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PERIOD

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STUDIES OF RADIATION-PRODUCED RADICALS AND RADICAL IONS

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I. PUBLICATIONS (1994-2000)

The following papers have been published or accepted for publication. Copies of these papers are included in this report. The names of the co-authors with the Principal Investigator are given in parentheses.

1. (with A. Marcinek, J. Rogowski, J. Gebicki, and G.-F. Chen) "Isomerization of Cubane Radical Cation," *J. Phys. Chem.*, in press.
2. (with T. Bally, S. Bernhard, S. Matzinger, L. Truttman, Z. Zhu, J.-L. Roulin, A. Marcinek, J. Gebicki, G.-F. Chen, H. D. Roth, and T. Herbertz) "The Radical Cation of *anti*-Tricyclooctadiene and Its Rearrangement Products," *Chem. Eur. J.*, **6**, 849-857 (2000).
3. (with T. Bally, S. Bernhard, S. Matzinger, J.-L. Roulin, G. N. Sastry, L. Truttman, Z. Zhu, A. Marcinek, J. Adamus, R. Kaminski, J. Gebicki, G.-F. Chen, and M. Fülcher, "The Radical Cation of *syn*-Tricyclooctadiene and Its Rearrangement Products," *Chem. Eur. J.*, **6**, 858-868 (2000).
4. (with T. Bally and L. Truttman) "Isomerizations of $C_8H_8^{+\bullet}$: Experiments and Calculations in Synergy," *J. Mol. Struct. (THEOCHEM)*, **398-399**, 255-263 (1997).
5. (with T. Bally, L. Truttman, and J. T. Wang) "Electronic Structure and Photochemical Interconversions of Dihydropentalene Radical Cations," *J. Am. Chem. Soc.*, **117**, 7916 (1995).
6. (with T. Bally, L. Truttman, and S. Dai) "The $C_8H_8^{+\bullet}$ Radical Cations of Cyclooctatetraene, Semibullvalene, and Their Common Bisallylic Rearrangement Product: Electronic Structure and Potential Energy Surfaces," *J. Am. Chem. Soc.*, **117**, 7923 (1995).
7. (with D. Vollmer, D. Rempel, and M. L. Gross) "Isomerization of the 4-Vinylcyclohex-1-ene Radical Cation: A Tandem Mass Spectrometry Study", *J. Am. Chem. Soc.*, **117**, 1669 (1995).
8. "Comment on the Whiffen Expression and Its Application to the Structural Characterization of the Radical Cation Derived from Semibullvalene", *J. Phys. Chem.*, **98**, 8258 (1994).
9. (with W. Adam, C. Sahin, J. Sendelbach, H. Walter, and G.-F. Chen) "Regioselective Rearrangement of Bridgehead-Methyl Substituted Radical Cations Derived from Bicyclo[2.1.0]pentanes and 2,3-Diazabicyclo[2.2.1]hept-2-enes through Photoinduced Electron Transfer and Radiolytic Oxidation: Product Distribution and Matrix ESR Studies," *J. Am. Chem. Soc.*, **116**, 2576 (1994).

10. "Inverted Potential Energy Surfaces in the Radical-Cation Cope Rearrangements of 1,5-Hexadiene and Semibullvalene," *J. Chem. Soc., Faraday Trans.*, **90**, 1681 (1994)
[Proceedings of *Faraday Symposium 29*, "Potential Energy Surfaces and Organic Reaction Paths," held at the University of Oxford, England, December 15-17, 1993].

II. Ph. D. Theses

1. Robert S. Pappas, "Vibronic Coupling Interactions in Organic Radical Cations: A Matrix ESR Study," University of Tennessee, August, 1995.
2. Bin Jiang, Part 1, "A Matrix ESR Study of Radical Cations of Acyclic Enediyne Compounds," University of Tennessee, December, 1999.

III. Summary

This summary covers work carried out during the original grant renewal period from July 15, 1994 to July 14, 1997 as well as during the subsequent no-cost extensions of the grant through December 14, 1999. Earlier work under this project is summarized in DOE Report No. DOE/ER/13852-201.

