

APPLICATIONS OF TECHNOLOGY IN TEACHING CHEMISTRY  
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PAPER 3

VISUALIZING CHEMICAL REACTIONS

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ABSTRACT

Conventional (paper) representations of chemical reactions suffer in that they generally show only the atomic connectivity (topology) of the product and reactant molecules. We train students to infer additional information not contained explicitly in these representations such as three-dimensionality, atomic size and steric factors, statistics of bimolecular collisions, and even the higher-energy transition-state complex. Our representations and our teaching, however, seldom include the facts that the molecular fragments undergo several cycles of vibrational motion during the time of interaction, that the course of reaction depends upon the phase of these motions, and (most importantly) that the molecular orbitals (electron distributions), which are the only factors other than billiard ball dynamics affecting the outcome of the reaction, are constantly shifting in response to both motion along the molecular interaction coordinate and the vibrational motions of the molecular fragments. Three HyperChem "movies" of the prototype SN<sub>2</sub> reaction showing both atomic motions and frontier molecular orbitals throughout the course of the reaction are presented together with commentary about features unrecognized by most students.

I. TEXTBOOK REPRESENTATIONS OF CHEMICAL REACTIONS

Figure 1 shows three representations, taken from standard organic chemistry textbooks, of the prototype SN<sub>2</sub> reaction in which a hydroxide ion replaces a halide ion in an alkyl halide. The amount of information that has been deliberately or thoughtlessly left out of the symbolism and the amount of misinformation seemingly implied should give all teachers (and publishers) pause.

The first representation seems to imply that the reactants are directly converted to products and the symbolism suggests no mechanism. The tetrahedral structure of the carbon atom and the

necessary inversions are not apparent to the novice and the unsymmetrical symbolism about the carbon atom could be taken to be a typographical convention only or even to suggest an ionic dissociation followed by recombination. With little additional attention, the tetrahedral structure could have been made explicit with wedge bonds. True, the solid and dotted wedges also represent a convention, but they are closely related to visual phenomena and are guessed correctly by most persons. Had the tetrahedral structure of the carbon atom been represented explicitly using wedge bonds, a mechanism might at least have been suggested.

The second representation emphasizes the transition state complex with some division of formal charge and suggests the transfer of charge. Again, the exact structure of the transition state complex could have been made explicit by the use of wedge bonds. As it stands, the transition complex can quite plausibly be interpreted as five atoms in a plane around the carbon atom. The glaring inconsistency of representing the transition complex in great structural detail while representing the reactant and product as only  $\text{H}_3\text{C-X}$  and  $\text{HO-CH}_3$  not only raises a question as to whether there is any meaning in this inconsistency but also hides essential structural information that could and should have been included in an introduction to this important reaction type. The third representation emphasizes the mechanism for charge transfer without any attention to the necessary inversion of configuration. Without careful explanation of the curved arrow symbolism, the equation seems to imply that electrons from the hydroxide somehow go directly to some mysterious R (Does the rest of the hydroxide ion go along?) while a BOND goes to the halogen atom to make it a halide ion.

One could present myriad other examples of poor representations of this or any elementary chemical reaction in introductory textbooks. Suffice it to say that:

- 1) Standard printed representations of chemical reactions frequently show less of the essential geometric information than is easily possible.

- 2) If the geometric rearrangement is shown at all, it is implied that the transition is smooth and direct.

- 3) The mechanism for electron transfer or rearrangement is either omitted or shrouded in mystery (How do the electrons know to follow the arrows?).

- 4) Except for the rearrangement due to the reaction, it is not even hinted that the reactant, product, and transition state complex are not static structures.

## II. ELECTRONIC SCREEN REPRESENTATIONS OF CHEMISTRY

Modern electronic screen representations of chemistry are superior to hand-written or printed representations in at least five important ways and remove so many of the usual limitations to representing chemical reactions that we should seriously reconsider the medium for introductory instruction in chemistry.

First, THE ATOMS CAN BE EASILY AND AUTOMATICALLY PRESENTED DISPLAYING THEIR CORRECT RELATIVE SIZE. In hand-written representations, and especially in printed representations, the alphabetical symbols for the elements all have exactly the same size and H is apparently as large as I. For brevity, we further write groups such as Et, Ph, and Ts which are rendered in the same uniform type face. Without correct visual representation, it is easy to overlook the immense size of groups such as t-Bu or Ar (aryl) and beginning students frequently fail to recognize the (hidden) size factor altogether.

