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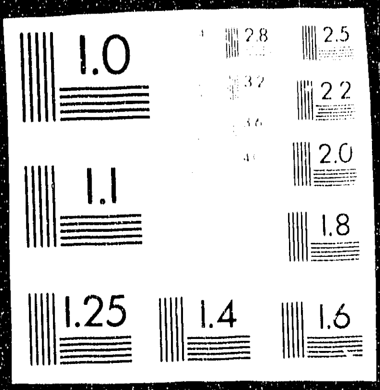

PROGRESS REPORT

SUBMITTED UNDER GRANT NO. DE-FG05-88ER13852

BETWEEN THE

DEPARTMENT OF ENERGY

AND

THE UNIVERSITY OF TENNESSEE
Knoxville, Tennessee 37996-1600

DOE/ER/13852--192

DE92 011807

PERIOD

SEPTEMBER 1, 1990 TO OCTOBER 15, 1991

STUDIES OF RADIATION-PRODUCED RADICALS AND RADICAL IONS

Principal Investigator

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DOE REPORT NO.

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I. PERSONNEL

(1) *T. Ffrancon Williams*: Professor of Chemistry and Alumni Distinguished Service Professor.

(2) *Jih Tzong Wang*: Postdoctoral Research Associate. Dr. Wang's association with this project started in 1966 and he received both his M.S. (1968) and Ph.D. (1972) degrees from The University of Tennessee. He was a postdoctoral research associate from 1978 to 1982, and rejoined the project again in May, 1985. Dr. Wang has held academic positions in Taiwan at the Chung Shan Institute of Science and Technology and the Chung-Jen Institute of Technology, and most recently he was a Professor of Chemical Engineering at the Tatung Institute of Technology in Taipei.

(3) *Guo-Fei Chen*: Visiting Research Associate. Mr. Chen is a visiting researcher from Professor Xikui Jiang's group at the Shanghai Institute of Organic Chemistry, and joined this project on May 1, 1989. His past experience in free radical chemistry and ESR spectroscopy provided him with an excellent background to our current research studies, and Mr. Chen has quickly become a productive member of the group.

(4) *Robert S. Pappas*: Graduate Teaching and Research Assistant. Mr. Pappas was an undergraduate research participant in our group from Indiana University Southeast, New Albany, Indiana, during the summer terms of 1989 and 1990, when he was the recipient of fellowships under the State of Tennessee's Centers of Excellence Program. He entered The University of Tennessee as a graduate student on August 1, 1990, and passed all four entrance examinations. He has made excellent progress in his graduate work, as can be judged from his current GPA of 4.0. Mr. Pappas has also nearly completed the cumulative

examination requirements in less than a year, as compared to an average time of 2-3 years taken by our graduate students.

II. FACILITIES AND EQUIPMENT

The major equipment used in this project consists of two ESR spectrometer systems, two cobalt-60 γ radiation sources, two liquid helium cryostat systems for use with the ESR spectrometers, a liquid chromatograph, and a portable glove box system. These items were described in detail in last year's Progress Report (DOE/ER/13852-188).

This research project depends particularly on the use of the BRUKER ER 200D SRC electron spin resonance spectrometer acquired with the aid of an NSF instrumentation grant in 1982. This instrument is dedicated to our research activities, and is operated only by experienced personnel within the group. No serious problems occurred during the past year and there was virtually no "downtime" on the instrument. The Systron-Donner Model 6054 B microwave frequency counter used in conjunction with the ESR spectrometer became inoperable, however, and the counter had to be returned to the manufacturer for extensive repair.

The gamma irradiation facilities provided by two cobalt-60 sources also play a vital role in this research. The routine operation of these units can be affected by mechanical and electrical problems from time to time, but no serious difficulties were encountered in the past year.

III. PUBLICATIONS

The following reports have been prepared during the past year and submitted for publication; these preprints are included with this Progress Report.

1. [DOE/ER/13852-189] "Photochemical and ESR Spectral Evidence for a Stereoselective Rearrangement of Radical Cations Derived from Azoalkanes and Bicyclopentanes" by W. Adam, H. Walter, G.-F. Chen, and F. Williams, submitted to *J. Am. Chem. Soc.*

2. [DOE/ER/13852-190] "Radical Cation Rearrangement of 4-Vinylcyclohexene to Bicyclo[3.2.1]oct-2-ene: A Matrix-Isolation ESR Study" by G.-F. Chen and F. Williams, *J. Am. Chem. Soc.* **1991**, *113*, 7792-7794.