1. *Electronic Structure and Photochemical & Thermal Interconversions of $C_8H_8^{+\bullet}$ Species*

Considerable progress has been made in this general area. Starting with our discovery in 1990 of the photorearrangement of the cyclooctatetraene radical cation ($COT^{+\bullet}$) by cycloaddition to the oxidized form ($BOD^{+\bullet}$) of the bisallylic biradical, bicyclo[3.3.0]octa-2,6-diene-4,8-diyl [*J. Am. Chem. Soc.* 1990, *112*, 2837], the photochemistry of these species has been systematically explored by both ESR and EA (electronic absorption) spectroscopy, and several additional $C_8H_8^{+\bullet}$ isomers have been characterized. Thus, in a subsequent collaboration with the group of Thomas Bally (University of Fribourg, Switzerland), the photoproduct of $BOD^{+\bullet}$ formed consecutively from $COT^{+\bullet}$ was shown to be the 1,4-dihydropentalene radical cation ($1,4-DHP^{+\bullet}$) produced by two hydrogen shifts [*Chem. Phys. Lett.* 1993, *212*, 141-149] and not the highly strained tetracyclic diyl radical cation postulated by other workers [C. J. Rhodes and C. Glidewell, *J. Chem. Soc. Perkin Trans. (2)* 1992, 1481].

Additional studies have demonstrated a remarkable series of further photochemical interconversions among these dihydropentalene (DHP) radical cations. For example, 1,4-DHP^{•+} undergoes successive transformations into the 1,5-DHP^{•+} and 1,6-DHP^{•+} species. Moreover, the 1,6-DHP^{•+} can be converted quantitatively to regenerate 1,4-DHP^{•+}, thereby completing a photochemical cycle in which the separate activation steps are carried out in the visible and near infrared regions of the spectrum. These photoinduced hydrogen shifts are found to obey selection rules based on the symmetry properties of frontier molecular orbitals. In particular, the use of the orbital phase continuity principle determines whether a reaction is allowed or forbidden according to the nodal properties of the singly occupied molecular orbitals (SOMOs) in the reactant and product species. This MO-correlation approach is applicable to both thermal and photochemical reactions.

A comprehensive paper describing these studies was published [*J. Am. Chem. Soc.* 1995, 117, 7923-7934] together with a related full paper [*J. Am. Chem. Soc.* 1995, 117, 7916-7922] on the detailed mechanism for the photoconversion of COT^{•+} to BOD^{•+}. The driving force for this latter rearrangement by internal cycloaddition stems from a strong Jahn-Teller distortion of the ²E second excited state of COT^{•+}, a process that represents significant structural progress towards the product. In fact, there is a direct crossing from the potential energy surface of this second excited state of the reactant to the ground state surface of BOD^{•+} so that the photoreaction competes successfully against internal conversion to the lowest ²A₂ excited state of COT^{•+}, in violation of Kasha's rule.

In further investigations on $C_8H_8^{2+}$ isomers, recent work has focussed on the radiolytic oxidation of *syn*- and *anti*-tricyclo [4.2.0.0^{2,5}]octa-3,7-diene, and we have also studied the highly symmetrical cubane. Full accounts of these detailed studies have recently been published [*Chem. Eur. J.* 2000, 6, 849-857 and 858-868] or are in press [*J. Phys. Chem.*], and the papers are included in this report.

2. *Vibronic Coupling Interactions in Organic Radical Cations*

This topic serves as an intellectual framework for much of our current work on both the structural and reactivity properties of organic radical cations, and is the subject of a dissertation (Robert S. Pappas, Ph.D. Thesis, University of Tennessee, August 1995). Vibronic coupling between ground and excited states is inversely proportional to the energy gap between these states. Consequently, many organic radical cations, which frequently possess a close-lying excited state within 1-2 eV of the ground state, are natural candidates for the exhibition of strong interactions.

Evidence for these vibronic coupling effects has been obtained from structural studies of geometric distortions carried out in collaboration with the group of Stephen F. Nelsen (University of Wisconsin), and also from the detailed analysis of reaction pathways for the radical cations of highly strained molecules. As representative of a vibronically-induced geometric distortion, the bicyclo[2.2.2]oct-2-ene radical cation is found by ESR studies to exhibit an alternating linewidth effect which can be interpreted in terms of a double minimum. The ESR evidence for the hyperfine splitting by only two *exo*-hydrogens at low

temperature clearly shows that these minima correspond to the two equivalent forms of the radical cation produced by twisting the olefinic bond such that the symmetry is reduced from C_{2v} to the C_2 point group. This is precisely what would be anticipated according to the theory of vibronic coupling since the a_2 torsional mode represents the vibration that couples the 2B_1 (π) ground state with the low-lying 2B_2 (σ) excited state.