Second, THE ELECTRONIC REPRESENTATION, ALTHOUGH FLAT IN PRESENTATION, CONTAINS MANY VISUAL CUES TO REMIND US CONSTANTLY AND ASSIST US IN DEALING WITH THE THIRD DIMENSION. We think we become adept at imagining the third dimension, but which of us has not been surprised from time to time by a new insight gained from a particularly good three-dimensional model? Which of us, as a practicing chemist, does not keep a three-dimensional model kit near at hand to construct models that we may hold in our hands and ponder from different perspectives? The electronic screen presents us with a direct view of a three-dimensional molecule from a particular visual perspective with opacity and perhaps shadowing as further cues to the third dimension. Because the model can be grabbed and rotated to see what has been obscured, there is no need to distort the representation into two dimensions in an odd way to display all the features simultaneously. The presentation of the geometry is visually correct and needs no implied Fischer conventions; that which required abstraction for representation in typography can be represented concretely (and more realistically) in the electronic medium.

The electronic representation is not permanent, but is volatile and in need of constant refreshment. Because the refreshment must be accomplished by computation, there is no need to refresh exactly the same structure every time. MOLECULES MAY BE PRESENTED ELECTRONICALLY AS DYNAMIC OBJECTS with little computational overhead. This is especially important in representing chemical reactions. The conventional chemical equation on the printed page seems to imply that the reactants proceed directly to products and does not betray the several cycles of thermal vibrations the reactants and products undergo during even the brief course of a reaction or the alignment and phasing of these vibrations that is necessary if the reactants are to achieve the transition complex and cross over the reaction barrier. All this is simply swallowed up in a number called the Arrhenius pre-exponential factor and is nowhere in evidence in the representation of the reaction.

One of the most important representational issues in chemistry is still difficult in the electronic medium. Chemistry is the interaction between molecules. As one molecule approaches another, its electronic periphery encounters another electronic periphery. CHEMICALLY, A MOLECULE WOULD BEST BE SHOWN BY SOME DISPLAY OF THE ABSOLUTE AND RELATIVE DENSITY AS WELL AS THE DEFORMABILITY OF THIS ELECTRONIC PERIPHERY. The problem is that we must simultaneously present several properties that vary

continuously throughout three dimensions. These properties may be mapped to the new electronic dimensions of color and intensity. The eye is quite sensitive to GRADATIONS in both color and intensity and this aids greatly in representing the continuous nature of these variables. The real problem resides in representing these continuous functions IN THREE DIMENSIONS. Several conventions, including partial transparency, isosurfaces, slicing, and contour mapping seem difficult representations at best, but these must be compared to the limited options available to the printed medium in which representation of these properties remains nearly impossible.

Finally, the electrons which constitute the chemically reactive periphery of the molecule exist in different energy states and each state has its own distribution and properties. Electron orbitals are central to understanding the properties of a molecule and the electron orbitals are constantly changing in response to the dynamic positions of all the nuclei in the neighborhood. THE ELECTRONIC MEDIUM PROVIDES FOR THE CONSTANT RECOMPUTATION AND DISPLAY OF THESE DYNAMIC ELECTRON ORBITALS, but presentation of orbitals has all the problems noted in the previous paragraph PLUS the difficulty of distinguishing among different electron orbitals when it is necessary to display more than one simultaneously.

### III. CHEMICAL REACTIONS AS MOVIES

As an alternative presentation of SN2 reactions, I have created three 100-frame computer "movies" using the molecular dynamics and quantum mechanical features of HyperChem, a molecular modeling program developed by HyperCube and distributed by Autodesk, Inc. The first movie (PAP3SN2.FLC) shows the van der Waals surfaces of the atoms throughout the course of the reaction. The second and third (PAP3HOMO.FLC and PAP3LUMO.FLC) display also the frontier molecular orbitals through the entire course of the reaction.

