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## DESCRIBING REACTIVITY WITH STRUCTURAL FORMULAS, OR WHEN PUSH COMES TO SHOVE

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**ABSTRACT:** This short note reflects upon the widespread practice, in the classroom, of the paper tool of reaction mechanisms, taught with Lewis structural formulas, using curved arrows to denote motions of electrons. It is concluded that this practice, while assuredly improving upon the rational understanding of chemical reactions and their underlying logic, can easily become a modern counterpart to medieval scholastics. It has many of the features of slang with respect to more thoughtful and dignified speech. And it may breed cynicism and skepticism on the part of the students when they see this paper tool turned into a universal explanatory device. [*Chem. Educ. Res. Pract. Eur.*, 2002, 3, 113-118]

**KEY WORDS:** *heuristic tool; reaction mechanisms; curved arrow; pushing electrons; slang speech*

### INTRODUCTION

Chemistry teaching has two main channels, viz. to train future chemists, and to present chemistry to nonscientists. Throughout the world, the latter, service teaching performed by departments of chemistry to students who will become physicians, nurses, veterinarians, geologists or nutritionists, etc. is predominant. However, a widespread perversion is to treat nonscientists as if they were future chemists, and to insist that they learn and become fluent in chemical language. This pitfall is made all the more unavoidable that chemists are not used to describing chemistry in other than chemical language. This is one of the reasons for chemophobia on the part of the public, since chemists too seldom make the effort of conveying in everyday words what their work entails.

Even though the two topics, science communication and science teaching, are obviously closely related, I won't deal here with the former, only with the latter. I shall focus on an important segment of chemical language, structural formulas. Indeed these little icons which the public is used to see chemists scribbling on a blackboard or on a piece of paper, are taken by it to be emblematic of the chemist—just as a white lab coat used to be, in the not-too-distant past.<sup>1</sup>

I shall concern myself here with one particular use of structural formulas, a specialized usage which has become generalized, the writing of reaction mechanisms in which curved arrows denote electronic motions, most often movements of spin-paired electrons in molecules. My goal is to increase awareness of the historical contingency of these iconic representations, of their constraints too. It is to make fellow-educators realize

that this sub-text of chemical language is not unlike a pidgin language or a slang. It is very often incorrect. Our spontaneous recourse to it, in communicating with outsiders especially (such as undergraduate students who are not chemistry majors), is a form of laziness, a bad habit.

Which explains my title, with the pun on electron-pushing: by training innocent minds in the writing of curved arrows, we are bullying them into the erroneous identification of a description of reality, beset with all kinds of liabilities, to reality. Which runs exactly opposite to what is the goal of any science education, whether for scientists or for nonscientists, a training in critical evaluation of data.

### THE HISTORICAL BACKGROUND. A BRIEF SKETCH

Chemistry educators are well-advised to steep themselves in history. Only with its perspective can they properly convey to their students the dynamic dimension of science, the extent to which it is alive and throbbing as an organic whole, rather than a dried-up and dead subject. Furthermore, history demands the broad sweep, the *longue durée* as Fernand Braudel has termed it.<sup>2</sup>

In the case of the curved arrow notation and of its use in depicting a reaction mechanism, it was introduced by Robinson,<sup>3</sup> prior to the Hughes-Ingold studies in the 1930s. It was made popular after World War II when, under the influence of the American school (Paul D. Bartlett – Saul Winstein – John D. Roberts, in particular), it conquered mainstream organic chemistry. From the 1950s on, this paper tool took over chemical education as well. When other manuals started in the 1970s to displace Morrison and Boyd's as standard textbook for pre-medical students, this graphic device came into widespread use for teaching the subject to nonchemistry majors as well.

But a wider historical view is necessary to the remarks which will follow. Indeed, the whole span of the discovery and use of structural formulas by chemists is necessary to recall, not only for the telling of the story, but to a full understanding of the issues.

After the discovery of these two-dimensional iconic representations of the molecules of organic chemistry by Crum Brown, during the writing of his doctoral dissertation (1861),<sup>4</sup> such constitutional formulas were embraced by Frankland (first in his 1866 textbook<sup>5</sup>) who, in the public eye, became their progenitor.<sup>6</sup> They came to be known as «Frankland formulas.»