Turning now to an example of how reactivity can be influenced by vibronic interactions, the rearrangement of the bicyclo[1.1.1]pentane radical cation to the 1,4-pentadiene radical cation affords a clearcut illustration. Considerations based only on the ground state of the bicyclo[1.1.1]pentane radical cation provide no inkling that the bicyclic rings would tend to open. Indeed, to the contrary, one might have expected this bicyclic radical cation to be relatively unreactive since the highest occupied molecular orbital in the neutral molecule is antibonding between the bridgehead carbons, and therefore ionization from this orbital should in principle stabilize the radical cation.

However, vibronic coupling brings about an admixture of an excited state in which the unpaired electron now occupies a strongly bonding orbital between the bridgehead carbons and the CH_2 groups. Consequently, the bonding in the radical cation is weakened. Moreover, a detailed analysis shows that the vibrational coupling mode becomes the natural reaction coordinate for the rearrangement by the concerted opening of the two rings to give the acyclic 1,4-pentadiene radical cation. Thus, the combination of the appropriate reaction coordinate together with the admixture of excited-state character that is introduced along this coordinate profoundly affects the dynamics by creating a low-energy path for the reaction.

A similar study on the radiolytic oxidation of the closely analogous [1.1.1]propellane molecule has also been carried out by Pappas, and this gave further evidence for the influence of vibronic mixing in promoting reactivity by the lowering of potential energy barriers. Essentially this comes about as a result of the lowering of overall symmetry which facilitates an "avoided crossing" instead of a symmetry-constrained pathway proceeding right up to the conical intersection of the ground-state and excited-state surfaces. It is also noteworthy that the photoelectron spectrum of [1.1.1]propellane provides a strong independent indication that vibronic mixing is important, as evidenced by the unusual vibrational structure of the first band in the study reported by Heilbronner and Wiberg [*J. Am. Chem. Soc.* 1985, 107, 7172].

3. *The "Open-Chain" Radical Cation of 1,1,2,2-Tetramethylcyclobutane*

In a joint project with the group of Joshua L. Goodman (University of Rochester), we have been successful in characterizing the title species by ESR spectroscopy following its generation by the radiolytic oxidation of 1,1,2,2-tetramethylcyclobutane and also of 3,3,6,6-tetramethyl-1,2-diazacyclohex-1-ene. The spectrum consists of a well-defined septet with a hyperfine splitting of 27.2 G(6H) at temperatures below 100 K, but this pattern changes reversibly to a multiplet of some 17 lines with a spacing of 12.1 G at 160 K. At the intermediate temperature of ca. 135 K, the spectrum consists of a broad unresolved envelope.

These results are consistent with an open form of the radical cation having C_2 symmetry. Using the 1,1,4,4-tetramethylbutane-1,4-diyl radical cation nomenclature, the butane-diyl cation conformation at C(2) - C(3) is *gauche* such that the C_2 axis is perpendicular to the plane containing the *anti* methylene hydrogens and this C(2) - C(3) bond. The low-temperature 7-line pattern is then readily interpreted as resulting from hyperfine interaction with 6 hydrogens that are aligned parallel with the diyl p orbitals at C(1) and C(4), one each from the four methyl groups and the other two being the *gauche* methylene hydrogens at C(2) - C(3). The multiplet at higher temperature is then assigned to the onset of free rotation in the methyl groups; this is probably accompanied by an outward rotation of the diyl p orbitals about the C(1) - C(2) and C(4) - C(3) bonds to render the four methylene hydrogens approximately equivalent in hyperfine coupling as a result of the change in alignment. The broad spectrum seen at intermediate temperatures is consistent with the dynamics for reversible conformational changes of this kind.

