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"Studies of the Stabilities and Reactions of Solution Phase Organic Radicals"

DE-FG02-91ER14186

TECHNICAL REPORT OF RESEARCH PROGRESS

for the time period July 1, 1992 - June 30, 1993

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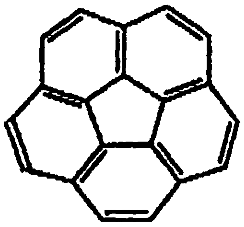
This technical report summarizes recent progress in four areas of our DOE-BES sponsored research.

- PROPERTIES OF RADICALS AND RADICAL IONS DERIVED FROM NOVEL AROMATIC SUBSTRATES

With the aid of samples provided by Profs. Larry Scott, Peter Rabideau, and Mordecai Rabinowitz, the redox properties of corannulene (**1**), acecorannulene (**2**), *iso*-propylcorannulene, and *tert*-butylcorannulene have been investigated and compared to the redox properties exhibited by buckminsterfullerene (C_{60}). Of significance is our observation that corannulene accepts three electrons in the low temperature cyclic voltammetry (CV) experiment (the signal resulting from acceptance of a fourth electron is probably hidden near the solvent window); at room temperature the second and third reductions are not well-resolved. The CV results from room temperature reductions carried out on *iso*-propylcorannulene and *tert*-butylcorannulene are indistinguishable from analogous experimentes carried out on corannulene. The latter results suggest that the five-fold symmetry of the corranulene moiety is not specifically responsible for its reductive properties.



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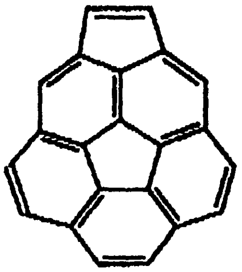

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The redox properties of acecorannulene are, however, substantially different from corannulene. Inspection of the room temperature cyclic voltammogram arising from the reduction of acecorannulene reveals the presence of four well-defined reversible signals. These results suggest that the presence of the "extra" double bond in acecorannulene results in redox properties much closer to those displayed by C_{60}. In collaboration with Profs. Scott, Rabideau, and Rabinowitz, electrochemical investigations of the properties of corannulene, corannulene derivatives, and other

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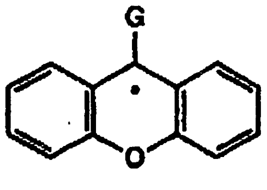
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED interesting aromatic molecules (such as hexaphenylbenzene) are ongoing.

- DETERMINATIONS OF THE RATES OF SELF-REACTIONS OF DELOCALIZED CARBON-CENTERED RADICALS USING FAST SCANNING CYCLIC VOLTAMMETRY (FSCV) TECHNIQUES

Second order rate constants have been determined for the room temperature solution phase self reactions for radicals **3** and **4**. Analysis of the rate data reveals that **3** and **4** (where G=cyano) react at comparable rates (ca. 10^7 $M^{-1}s^{-1}$), despite the fact that the xanthenyl framework in **3** provides thermodynamic stabilization not present in the fluorenyl framework (**4**). These results, combined with self reaction rates for the 9-phenylxanthenyl (**3** where G=phenyl) and 9-*tert*-butylfluorenyl (**4** where G=*tert*-butyl) radicals (4×10^4 $M^{-1}s^{-1}$ and 5×10^5 $M^{-1}s^{-1}$, respectively), are important and new evidence for the hypothesis that steric effects play a dominant role in the rates of self reaction for large delocalized carbon-centered radicals. A manuscript that summarizes this research is nearly ready for submission.



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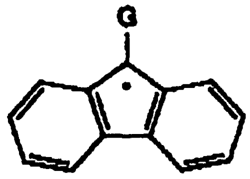

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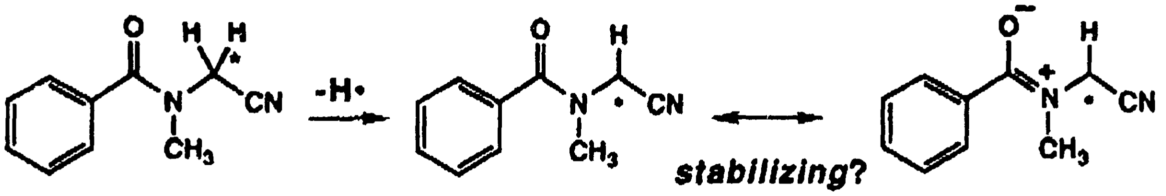
- HETEROATOM-RELATED RESEARCH TOPICS: CARBON-CENTERED AND NITROGEN-CENTERED RADICAL STABILITIES

