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COMPLETED PROJECT SUMMARY

TITLE: Dynamic Constraints on Stochastic Behavior in the Chemistry of Highly Excited Molecules.

INCLUSIVE DATES: April 15 1987 - April 14 1990

GRANT NUMBER: AFOSR-87-0165

SENIOR RESEARCH PERSONNEL: Barry K. Carpenter, John R. Wiesenfeld

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PUBLICATIONS:

Williams, F.; Guo, Q.-X.; Bebout, D. C.; Carpenter, B.K. *J. Am. Chem. Soc.* **1989**, *111*, 4133.

Newman-Evans, R.H.; Simon, R.J.; Carpenter, B.K. *J. Org. Chem.* **1990**, *55*, 695.

Lyons, B.A.; Pfeifer, J.; Carpenter, B.K. *J. Am. Chem. Soc.* submitted.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

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Project Number	AFOSR-87-0165
Project Title	Dynamic Constraints on Stochastic Behavior in the Chemistry of Highly Excited Molecules
Principal Investigator	Barry K. Carpenter
Co-Investigator	John R. Wiesenfeld
Project Period	April 15 1987 - April 14 1990
Project Status	Completed
Project Location	Stanford University
Project Funding	AFOSR-87-0165
Project Budget	\$1,000,000
Project Personnel	Barry K. Carpenter, John R. Wiesenfeld, Deborah C. Bebout, Barbara A. Lyons, Jörg Pfeifer, Reyna J. Simon
Project Publications	Williams, F.; Guo, Q.-X.; Bebout, D. C.; Carpenter, B.K. <i>J. Am. Chem. Soc.</i> 1989 , <i>111</i> , 4133. Newman-Evans, R.H.; Simon, R.J.; Carpenter, B.K. <i>J. Org. Chem.</i> 1990 , <i>55</i> , 695. Lyons, B.A.; Pfeifer, J.; Carpenter, B.K. <i>J. Am. Chem. Soc.</i> submitted.
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Project Evaluation	A-1



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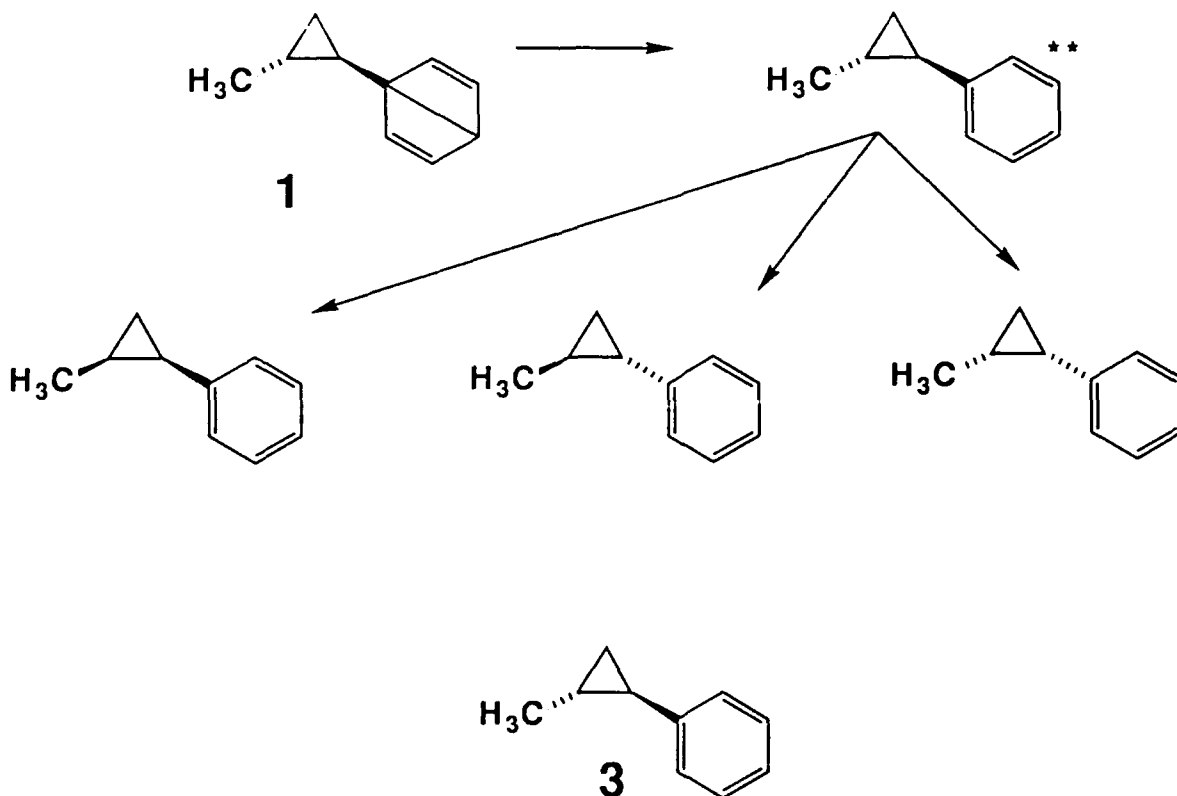
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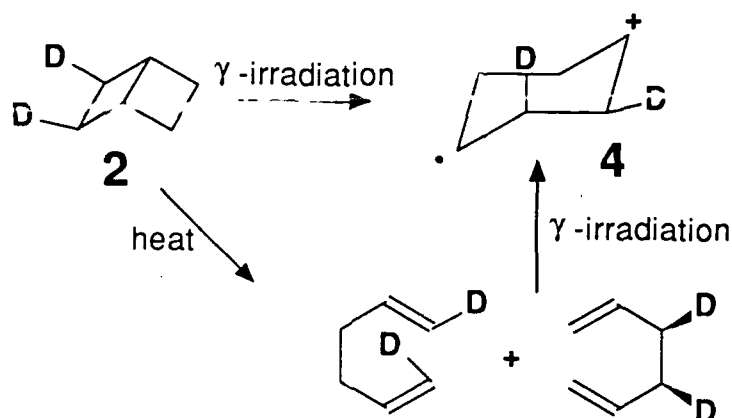
*Dynamic Constraints on Stochastic Behavior
in the Chemistry of Highly Excited Molecules*