But their significance to organic chemists was not identical to what it has become for us. When we look at a structural formula, say that of morphine, we see a network of interconnected atoms. In other words, we contemplate a molecular architecture. In the terminology of the philosopher, we are naive realists. And as naive realists, we look at a molecular object. Our training indeed even allows us, by a leap of imagination, to go from the two-dimensional formula written or printed on a page to what the molecule may look like, as a «real» object in three-dimensional space.<sup>7</sup>

Constitutional formulas had quite a different meaning, or rather set of meanings, to chemists at the end of the nineteenth century, already in the 1880s and until the time of World War I. First and foremost, they saw it as a convenient shorthand notation, and a recapitulation both, of all the chemical reactions which had been performed on an individual chemical compound. These organic chemists of the late nineteenth century were very explicit on this point: a formula was to them a convenient means for encapsulating the chemical history of a molecule.<sup>8,9</sup>

History is the keyword. Allow me an analogy here: the formula was like a map.<sup>10</sup> In like manner as surveyors of a land, or as the explorers seeking the Northwest Passage and

mapping heretofore unknown lands in the Arctic,<sup>11</sup> organic chemists with their reactions were painstakingly determining for a given molecule (such as morphine) the identity of its component parts, piece by piece, segment by segment, chemical group by chemical group.

The other and equally strong meaning of a structural formula in the 1880s was as a word—we leave now the analogy from history and geography, and we turn to linguistics—in the newly-formed lexicon of organic chemistry. The organic chemists of the time had established a whole language based on this paper tool of the formula. It was a coherent language, understandable by all, printable. They did not have to worry about for instance the real existence of atoms, since they were well aware that any language has arbitrary and conventional foundations. But sharing this language, in Baltimore, Berlin, London, St Petersburg or Rome, gave them an elation, a wonderful sense of community and of a disciplinary identity. They were quite explicit about this other feature of structural formulas too. They knew them to be emblematic of organic chemistry.<sup>12</sup>

The next historical stage was the devising by Gilbert N. Lewis in the 1910s of what we now term Lewis formulas. His insight was to equate the bonds between the atoms in the Frankland formulas with pairs of electrons.<sup>13</sup> Thus, the distinction emerged quite naturally between bonding and non-bonding electrons, the latter on heteroatoms and on atoms bearing net electric charges.

The conceptual system of Lewis formulas, as it carried the day, together with the adequate rules for writing them, crystallized in the 1930s after Linus Pauling launched valence bonds<sup>14</sup> as the translation, for chemists, of quantum physics ideas into that language which chemists had learned to communicate with since the 1860s.<sup>15</sup> That Pauling was also an educator, that he relied heavily on graphics, and that he published all these textbooks of his, was the final step in the popularization of VB theory and of its essential ingredient, the Lewis formula.

### **A useful parallel**

This cannot be a blow by blow, year by year account of the history of the penetration of organic chemistry by mechanistic ideas, first in a few academic laboratories during the 1940s and the 1950s, leading then to a short-lived hegemony of physical organic chemistry during the 1960s, when classroom teaching started to become infused also with mechanistic explanations and notations.

Instead, I wish to submit a parallel with another shorthand notation, equally simple as that of the curved arrow, equally powerful and probably equally open to criticism, the VSEPR (valence shell electron pair repulsion) heuristic devised by Gillespie, from ideas originally brought forward by Nyholm and a few others.

Electron-pushing with curved arrows and the VSEPR rationale for molecular geometry share a view of organic molecules as consisting of a set of atoms connected with bonds consisting of localized electrons. They both view electronic density as a static distribution around each atomic nucleus. This distribution of electric charge can be shifted, either in relative terms when comparing, in the VSEPR framework, bonding and non-bonding electrons (the latter being closer to the nucleus and thus «larger»), or from the polarization associated with attack by a reagent such as a proton, the initial step in the sequence of events involved in the mechanism of a reaction.

Thus, both the curved arrow and the VSEPR formalisms deliberately ignore a key feature of electrons, basic to the alternate description, that of molecular orbital theory: electrons are mobile and delocalized over the entire molecule. And such a myopia is all right: any formalism has a formal aspect, it is by necessity no more than an approximation, a

travesty of reality. And indeed, if it is to be of heuristic value, then it has to be an oversimplification. It is all right, provided that one always keep in mind the precise limitations of the formalism which, like the cane an old person leans on, we rely upon. We should always remember that such paper tools are mere prosthetic devices.

My remarks are not to be misconstrued as denying merit, or validity, to these formalisms of the curved arrow and the VSEPR model. Each in its way reaches deep and catches important features of the physical phenomenon it attempts to describe. Furthermore, bridges can be built (and have been built) between valence bond and molecular orbital theories. The article by Karafiloglou in this issue exemplifies it, expressing electronic transfer through resonance structures. Other bridges also exist to connect the Lewis and VSEPR models with quantum chemistry, through the Laplacian of the electron density.<sup>16</sup>

Before going further, another point must be made with respect to an intrinsic defect of structural formulas, of Lewis formulas as used both to write a reaction mechanism or to predict molecular geometry. This limitation was already painfully obvious to the organic chemists in the 1880s: these are static structures, whereas of course any molecule at any temperature is a jelly-like pulsating, librating and vibrating entity. Only a terribly simplistic eye would see a molecule frozen into this Platonic archetype of the structural formula.