3. [DOE/ER/13852-191] "Matrix ESR Evidence for the Formation of the Bicyclo[3.2.0]hepta-2,6-diene Radical Cation Both from Ionized Quadricyclane and as an Intermediate in the Radical Cation Photoisomerization of Norbornadiene to Cycloheptatriene" by G.-F. Chen, J. T. Wang, F. Williams, K. D. Belfield, and J. E. Baldwin, submitted to *J. Am. Chem. Soc.*

Two other preprints are included with this Progress Report as follows:

4. "Radical Cation Photoisomerization of Norbornadiene to Cycloheptatriene in Freon Matrices. ESR Evidence for Consecutive Reactions Through the Bicyclo[3.2.0]hepta-2,6-diene Radical Cation" by G.-F. Chen, J. T. Wang, F. Williams, K. D. Belfield, and J. E. Baldwin. This preprint provides additional experimental evidence for the role of the bicyclo[3.2.0]hepta-2,6-diene radical cation in the thermal and photochemical interconversion of $C_7H_8^{\cdot +}$ isomers. This material will be incorporated in an eventual full paper on the subject of the Communication listed under (3) above. Because of size limitations, only one paragraph of the subject matter of (4) could be included in (3).

5. "Photochemical Interconversions of Dihydropentalene Radical Cations" by T. Bally, S. Dai, L. Truttmann, J. T. Wang, and F. Williams. This preprint describes a series of photochemical transformations starting from the bicyclo[3.3.0]octa-2,6-diene-4,8-diyl radical cation which was characterized by previous studies in our group (S. Dai, J. T. Wang, and F. Williams, *J. Am. Chem. Soc.* **1990**, *112*, 2835-2837 and 2837-2839). The material of this preprint will form one of two full papers dealing with the thermal and photochemical interconversions of the family of $C_8H_8^{\cdot +}$ isomers.

IV. PRESENTATIONS AND OTHER SCIENTIFIC ACTIVITIES

Conference presentations were made by Dr. Williams as follows:

(1) Invited lecture on "Orbital Reorganization in the Transformations of Radical Cations: Electron Spin Resonance Studies in Matrices" at the 8th Asilomar Conference on Mass Spectrometry, Pacific Grove, California, September 23-27, 1990.

(2) Invited lecture on "Electronic Structures and Reactions of Some Organic Radical Cations" at the Division of Organic Chemistry Symposium on "Single-Electron Transfer Initiated Reactions," 201st National Meeting of the American Chemical Society, Atlanta, Georgia, April 17, 1991.

(3) Talk on "Matrix ESR Studies of Organic Radical Cations and Their Thermal and Photoinduced Rearrangements" at the Fifteenth DOE Solar Photochemistry Research Conference, Snowmass Village, Colorado, June 2-6, 1991.

(4) Invited talk on "Thermal and Photoinduced Radical Cation Rearrangements" at the 1991 Miller Conference, Giens, France, September 16-20, 1991.

Abstracts of the papers presented at the ACS Symposium and the DOE Conference are included with this report.

Dr. Williams served as a Member of The University of Chicago 1991 Review Committee for the Chemistry Division at Argonne National Laboratory, May 6-8, 1991. Also, he was an internal member of the Mid-Cycle Review Committee for the Department of Materials Science and Engineering at The University of Tennessee, October 14 & 15, 1991.

Research seminars were presented by Dr. Williams at the IBM Almaden Research Center, Almaden, California (September 28, 1990), the Institute of Organic Chemistry at the University of Würzburg, Germany (September 12, 1991), and the Institute of Physical Chemistry at the University of Fribourg, Switzerland (September 23, 1991).

