# Practitioner development in organic chemistry: how graduate students conceptualize organic acids

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**Abstract:** Using a model-eliciting activity (MEA) focused on Brønsted acids, this study probed organic chemistry graduate students' mental models regarding one of the important theoretical constructs of their field. The salient finding of this work is that the graduate students in this study considered acidity primarily as a function of bond polarization. Furthermore, although they referred to resonance and inductive effects in their explanations, the participants had difficulty characterizing each phenomenon. Overall, the participants' expressed models suggested that they didn't have well-developed conceptions of acids in their minds; rather, their models reflected a rationalization of the data provided in MEA. As a result the participants' mental models (a) showed little evidence of the anticipated hybridization of theoretical constructs; (b) were not applicable beyond the MEA data; and (c) lacked the predictive capability needed to produce new science. [*Chem. Educ. Res. Pract.*, 2006, **7** (4), 240-247]

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## Introduction

In traditional chemistry instruction theoretical constructs are taught as a steadilyimproving collection of paradigms (Kuhn, 1970). Instead of using the most sophisticated single model, however, practicing organic chemists tend to use a 'best-fit' model approach in which they freely combine different — even mutually incompatible — paradigms to create hybrid models that highlight a particular aspect of a molecule's chemical behavior (Samarapungavan et al., 2006). Schön (1987) calls these types of eclectic mental models as 'theories-in-use'. Practitioners routinely use these mental models to integrate and apply the breadth of theories to which they are exposed, since no single, simple model can describe every aspect of the chemical behavior of 'real-world' molecules.

In organic chemistry generating theories-in-use primarily requires the practitioner to engage in two types of multi-variate thinking. In one type, a single chemical phenomenon is described using two or more scientific models, even seemingly incompatible ones. For example, chemists invoke the creation of  $\sigma$ -bonds — a construct of Molecular Orbital (MO) Theory — from the interaction of one or more hybridized orbitals — an outcome of Valence-Bond Theory (VBT) (Fleming, 1976), even though MO Theory is based on a delocalized model of bonding and VBT is based on a localized model of bonding. The second type of multi-variate thinking involves balancing different chemical effects, such as steric and electronic, to explain outcomes of chemical processes.

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Although practicing organic chemists routinely use theories-in-use that reflect these types of multi-variate thinking, students, on the other hand, have a tendency to invoke a single model or effect to explain every case of a chemical phenomenon (Coll and Treagust, 2002). Previous work shows, for example, that first-year graduate students tend to focus solely on steric effects when explaining or predicting stereochemical outcomes of organic reactions (Bhattacharyya and Bodner, 2005).

As part of ongoing efforts aimed at understanding how students develop into practicing organic chemists, this paper reports an investigation of organic chemistry graduate students' mental models of organic acids. Brønsted acids were the primary topic because it is not possible to describe the acidities of a variety of compounds without addressing both types of multi-variate thinking addressed above. Thus, it requires individuals to invoke theories-in-use. Furthermore, practicing organic chemists emphasize the use of acid-base theory to their graduate students because comparing  $pK_{as}$  of conjugate acids is a useful method for describing the relative reactivity of bases, which, in turn, can help predict and explain the outcomes of many classes of reactions. The goal of this work, therefore, was to understand better how immersion in graduate-level research affects early-career organic chemists' theories-in-use regarding one of the important theoretical constructs of their field.

# Methodology

The theoretical framework that guided this study was models and modeling (Bodner et al., 2005). The term 'model' in the science education literature corresponds to a number of definitions. For the purposes of this research, 'model' refers to an individual's mental model. Bower and Morrow (1990) define mental models in the following statement: "We build models that represent significant aspects of our physical and social world, and we manipulate elements of those models when we think, plan, and try to explain events of that world" (p 48). Since some researchers (Greca and Moreira, 2000) have suggested that it is impossible to access an individual's mental models, this research was based on Gilbert's (1997) notion of an 'expressed model', which is a mental model that an individual attempts to make public by some mode of communication.