In this proposed *gauche* or *cisoid* structure for the butane-diyl radical cation; delocalization over the two diyl centers is achieved by through-space coupling involving the direct overlap of the p orbitals. An *anti* or *transoid* butane-diyl cation structure would allow through-bond coupling for delocalization, but the ESR spectrum at low temperature is difficult to reconcile with such a structure in which all four methylene hydrogens would be equivalent. Clearly, the coupling to six equivalent hydrogens in the low-temperature spectrum strongly supports the *gauche* or *cisoid* structure. As far as we are aware, this study represents the first direct evidence for an open diyl radical cation of this type,

although just such an intermediate has long been postulated as the first product in the 2 + 1 cycloaddition of vinyl compounds such as *N*-vinylcarbazole which takes place via a chain reaction [Ledwith, *Acc. Chem. Res.* **1972**, *5*, 133]. In such reactions, this intermediate is likely to function as the propagating species which undergoes an electron transfer reaction with the vinyl monomer. In this way the monomer radical cation is regenerated and the diyl cation is converted to a biradical which can undergo rapid ring closure to give the diamagnetic cyclobutane product. Such a mechanism does not require the postulation of both open-chain and closed cyclobutane radical cation intermediates, as has been previously proposed.

Moreover, our finding that the oxidation of the diaza compound (3,3,6,6-tetramethyl-1,2-diazacyclohex-1-ene) yields the same signal carrier as that obtained directly from the oxidation of 1,1,2,2-tetramethylcyclobutane also argues against the existence of separate open and closed forms of a substituted cyclobutane radical cation. Since the oxidation of the diaza compound must initially generate an open radical cation following the extrusion of molecular nitrogen from the parent cation, these experiments with the two different precursors were designed to probe the possible existence of two different species. Thus the conclusion in favor of the single (open) species is supported by the similar results for these two precursors.

4. *Radical Cations of Pyridinophane and Pyridine*

In a joint project with the group of Vincenzo Barone (University of Naples, Italy), we have characterized the radical cations of [2,2] (2,6)pyridinophane and pyridine through the combination of experimental ESR spectroscopy and theoretical calculations using density functional theory (DFT). The pyridinophane molecule consists of 2 pyridine rings linked together at the 2,6 positions by dimethylene ($-\text{CH}_2\text{CH}_2-$) bridges. In the neutral species, the pyridine rings avoid each other because of the strong repulsion between the filled lone-pair orbitals on the nitrogens. Our interests in this molecule was to determine whether the radical cation would adopt a much “flatter” geometry than that of the neutral molecule corresponding to the idealized formation of a 3-electron bond between the two nitrogen atoms.

First, we note below the excellence of the agreement between the experimental and theoretical values of the nitrogen hyperfine coupling constants (hfcc) for pyridine and pyridinophane.

Radical Cation	Method	isotropic ^{14}N hfcc/G	anisotropic ^{14}N hfcc/G
Pyridine	ESR (expt.)	41	[22.4, -10.0, -12.4]
Pyridine	DFT (theory)	41.5	[24.8, -10.9, -13.9]
Pyridinophane	ESR (expt.)	63.2	[14.9, -7.5, -7.5]
Pyridinophane	DFT (theory)	59.7	[14.0, -7.7, -6.3]

It is striking that in the pyridinophane radical cation, the magnitude of the hyperfine couplings is consistent with most of the spin density being localized on the two nitrogens. Thus, using the standard atomic values of 645.9 G and [39.6, -19.8, -19.8] G for unit spin densities in the nitrogen 2s and 2 p orbitals, respectively, the above results indicate nitrogen spin populations of 0.196 (2s) and 0.76 (2p) in the pyridinophane radical cation, for a total population of 0.96, which is what would be expected for a structure approximating to a 3-electron N-N bond.

It is also instructive to compare the calculated inter-ring and N...N distances for the radical cation with those obtained from calculation and experiment for the neutral molecule. These results are shown below.

Molecule	Inter-ring Distance/pm	N N Distance/pm
Neutral Pyridinophane (expt.)	222	254
Neutral Pyridinophane (calc.)	241	252
Pyridinophane Radical Cation (calc.)	87	203

It is clear from the above data that there is a significant difference between the geometries of the neutral molecule and the radical cation, the separation distances between the rings and between the nitrogens being, as expected, a lot closer in the radical cation than in the neutral molecule. Further examination of these structural results indicates that the limiting

factor preventing the approach of the two nitrogens towards a fully planar D_{2h} structure in the radical cation results from the unfavorable energetics associated with the synchronous formation of eclipsed conformations in the dimethylene bridges. Thus, it is reasonable to conclude that the pyridinophane radical cation adopts a C_{2h} structure in which these dimethylene bridge hydrogens remain slightly staggered at the energy minimum where the two nitrogens are situated at the closest optimum distance.