V. RESEARCH ACCOMPLISHMENTS

(1) By employing compounds with a stereochemical label, the precise pathway of

hydrogen (or methyl) migration has been demonstrated unequivocally in a radical cation rearrangement for the first time. ESR studies revealed that matrix-isolated cyclopentane-1,3-diyl radical cations produced by the radiolytic oxidation of bicyclo[2.1.0]pentanes adopt puckered (C_s) conformations in which the *pseudo-axial* substituent originally in the *syn* position on the methylene bridge is in almost perfect coplanar alignment with the radical cation 2p orbital lobes at the bridgehead positions. This alignment might be expected to facilitate migration, and it was shown that in the subsequent rearrangement, the pseudo-axial substituent does in fact migrate stereospecifically to one of the bridgehead positions to form the corresponding olefin radical cation. Thus, the radiolytic oxidation of *anti*-5-methylbicyclo[2.1.0]pentane gives the 1-methylcyclopentene radical cation as the sole rearrangement product by H migration whereas oxidation of its *syn* isomer results in the highly selective formation of the 3-methylcyclopentene radical cation by methyl group migration. Since exactly the same stereoselectivity of olefin formation was observed in corresponding PET (photosensitized electron transfer) studies in the liquid phase, it is concluded that the rearrangement in this case also occurs through the intermediacy of radical cations. Clearly, the radical cation rearrangement must occur very rapidly (10^{-8}-10^{-9} s) under liquid-phase conditions at room temperature to compete with back electron transfer, and therefore the hydrogen (or methyl) migration is a fast process under these conditions. Further details are given in report DOE/ER/13852-189 included as preprint (1).

Although the observed selectivity of *pseudo-axial* substituent migration vicinal to the carbon radical center fully accords with chemical expectation, there is no precedent for this finding. The only comparable study of stereochemical preference in radical reactions that we are aware of concluded that in the disproportionation of two cyclohexyl radicals within a solvent cage, it was the *pseudo-equatorial* hydrogen that migrated to the attacking radical center (Livant, P.; Lawler, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 6044-6045). The authors recognized the surprising nature of this result and attributed it to steric effects or a distorted transition state connected with the bimolecular nature of this particular reaction.

(2) An intramolecular cycloaddition reaction was demonstrated in the radical cation rearrangement of 4-vinylcyclohexene to bicyclo[3.2.1]oct-2-ene (Chen, G.-F.; Williams, F. *J. Am. Chem. Soc.* **1991**, *113*, 7792-7794). A feature of this study was the identification of the product radical cation from a potential list of more than sixteen $C_8H_{12}^{\cdot+}$ isomers by using the structural information (coupling constants) in the ESR spectrum to narrow the field of suitable candidates to two or three. As well as being scientifically satisfying, this approach is the only practical way to solve the problem when the radical cation rearrangement (as in this case) is so unusual that the product species is not easily predictable on chemical grounds. These remarks also apply with particular force to the photoisomerization of the norbornadiene radical cation discussed below under (3).

(3) As described in preprint (3), ESR studies show that the radiolytic oxidation of quadricyclane in Freon matrices under conditions of high substrate dilution leads to the bicyclo[3.2.0]hepta-2,6-diene radical cation as well as the previously reported norbornadiene radical cation, the former species predominating at sufficiently low concentrations. These results are interpreted in terms of vibrationally excited quadricyclane ions undergoing two reaction paths, one of low energy to give the norbornadiene radical cation and the other of high energy to the bicyclo[3.2.0]hepta-2,6-diene radical cation. The concentration

dependence of the results is attributed to vibrational energy transfer from the excited quadricyclane ion to neutral quadricyclane in the matrix, thereby favoring the low-energy pathway at high concentrations. The two pathways represent the two alternate ways for the simultaneous opening of identical C-C bonds in the cyclopropane rings of the quadricyclane radical cation, and correspond to the potential reactivities of the $^2B_1$ ground state and the $^2A_2$ excited state. The bicyclo[3.2.0]hepta-2,6-diene radical cation has also been detected as an intermediate in the radical cation photoisomerization of norbornadiene to cycloheptatriene. Its formation is again attributed to a pathway from an excited quadricyclane radical cation precursor, the latter being formed in this system by the photoactivation of the norbornadiene radical cation.

There are two notable results from this work. First, the detection of the bicyclo[3.2.0]hepta-2,6-diene radical cation as an intermediate in the photoisomerization of the norbornadiene radical cation to the cycloheptatriene radical cation was quite unexpected on simple chemical grounds since its formation requires a drastic rearrangement of the $C_7H_8^{\cdot+}$ carbon framework. This rearrangement becomes understandable, however, by recognizing that the $^2A_1$ photo-excited state of norbornadiene can be transformed to an excited state of the quadricyclane radical cation which can then rearrange by suitable opening of the cyclopropane rings to the bicyclo[3.2.0]hepta-2,6-diene radical cation. Nicely interlocking with this interpretation is the second finding that the bicyclo[3.2.0]hepta-2,6-diene radical cation is in fact produced thermally from the oxidation of quadricyclane under matrix and solute conditions where vibrational energy loss is minimized. Thus it appears that an **electronically excited state** of the quadricyclane radical cation is generated by vertical ionization in a matrix. As far as we are aware, this is the first time that experimental evidence has been obtained for such a process.

Reprints + Preprints removed

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