Substance	pK <sub>a</sub> in H <sub>2</sub> O
Water	15.7
Methanol	15.1
Ethanol	15.9
Propanol	16.2
Butanol	16.1
iso-Propanol	17.1
<i>tert</i> -Butanol	19.2
F <sub>3</sub> C–CH <sub>2</sub> –OH	12.4
F <sub>3</sub> C–CH <sub>2</sub> –CH <sub>2</sub> –OH	14.6
F <sub>3</sub> C–CH <sub>2</sub> –CH <sub>2</sub> –CH <sub>2</sub> –OH	15.4
Phenol	9.95
para-Nitrophenol	7.14
para-Methoxyphenol	10.20

Figure 1. The model-eliciting activity (MEA) that was used to probe the participants'

concept	ualizations	of a	cids.	

"One evening, while you are working in the lab, a fellow graduate student in the organic division calls and asks you to explain the trends in the acidities of these compounds. To help her out, create a set of rules that could explain acidities of organic molecules from these data."

The instrument used to probe the participants' conceptions was the model-eliciting activity (MEA) shown in Figure 1.

Lesh and co-workers have suggested a set of six criteria that should be used in designing MEAs (Lesh, et al, 2000). Because the goal of this research was probing the participants' theories-in-use, the design of the MEA focused on two principles:

- Construct documentation: the MEA aimed to evoke the participants' thought processes.
- Construct shareability/reusability: analysis of the MEA aimed to determine whether the participants' models were generalizable beyond the situation provided.

The choice of molecules was limited to a single functional group because the primary goal of this research was to elucidate the participants' ability to incorporate multi-variate thinking into their theories-in-use. Multiple functional groups would have likely made it more difficult to concentrate the discussion on the primary topic of this investigation. Alcohols were chosen because they contain members that highlight inductive— the trifluoroalcohols — and resonance effects — the phenols. Furthermore, the differences in acidities of the primary, secondary, and tertiary alcohols are believed also to be influenced by different states of solvation of their conjugate bases which, in turn, are affected by the steric bulk of the respective alkyl groups. Thus, creating a set of rules for characterizing the acidities of the set of alcohols presented in the MEA would require considering both types of multi-variate thinking discussed in the introduction.

The participants in this study were ten graduate students recruited on a voluntary basis from the population of organic chemistry doctoral students in the Department of Chemistry at a large, state-supported, research-oriented university. The participants were interviewed using the think-aloud protocol as they worked on the MEA (Ericsson and Simon, 1984). All the interviews were conducted by the author whose primary role was to help the participants make their reasoning explicit. Although content knowledge can be a confounding variable in learning research in chemistry, no resources were made available during the interviews as the goal was to elicit the participants' personal models of organic acids.

The interviews were audio-taped and then transcribed. Key observations in the form of field notes written during the interviews or immediately afterwards provided a second source of data. The participants' written artifacts represented a third source of data. Analysis of all three sources of data — interview transcripts, field notes, and written artifacts — yielded a mental model of acidity for each participant. Due to the similarity between the individual models, a composite model representing the essence of the participants' individual models could be generated. The participants' conceptions of the chemical principles invoked in the supporting data. The composite model and participants' conceptions, which are addressed in the following section, were discussed with the professors who mentor these participants as a validity check, to ensure that the researcher's interpretations of the data were consistent with their experiences with the students.

# Results

Although there were minor individual differences, the participants' expressed models were remarkably similar. Hence a sample reflecting the essence of the participants' individual models is shown in Figure 2.

In describing the salient features of the participants' models, the claims made below are supported by the participants' utterances. These quotes are taken directly from the interview transcripts without correction of grammar and/or syntax. To protect their confidentiality, the participants are referred to by a pseudonym. When an exchange is shown, the letter "I" is

used to denote statements made by the interviewer. Annotations to quotes are placed in square brackets

Figure 2. A summary model representing the essence of the participants' individual models.