In the atoms-only movie (PAP3SN2.FLC), the symmetric bending of the hydrogens in the methyl is clearly seen in frames 1 through 38 and again in frames 53 through 100. At about frame 50 it appears that after a firm collision, the hydroxide ion is about to rebound without reacting, but then (frame 70) the movement of mass associated with the next vibratory half cycle of the methyl group brings the carbon and oxygen atoms together while separating the carbon and chlorine atoms and this arrangement persists.

Because one is interested in electron distribution as well as the overall shapes of the orbitals, I have presented the orbitals in PAP3HOMO.FLC and PAP3LUMO.FLC as contour maps. Although contour maps represent the orbital in a single plane only, I have arranged the reaction fragments so that the reaction is cylindrically symmetrical about the O-C-Cl axis except for the hydroxide hydrogen which I have placed in the orbital plane. The total electron distribution in orbitals relating to the methyl hydrogens is (except for asymmetric vibrations) cylindrically

symmetrical.

In frame 1 of the HOMO movie, the reactive electrons in the hydroxide ion are seen to reside in p orbitals perpendicular to the O-H bond (not at tetrahedral positions as suggested by VSEPR theory). Very early in the encounter and while the hydroxide is still quite far away (frame 10) the vibratory motions of the methyl group have "opened" the carbon atom to the approaching reactant and the HOMO extends over the carbon and chlorine atoms (actually, the hydrogens have moved to the nodal plane of the 2p orbital on the carbon and the 2p orbital extends to mix with the 2p orbital on the hydroxide ion). Throughout the movies, the HOMO and LUMO are seen to adjust constantly to the wagging of the hydrogens as well as to the O-C and C-Cl bond distances.

The HOMO is seen to be a bonding orbital between O and C in frames 10 through 75 and between C and Cl in frames 33 through 80. Throughout, the LUMO is seen to be anti-bonding (lobes of opposite sign extending toward each other) between C and Cl, though the nature of the orbital between C and OH is not always clear. The HOMO begins on the hydroxide and ends on the chloride; the LUMO remains with the methyl throughout (HOMO = nucleophilic; LUMO = electrophilic!).

#### QUESTIONS FOR READERS

- 1) Aside from presenting other simulations in which collisions do not result in successful reaction, what other features can or could be seen in movies such as these?
- 2) What other orbital representations might be superior to contour maps? Contour maps show interior distributions but contour surfaces do not; contour surfaces show three-dimensional geometry explicitly, but show nothing of the interior. Cloud and voxel representations can appear featureless and, therefore, indistinct.

#### DESCRIPTION OF FIGURE AND MOVIES

PAP3FIG1.GIF

CAPTION: Figure 1. Representations of SN2 reactions found in current organic chemistry textbooks.

Black & white bitmap; 640 x 241 pixels x 2 bits per pixel.

|              |                 |                              |
|--------------|-----------------|------------------------------|
| PAP3SN2.FLC  | 1,288,578 bytes | 640 x 480 VGA animation file |
| PAP3HOMO.FLC | 2,153,172 bytes | 640 x 480 VGA animation file |
| PAP3LUMO.FLC | 2,440,578 bytes | 640 x 480 VGA animation file |

are obtained by "unzipping" the three files

PAP3SN2.ZIP  
PAP3HOMO.ZIP  
PAP3LUMO.ZIP

The three animation (\*.FLC) files may be played back using the "free distribution" DOS Autodesk Animator Pro Player (TM). [Autodesk also provides an animation player for Windows but the overhead computation associated with the Windows multitasking system makes the animations a bit "jerky." The DOS animation player is more satisfactory.]

The Autodesk Animator Pro Player (TM) and associated support files and drivers is obtained by "unzipping" file ANIPLAY.ZIP. To run the animation player, "CD" to the main directory and type "ANIPLAY". The screen size is preset for 640 x 480. If this is compatible with your system everything is fine; if not, select an appropriate "SCREEN SIZE" from the "FILE" menu. (Note that if you choose a screen size smaller than 640 x 480, the frames will be "clipped.") Then select "LOAD FLIC" from the "FILE" menu and specify the appropriate .FLC file. The animation is run with typical VCR type controls. Click the right mouse button to suspend the animation at any point. "QUIT" is on the "PLAYER" menu.

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