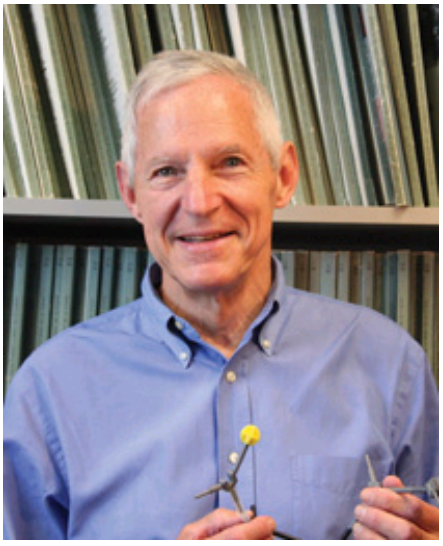
John Baldwin

Distinguished Professor of Chemistry



Email: ***jbaldwin@syr.edu***

Chemistry
4-014B Center for Science and Technology
Phone: 315-443-3743 / fax: 315-443-4070

Research Interests

Organic chemistry and physical organic chemistry; stereochemistry and mechanisms of thermal reactions of simple hydrocarbons

Education

- A.B., 1959, Dartmouth College
- Ph.D., 1963, California Institute of Technology

Honors & Awards

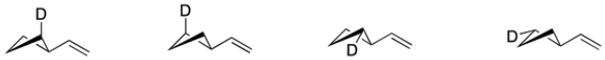
- 2010 James Flack Norris Award in Physical Organic Chemistry,
- William R. Kenan Jr. Professor of Science, Daniel Webster National Fellow,
- The Charles Lathrop Parsons Scholar, National Science Foundation Predoctoral Fellow,
- Alfred P. Sloan Fellow, John Simon Guggenheim Memorial Foundation Fellow,
- Senior U.S. Scientist Awardee of the Alexander von Humboldt Foundation

Research Focus

Creditable mechanistic descriptions to account for simple organic chemical reactions remain elusive in spite of serious efforts to gain them. Detailed experimental characterizations of reactions exhibiting more than one reaction path from reactant to product can contribute to attaining fresh mechanistic insights on just how specific transformations take place. Examples of published work representative of our efforts along these lines include studies of thermal stereomutations of cyclopropanes, structural isomerizations of vinylcyclopropanes to cyclopentenes and vinylcyclobutanes to cyclohexenes, and degenerate isomerizations of cycloalka-1,3-dienes. Current reactions under study include the

thermal stereomutations and [1,3] carbon sigmatropic shifts of deuterium-labeled vinylcyclobutanes and the fragmentation of ethylcyclopropane to form, among other products, butadiene and methane.

Studies of the reactions of vinylcyclobutanes labeled with deuterium could enable dynamic modeling of intermediate diradicals, but they would present considerable synthetic and analytical difficulties. How, for instance, could one determine the time-dependent relative concentrations of the four stereoisomers of 2-*d*-vinylcyclobutane in thermal reaction product mixtures? The usual spectroscopic methods would not be efficacious. A novel analytical method dependent in part on $^{13}C\{^{1}H,^{2}H\}$ NMR spectroscopy is now being essayed and has afforded promising initial results.



The conversion of ethylcyclopropane to butadiene and methane has been known for more than 40 years but has not been mechanistically clarified. Through studies of the reactions of isotopically labeled ethylcyclopropanes under shock-tube conditions, progress toward securing data affording mechanistic insights is being secured.

Such studies and findings, and related theory-based developments seeking to test and extend the mechanistic perceptions prompted by the experimental results, serve to deepen understandings of chemical reactivity. Whenever such experimental studies are forced to deal with some novel challenge presented by inherent kinetic complexities or extreme analytical requirements or demanding labeling schemes and synthetic requisites, the work also contributes to augmented appreciations of new tools mechanistic organic chemistry can apply to ferret out the not-so-obvious characteristics of chemical reactions.

Selected Publications

- Baldwin, J. E; Kiemle, D. J.; Kostikov, A.

P. Quantitative Analyses of Stereoisomeric

- 3,4-d_2-Cyclohexenes in the Presence of 3,6-d_2-Cyclohexenes. *J. Org. Chem.* **2009,** *74,* 3866-3874.
- O'Leary, D. J.; Allis, D. G.; Hudson, B. S.; James, S.; Morgera, K. B.; Baldwin, J. E. Vicinal Deuterium Perturbations on Hydrogen NMR Chemical Shifts in Cyclohexanes. *J. Am. Chem. Soc.* **2008,** *130,* 13659-13663.
- Baldwin, J. E.; Leber, P. A. Molecular Rearrangements Through Thermal [1,3] Carbon Shifts. *Org. Biomol. Chem.* **2008,** *6,* 36-47.
- Baldwin, J. E. Organic Chemical Reaction Mechanisms Clarified for Deuterium and Carbon-13 Labeled Hydrocarbons. *J. Label. Compd. Radiopharm.* **2007,** *50,* 947-960.
- Baldwin, J. E.; Raghavan, A. S.; Hess, Jr., B. A; Smentek, L. Thermal [1,5] Hydrogen Sigma-tropic Shifts in *cis,cis*-Cyclonona-dienes Probed by Gas-Phase Kinetic Studies and Density Functional Theory Calculations. *J. Am. Chem. Soc.* **2006,** *128,* 14854-14862.
- Baldwin, J. E.; Leber, P. A.; Powers, D. C. Thermal Reactions of 7-*d*- and 8-*d*-Bicyclo[4.2.0]oct-2-enes. *J. Am. Chem. Soc.* **2006,** *128,* 10020-10021

» View all Publications

College Directories

Arts and Sciences Faculty

Full Time Faculty, By Department

Instructors, By Department

Humanities Faculty

Fellows

Syracuse University Directory

Arts and Sciences Directory Lists

Research Spotlight

Chemistry Website Home Page

- Research Overview
- Faculty Listing
- Undergraduate Program
- Graduate Program
- Events
- News