of specific mechanistic details when provided with a set of possible RCDs. Specific resources were activated after prompting, including carbocation formation, the formation of the carbocation as the rate-determining step, and an addition reaction, which is a stepwise mechanism. While resource activation from the provided RCDs was more evident, possible improvements in RC were observed with some students. However, we did observe similar challenges with students’ understanding of the x-axis, as reported in previous literature.

LIMITATIONS

The Qualtrics survey was assigned as a homework assignment and was not given as a proctored assignment in the classroom. Therefore, it is possible that students reviewed textbooks and other materials to answer the problems. However, the grades were based on participation, and it was emphasized that the responses would only be reviewed at the end of the term for research purposes. A multiple-choice format was used that provided a partial list of options. For the Zaitsev and Hofmann eliminations, the RCD options were all concerted, limiting the total responses landscape by removing E1 as a possible mechanism.

The interviews were conducted with students at the end of organic chemistry I. The instructors vetted the content of the interviews. The interview questions were designed from the Qualtrics survey and did not correct for activities done on homework and specific lecture examples. The interviews were designed to collect and analyze how students construct RCDs. For coding purposes, we only coded explicit statements. Data saturation is not guaranteed in the study, although data saturation of metathemes can be attained by as little as six interviews.46
Since the sample may not encompass a representative distribution of undergraduate students, the study cannot make generalizable claims about the relative frequencies of observed beliefs. However, the aim of this research does not rely on identifying the prevalence of different concepts in a population but rather on how students work through the relationships between chemical reactions, RCDs, and problem-solving resources.

**IMPLICATIONS FOR TEACHING AND FUTURE RESEARCH**

RCDs are the foundation for the EPF mechanisms we introduce to students. In introducing reactions, we can use limited resources to account for the outcome of chemical reactions without discussing thermodynamics and kinetics. Carbocation stability accounts for the major and minor products formed in addition reactions. Thermodynamic stability explains why the Zaitsev product is formed with less sterically hindered, strong bases. Using limited resources provides students with a narrow understanding of all energy changes observed in the reaction. As instructors, we aim to provide a more complete picture outlining both kinetic and thermodynamic factors to enhance mechanistic reasoning skills. The interplay of kinetics and thermodynamics appears throughout the curriculum, and by using a complete approach from the beginning, students will be more primed to analyze the kinetics and thermodynamics of more complex reactions such as the Diels-Alder reaction, the Michael addition, and the Wittig reaction—all of which require discussions of kinetic and thermodynamic control to explain why specific products are formed.

A future strategy will include developing scaffolded problem-solving activities designed to activate critical resources. Future research will focus on developing these scaffolds, using a flow chart like Figure 10, and implementing these within large-scale assessments via Qualtrics and individually in interviews. Although the interactive interview format provides the opportunity to ask clarification questions for students’ reasoning, additional types of data, such as eye-tracking and prompt diversification during interviews,
would enable researchers to pinpoint the specific resources students apply while solving problems.

**Figure 10.** A flow chart to use to assist with scaffolding activities for constructing RCDs.

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**REFERENCES**

3. Bhattacharyya, G.; Bodner, G. M., "It gets me to the product": How students propose organic mechanisms. *Journal of Chemical Education* 2005, 82 (9), 1402.
5. Graulich, N., Intuitive Judgments Govern Students’ Answering Patterns in Multiple-Choice Exercises in Organic Chemistry. *Journal of Chemical Education* 2015, 92 (2), 205-211.
18. Parobek, A. P.; Chaffin, P. M.; Towns, M. H., Location-thinking, value-thinking, and graphical forms: combining analytical frameworks to analyze inferences made by students when interpreting the points and trends on a reaction coordinate diagram. *Chemistry Education Research and Practice* 2021, 22 (3), 697-714.
21. Taştan, Ö.; Yağıcıkaya, E.; Boz, Y., Pre-Service Chemistry Teachers’ Ideas about Reaction Mechanism. *Journal of Turkish Science Education (TUSED)* 2010, 7 (1).
38. Braun, I.; Graulich, N., Exploring diversity: student's (un-)productive use of resonance in organic chemistry tasks through the lens of the coordination class theory. *Chemistry Education Research and Practice* 2024.
40. 2023, D.
46. Fusch Ph D, P. I.; Ness, L. R., Are we there yet? Data saturation in qualitative research. 2015.