In light of the importance of heteroatoms in fossil fuel chemistry, we have embarked on a program that aims to evaluate the effects of heteroatomic substituents on the homolytic strengths of C–H bonds (as in **5**). Of importance here is the fact that heteroatomic substituents placed between π-electron withdrawing substituents and C–H bonds are known to have substantial effects on the *heterolytic* strengths of the C–H bonds. This phenomenon has been referred to as the stabilization of carbanions *via* dipole stabilization. *The main goal in this research is the determination of the nature and degree of dipole stabilization as it applies to carbon centered radicals.* A secondary aim of this study is our continued interest in the phenomenon of charge separation as far as radical



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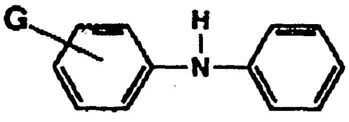
stabilities are concerned. Comparison of C–H bond strength results obtained for **5** reveals that neutral carbon-centered radicals **are not** stabilized *via* dipole stabilization, since the indicated C–H bonds is nearly equal in strength to the analogous C–H bond in acetonitrile. Work in this area is continuing using nitrogen-centered radicals as substrates.

Also underway are investigations of the solution phase chemistry of two dozen variously substituted diphenyl amines (**6**) and six variously substituted perimidines (**7**). Note that the perimidine framework is the nitrogen analogue of the phenalene substrate, a coal-relevant substrate which we have investigated previously. The experiments required to evaluate the N–H bond strengths for **6** and **7**, and the evaluation of the stabilities of the nitrogen-centered radicals derived from these species, have not been completed at this time. Preliminary results suggest that substituent effects on the homolytic strengths of the N–H bonds in these species are much different, and generally smaller in magnitude, than analogous substituent effects in the carbon-centered diphenylmethyl and benzyl analogues.



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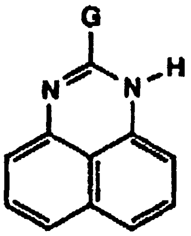

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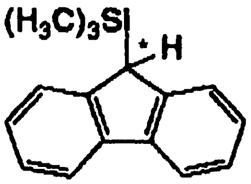
The #9C–H bond strengths in **8** and **9** have also been determined. The homolytic C–H bond strength data indicate that an α-silicon substituent has little effect on the indicated C–H bond in **8**, while a β-substituent weakens the indicated bond in **12** by ca. 7 kcal/mol. Silicon effects in physical organic chemistry have played a large role in the elucidation of theories relating to ion and radical stability. The β effects observed in **9** are the largest of their kind, and contrast with dipole stabilization results described earlier in this summary. *The results dramatize the importance of hyperconjugation as it relates to the stabilization of carbon-centered radicals.* Additional experiments using these and related silicon-containing substrates are planned prior to publication.



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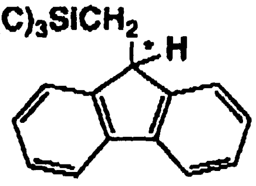

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- OXYGEN RADICALS: HYDROQUINONE/BENZOQUINONE and CARBONIC

ACID/CARBONATE CHEMISTRY

Hydroquinone /benzoquinone mixtures are likely candidates to serve as "hydrogen shuttling" reagents in various coal liquefaction processes. The physical organic properties of these species are therefore of great interest to organic chemists. Carbonate (CO_3^{-2}) is another seemingly simple molecule whose properties are of interest to organic chemists. We have utilized our techniques and strategies to evaluate the first and second (O–H) homolytic bond strengths in 1,4-hydroquinone (82 and 70 kcal/mol, respectively) as well as some of the fundamental properties of carbonic acid, bicarbonate, and carbonate, in DMSO solution. Of particular interest are comparisons of the properties of these species in different solvents. For example, the carbonate dianion (CO_3^{-2}), when dissolved in DMSO, is about twenty powers of ten more basic than when dissolved in aqueous solution. The free radical thermochemistry of these species, however, is solvent-independent. This work is a continuation of our publications that evaluate the effects of solvent on heterolytic as well as homolytic bond strengths. A new manuscript describing these and related results in DMSO and aqueous solution is nearing completion.

SUMMARY OF PUBLICATIONS RESULTING FROM DE-FG02-91ER14186: During the period of time beginning July 1, 1992, and ending June 30, 1993, no publications resulted from our work.

PLANS FOR THE NEXT FUNDING PERIOD: We are continuing our efforts to understand the reactions of solution phase free radicals. As described above, work is ongoing on projects with kinetic as well as thermodynamic emphases. Additional experiments will be completed enabling evaluation of the homolytic strengths of N–H bonds. Particular attention has been and will continue to be paid to our fast scanning cyclic voltammetry experiments. Data resulting from the use of this technique are unique and enable the collection of new facts regarding solution phase free radicals. We also plan to continue our collaborations with Profs. Scott, Rabideau, and Rabinowitz in the general area of aromatic hydrocarbon chemistry.

There are no changes in the original budget for the funding period January 1, 1994-December 31, 1994.

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