Barry K. Carpenter and John R. Wiesenfeld

- We accomplished the synthesis of optically active compounds **1** and **3**. The thermal chemistry of both compounds was being investigated and compared when the financial support was terminated. The statistical theories of kinetics would require that the branching ratios to stereoisomeric products be identical from these two compounds; demonstration of a difference would have constituted an incontrovertible illustration of dynamic effects in thermal chemistry. Such a phenomenon would be of profound importance in the thermal reactions of the high-energy-density materials currently being designed as advanced propellants. Lack of continued support for the project will not now permit the investigation of this phenomenon.

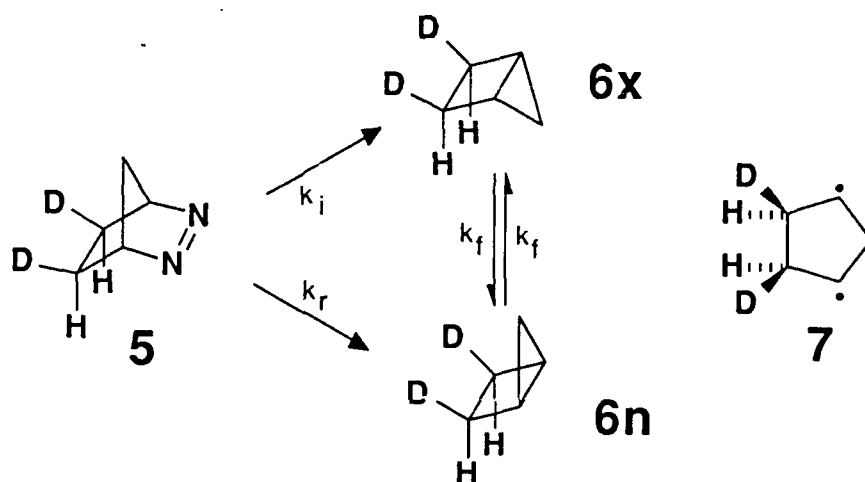


- In the process of development of the synthetic techniques for the preparation of 1 we found ways to prepare deuterium-labeled compound 2. This material was used, in collaboration with Professor Ffrancon Williams at the University of Tennessee, Knoxville, to generate and characterize the radical cation 4. This study has been published.¹ The results indicate that 4 has a chair-like geometry and that it is formed in this geometry from 1,5-hexadiene.



- We have prepared and pyrolyzed azo compound 5. We have solved the kinetics for its conversion to the interconverting products 6x and 6n in closed form and have thereby deduced the ratio of rate constants k_i and k_r as a function of temperature. Both in the gas phase and in solution the ratio of these rate constants is found to be temperature independent within experimental error.² Such a result is inconsistent with a branching ratio determined by exit-channel differences, but is consistent with a dynamically determined ratio.³ The influence of the solvent is interpreted as a randomizing influence on the ballistic trajectories of the molecules passing through biradical 7 (see diagram on page 3).

The reaction was being used as a probe for efficiency of energy transfer between the reacting molecule and surrounding solvent molecules. The dependence of efficiency of quenching of the ballistic effects on the availability of low-frequency vibrations in the solvent was being studied. This work would have been at the forefront of problems being considered by theorists in statistical mechanics. Again, its implications for the analysis of energy disposal in thermal reactions of high-energy-density materials are profound, but cannot now be investigated because of lack of continuing financial support from AFOSR.



¹ Williams, F.; Guo, Q.-X.; Bebout, D.C.; Carpenter, B.K. *J. Am. Chem. Soc.* **1989**, *111*, 4133.

² Lyons, B.A.; Pfeifer, J.; Carpenter B.K. *J. Am. Chem. Soc.* **1991**, submitted.

³ Newman-Evans, R.H.; Simon, R.J.; Carpenter B.K. *J. Org. Chem.* **1990**, *55*, 695.