#### Rule 1. Polarization of the H–A bond.

The greater difference in electronegativity between the proton and the atom it's bonded to, the stronger the acid.

#### Rule 2. Resonance stabilization of the conjugate base.

The more resonance delocalization is present in the conjugate base, the stronger the acid.

### **Rule 3 Electronic effects.**

Inductive effects of the rest of the molecule. The greater number and proximity of electronegative atoms, the stronger the acid.

According to this model, the most important characteristic needed to describe the molecules' acidities was bond polarization. It is important to note that the participants used the term 'bond strength' to describe this effect. Consider the following quotes from Carl, a first-year student who came to the program with a Master's degree in chemistry from another institution, and Frances, a second-year student:

Carl: Uh, and so with uh, say if you remove electron density from that proton, you're weakening a covalent bond it and the oxygen and therefore would be more acidic.

Frances: I tend to, I'm really visual. So what I'll tend to do is imagine what's actually happening with individual molecules. So, OK, this is a stronger acid. Why? And what's actually happening with that proton? And, it's interacting with the solution and so is it coming off or becoming more strongly attached? So, I'm kind of imagining the bond stretching and shrinking and things based on the pKa. So I'll imagine something with a larger pKa, so a weaker acid, as having a proton as a lot closer to that oxygen.

Although they spoke of a 'weakening' of the O–H bond, 'polarization' would have been a more appropriate description. To practicing chemists the notion of bond strength corresponds to the homolytic cleavage of a bond in the gas phase. Technically, therefore, comparing bond polarization would be a more scientifically appropriate approach than comparing bond strength. Hence, the word 'polarization' was used in Figure 2.

Irrespective of the semantic issue, describing acidity from the standpoint of bond polarization is problematic, because it cannot be generalized beyond the data presented in the MEA. For example, although the C–H bond of acetylene is stronger and more polarized than that of ethylene or ethane, acetylene is by far the strongest acid of the three.

The second and third most important characteristics used to describe the acidity of compounds were resonance and inductive effects, respectively. However, the participants' comments suggested incomplete understanding of these ideas. Consider the following exchange with Jeremy in which he explains his distinction between resonance and inductive effects:

I: What does, when you think of an inductive effect, what do you think of?

J: I think of inductive, I really think of an example. An electronegative atom like chlorine, like chlorobenzene pulling electrons out because it's more electronegative. So the more electronegative atom is going to have the greater electron density around it.

I: OK, and what does resonance mean to you?

J: Uh, delocalization of charge. ... So you can delocalize those lone pair of electrons into the ring.

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Although Jeremy was able to identify the compounds primarily exhibiting inductive effects versus those exhibiting primarily resonance effects, his comments suggest that he is not able to articulate clearly the difference between those two. Thus, the participants had a 'know it when I see it' approach to these two fundamental concepts of organic chemistry.

Interestingly, the participants' models could not completely explain the difference in acidities of primary, secondary, and tertiary alcohols. Although their models alluded to the electronic basis for the observed trend, the participants essentially ignored steric effects and didn't consider the solvent's interactions with any of the entities involved in the equilibrium. In addition to the electronic effects, it is believed that a major contributor to the observed differences in acidity is the solvation of the conjugate base. As the alkyl group of the conjugate base increases in steric bulk, stabilization by solvation decreases. Hence, *n*-propanol is a stronger acid than *iso*-propanol and *n*-butanol is a stronger acid than *t*-butanol. Consider the following comments:

Frances (a second-year student): So my general rule would be: the more electron-donating groups that you have, such as, we notice the *tert*-butanol has, there's a lot of donating character there and so that's likely to be a much weaker acid.

Eleanor (a first-year student): So, um, I guess back to the isopropanol and the *t*-butanol, um, let me see. So, would that have an electronic effect? I don't know how I would explain that to someone if they didn't understand how electronics could affect  $pK_a$  though?