And indeed, to think of it, when we write any reaction mechanism, what we are truly doing is to replace a dynamic phenomenon, which we little understand, with a stroboscopy of a succession of instantaneous successive static structures. The reaction mechanism, in an often made analogy, is movie-like. But the movie we build consists in a very small number of still frames, it is—we tend to forget—entirely a fake reconstruction.

## A critique

My intent in this paper is not at all that of an archaic conservative, who wants to return organic chemistry to the Dark Ages, prior to its fertilization by reaction mechanisms. It is to try to influence colleagues, who teach to non-chemists, to find the appropriate subject matter and language to communicate with this important segment of our collective audience. To use mechanistic language on such a public, worse to make the listeners become conversant in that specialized language, is to do them a disservice, on two counts: they are not future chemists; thus they don't need to master the language of the specialists; in so doing, willingly nillingly we present to them a caricature of both chemistry and of the scientific endeavor.

This last point needs some elaboration. Thus, let us remind ourselves that study of any reaction mechanism is experimental in nature. It is hard work, using a large number of diverse tools: kinetics, in order to determine the rate law and to identify the slow step; determination of the activation energy and entropy, of the volume of activation; spectroscopy such as infrared or nuclear magnetic resonance, in order ideally to follow the reaction in real time in the test tube; and for determining the structure of all the stable and metastable species, reaction products and intermediates; trapping (cold finger) and isolation of intermediates; substituent and isotope effects; solvent effects; etc.

Then and only then, after we have done all of this work, which may take months, sometimes years, do we allow ourselves to couch the results in the language of reaction mechanisms, shifting electrons around with curved arrows, in order to present to our peers our results in a, iconic format, that of the reaction scheme, which will make the findings understandable at a glance. But, before making use of the formalism, we conducted a study of reality. The experimental work was antecedent upon its description, as it had to be.

The word « caricature » above is apt: to replace a description of reality, with all of its wonderful unpredictability, with the «chemistry on paper» of a fictional reaction mechanism is indeed a caricature. We substitute to the time arrow that of the logical deduction, and to the historical contingency, with all its accidental occurrences, a formal scenario obeying a strict propositional logic, an account which for being step-by-step, superimposes upon the real our limited and conventional imagination. Worse, we give the kids the impression of being zealots of a language which has never been integrated in their minds. They may give us the illusion of mastery, having memorized a huge amount of discrete alphanumeric symbols, without these hieroglyphic signs holding any meaning to them.

The writing of reaction mechanisms on paper, which classroom presentation encourages, is liable to yet another two criticisms. In the mind of people totally lacking in the experience of the experimental determination of a reaction mechanism, it encourages confusion between a working hypothesis and a reliable conclusion, between the virtual and the real.

Moreover, the writing of a reaction mechanism on paper, by contrast to its laborious construction at the bench, not only suffers from a surfeit of pure logic; it is marked, too, by arguments and thinking based, at least implicitly, on thermodynamics-controlled equilibria, on acid-base chemistry primarily. Such a mode of thinking promotes prediction of the most probable occurrence, whereas a chemical system sometimes elects to follow an unpredicted and a priori unlikely kinetic route, because the energy barrier to be crossed happens to be less unfavorable than along the other, competing pathways. Electron-pushing and curved arrows encourage a confusion between equilibria and kinetics which, to a great extent, should be kept apart. Thus, giving students the habit of writing reaction mechanisms, besides artificiality, can become an exercise in futility.

### **Another, admittedly provocative analogy**

Writing reaction mechanisms is central to the language of chemistry. In making this statement, I refer to the *technical* language of *professional* chemists.

Professionals, whether they are chemists, medical doctors, lawyers or theologians, have to make a huge effort whenever they wish to communicate an issue to a wider public—or, equivalently, to students

The effort entails a full and imaginative reconstruction (not a mere translation, which does not wash), with recourse to analogies, coining of memorable formulas, etc. Out of laziness they are likely to fall back on the technical jargon they are used to.

Our electron-pushing jargon of reaction mechanisms is a lovely means for chatting among ourselves. It is an economical short-hand. To extend its use from the laboratory to the classroom, when we teach non-majors, is to force linguistically incompetent speakers to master a slang, when they are unable to express themselves in the parent language.

Any slang is an impoverished version of its parent language. We are aghast at teenagers expressing themselves with stereotyped and ultimately meaningless small messages (taught by the «music» they listen to all day long), such as, in Americanese, «this is cool», «this is cute», «this is OK» and a few other such, ultimately meaningless or meaningpoor, expressions.<sup>17</sup> We ought to be wary of us, behaving in like manner to a rap singer, when we explain chemical reactions to undergraduates with no intent of becoming chemists themselves. We may be doing a disservice, to both the students and the chemical science, in choosing this easy route.

## CONCLUSION

True, children love to learn dirty words. This is fine, when the dirty words serve to spice up their language. It is unacceptable when they do not know any other words.

In short, the curved arrow formalism amounts to a potent drug to be kept out of the reach of children!

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