Overall, the expressed models suggested that the participants didn't articulate conceptions of acids that were well-developed, or 'crystallized', in their minds; rather, their models reflected a rationalization of the data provided in MEA. Consequently, the models had a descriptive quality without much predictive capability. Generalizability is a key attribute of models which practitioners use to create new science. Furthermore, the participants intended their rules to be applied in a linear sequence, negating, thereby, any interplay between the different effects. Chemical effects such as steric and electronic, however, function on interrelated continua.

When asked to explain their reasons for focusing on the three effects mentioned in Figure 2, the participants' responses suggested that they made analogies with the MEA data and their classroom exposure to organic chemistry based on surface-level similarities. Consider the following comment by Jeremy, a second-year graduate student, who explained his reason for focusing on resonance effects to explain the differences in acidities of the compounds in the MEA:

I just have to say the, the way these compounds [referring to the phenols] were presented to me originally in class. The electronic effects of those substituents on the rings and how they react synthetically I think is how I would answer that question.

In the case of another participant, Shannon, a fourth-year student, the presence of *t*-butanol initially led her to think of a different reaction:

- I: So can I ask you one quick thing? What; you said that this *t*-butanol....
- S: That's the most stable. That cation [referring to *t*-butyl cation].
- I: OK, so you were thinking about the carbocation?
- S: I had it backwards. [Realizes that she was thinking of the wrong reaction.]

These statements suggested that the participants were cued to the simple contexts in which these molecules are typically presented in sophomore-level organic chemistry textbooks. Resonance effects are featured in the chemistry of aromatic compounds while *t*-butyl groups appear prominently in the discussion of the stability of carbocation intermediates in  $S_N1$  reactions (Bruice, 2004).

# **Discussion and Implications**

A major goal of doctoral programs in organic chemistry is helping students to construct a mutually beneficial relationship between theory and practice, since practicing chemists use theoretical constructs to create experiments, *and* use experimental results to promote their understanding of the underlying theory. The data reported in this paper, however, suggest that the participants' ideas of acids and bases were relatively unchanged from their classroom exposure to this topic. Through formal and informal discussions the participants' Ph.D. mentors stressed to their students the importance of acid-base theory, and demonstrated its use in resolving a variety of chemical problems. The participants' models, however, did not reflect the maturation that would have been expected from their immersion in the organic chemistry research group environment. The following exchange with Elizabeth, a third-year graduate student, reflects this disconnection:

I: And where do you think, you know, just from your definition of  $pK_a$  and from some of the things that you've talked about, where do you think that you've learned how to think about acids. I mean is it something that you've brought strictly from classroom experiences or your research?

E: More classroom I guess. Because I don't really, um, do a lot of things in water. And so I think of acids in water.

I: But in the sense that do you think about pK<sub>a</sub>s?

E: Do I think about it in my research?

I: Yeah.

E: No, I wouldn't necessarily. It's not really um. Sometimes when I'm using a base and I want to deprotonate something then I will. But, um, no I think it's more of something from the classroom that I um. Yeah.

Even though the participants in this study were deemed to have made excellent progress towards their doctoral degrees — over half had achieved candidacy at the time of the data collection — they did not attribute their conceptions of one of the basic theoretical tools of organic chemistry to any out-of-class activity. Additionally, at least in Elizabeth's case, they used  $pK_{as}$  in the limited way they are used in introductory organic chemistry. This parallels the observation by Coll and Treagust (2002), who in their study of high school, undergraduate and graduate students' conceptions of covalent bonding, noted that all three groups of participants used the simplest model – the octet rule – to describe covalent bonding in molecules.

Although much more research needs to be done to understand the lack of expected theoretical maturation, a preliminary speculation is provided here. Beyond their first year of study, graduate students spend most of their time in a research laboratory setting where they carry out original, scholarly work for their dissertations. In this phase of the degree, the primary goal for the student is to produce publishable results (Knorr-Cetina, 1983). Consequently, interactions between research mentors and students primarily occur to resolve problems associated with anomalous data, *i.e.*, to interpret the results of experiments that don't yield expected outcomes and to discuss and plan the next experiments (Preece Stucky and Bond-Robinson, 2004). In her work on the production of scientific knowledge, Knorr-Cetina (1999) uses the term 'blind variation' to describe the process by which problems with anomalous data are dealt with in small laboratory settings, i.e., laboratories with a single principal investigator. She suggests that when an experiment doesn't work, scientists in such environments rarely investigate the root cause of the problem. "Instead, they will try several variations in the belief that these will result in workable evidence" (Knorr-Cetina, 1999, p. 91). When practicing chemists use 'blind variation', they do so based on rationalization of the underlying process at the molecular level. Consider, however, the following exchange with Patrick, a second-year student:

P: 'Cause I'm starting to spend more time in the lab now than. Like most my training in the past is in the classroom. And there is a bit of a gap between the two I think that the individual has to fill. At least for myself. Transitioning from, taking the knowledge in the classroom and applying it in the lab.

I: What do you think are the barriers to that?

P: Comfortableness.

I: In what sense?

P: Being comfortable enough with what you're doing so that you can apply, so that you can resource, so being comfortable enough with a situation in what you're doing so that you can call forth whatever; so that you can retrieve other knowledge.

Patrick's words indicate his unease with applying theoretical knowledge to his laboratory activities. Thus, it is likely that his form of experimental variation is 'blinder', i.e., it is not based on the level of theoretical rationalization espoused by his research mentor. The 'blinder variation' of the students, therefore, is less conducive to promoting maturation of their understandings of the underlying chemical phenomena.

Two instructional suggestions are offered to mitigate this situation. First, based on the graduate students' reliance on their introductory organic chemistry classes, we need to ensure the accuracy of the presentation of chemical concepts and principles in textbooks and other instructional materials at that level. For example, many books show the reaction of ethylene and butadiene as the "trimmed-down" version of the Diels-Alder reaction. Under standard laboratory conditions, however, it would be impossible to effect this transformation. Second, in addition to traditional instruction, we need to make students explicitly aware of the necessity of creating of theories-in-use when attempting to solve 'real-world' problems. For example, standard textbook problems attempt to assess students' knowledge in a fragmented fashion; i.e., they pose questions that require the use of a single theoretical construct. In addition to these problems, it would be beneficial to give a few problems in which students have to learn how to combine theories.

Some examples of problems requiring multiple frameworks that the author has used are:

**Example 1**: "In class you were given the following order for the reactivity of carboxylic acid derivatives:

Acid chloride > Acid anhydride > Thioester > Ester (Acid) > Amide

Where would aldehydes and ketones fit into this spectrum? Clearly explain your rationale."

**Example 2**: "Please rank the following amines in order of basicity from strongest to weakest. Explain your trend fully. Please remember to reference the source of the relevant  $pK_a$  data."

Ammonia, Ethylamine, Diethylamine, Triethylamine, Pyridine, Aniline, Pyrrole

Another way to achieve the second goal would be to give students design problems and ask them to reflect on their strategies during and after the problem-solving process (Schön, 1987). Examples of design problems which the author has used in his organic chemistry classes are shown below:

**Example 3**: The fastest  $S_N^2$  reactions tend to occur in polar, aprotic solvents. Design an  $S_N^2$  reaction in which there is a rate acceleration in a protic solvent. Please explain your rationale in detail.

**Example 4**: Alkoxy (-OR) groups are said to be 'activating' in EAS reactions while nitro groups are said to be deactivating with respect to benzene. Design an experiment that would demonstrate this behavior. Please explain your rationale and include a set of expected results.

Action theorists suggest that such activities help individuals develop awareness of their mental models and are a step in changing subsequent behavior (Senge, 1994). Thus, instructors can help students build more robust and practicable mental models of chemical phenomena.

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