shows that the Fe atom in [Fe(TPP)(imidazole)$_2$]Cl is on the N_4 basal plane.[3] The electronic spectra of Fe(OEP)L_2 (L = imidazole and benzimidazole) show that both compounds are of low spin.[17] In fact, the magnetic moment of the imidazole complex was found to be 2.03 BM at room temperature.[17] Mössbauer data also indicate that the bis-imidazole complex is of low spin.[4] On the other hand, all the Fe(OEP)X type complexes are of high spin.[6,7,21]

In going from high- to low-spin complexes, electrons are shifted from the iron e_g* to t_{2g} orbitals. The iron atom in low-spin ferric porphyrin complexes is known to be a π-electron donor,[22] and its t_{2g} orbitals may overlap with vacant π-orbitals of the porphyrin ring to form π bonds.[23] Ligands such as imidazole are relatively good π donors in these complexes, reenforcing back-donation to the vacant porphyrin π orbitals.[24] This increase in π bonding may account for higher Fe–N(OEP) stretching frequencies of bis complexes relative to those of monocomplexes.[25]

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Thermochemistry, Calculations, and the Barrier to Ring Closure in Short-Chain-Length Diradicals[1]

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Abstract: A comparison of thermochemical and quantum chemical analyses of the energetics of short-chain-length diradicals is made. It is concluded that either all present quantum calculations inadequately treat diradical interactions or that 1,3 and 1,4 diradicals suffer a previously unrecognized destabilizing effect relative to a classical model.

Thermochemical and quantum chemical analyses of the properties of 1,3 and 1,4 diradicals have generated widely disparate points of view. The thermochemical analysis, due initially to Benson and coworkers,[2] depicts these diradicals as *intermediates* with substantial (6–10 kcal/mol) barriers associated with the ring-closure reaction, while numerous quantum calculations[3–6] show potential energy surfaces without minima in the region of bond-broken small ring compounds. In this paper we comment on the origin of this discrepancy and point out implications for diradicals associated with a combination of these two treatments.

Thermochemical Calculations

In recent years, the accumulation of a substantial body of experimentally based thermodynamic data for simple organic compounds and radicals has made the thermochemical approach to mechanistic problems an extremely attractive one. Using simple group and bond additivity relationships, Benson and coworkers[7] have accurately estimated heats and entropies of formation for a variety of species. A number of applications of this method have been summarized,[7] and it now appears that the practice of comparing calculated and experimental heats and entropies will join other more classical methods such as the use of stereochemistry as a primary tool in mechanistic work. However, it should be kept in mind that the thermochemical method is a formalism useful in evaluating the energy of *models* of chemical species. While well-chosen models often lead to energy evaluations closely matching experimental data, such matching cannot in general be interpreted *a priori* as evidence for the accuracy of the model in representing the details of the actual chemical entity under consideration.

Apparent exceptions to the wide applicability of the thermochemical method occur in analyses of cyclopropane and cyclobutane ring-opening reactions. Typical results (Scheme I) for the pyrolysis of cyclobutane and cyclopropane derivatives make clear the appeal which bond-broken species have in understanding the courses of these reactions. Benson and O'Neal[2] attempted to analyze these reactions in terms of *hypothetical* noninteracting 1,3 and 1,4 diradical intermediates and have calculated the heats of formation of such

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[1] The Chemistry of Diradicals. IV. For part III, see L. M. Stephenson and T. A. Gibson, *J. Amer. Chem. Soc.*, **94**, 4599 (1972).

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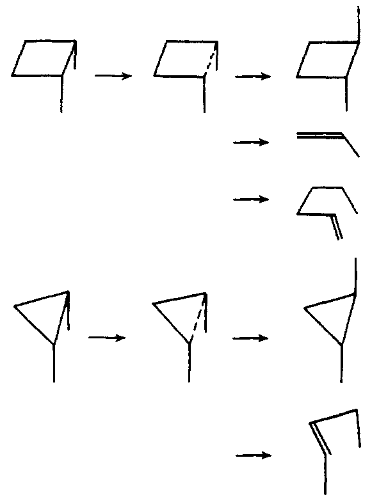
[5] (a) R. Hoffmann, *ibid.*, **90**, 1475 (1968); (b) R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *ibid.*, **92**, 7091 (1970).

[6] P. J. Hay, W. J. Hunt, and W. A. Goddard, III, *ibid.*, **94**, 638 (1972).

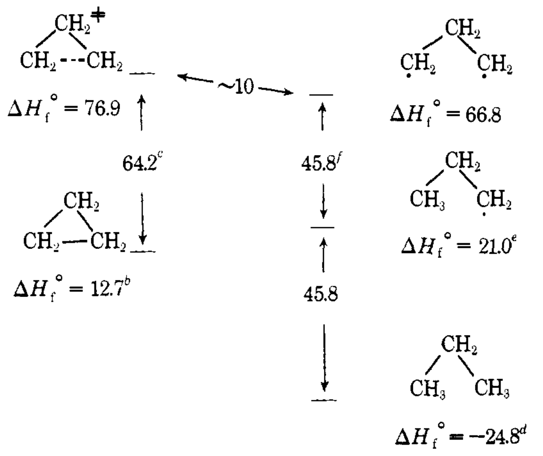
[7] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, and references contained.

Scheme I. Typical Cyclopropane and Cyclobutane Pyrolysis Products



species by successive removal of terminal hydrogen atoms from the parent linear hydrocarbons, propane or butane. It is important to note that the Benson–O'Neal procedure employs the same C–H bond dissociation energy in removing the second hydrogen as when removing the first. Whether or not one agrees that this procedure leads to an accurate representation of the true bond-broken species involved in the pyrolysis reactions, it does, *by definition*, generate the heat of formation for noninteracting diradicals. Curiously, the heats of formation of the activated complexes for ring opening of cyclopropane and cyclobutane are respectively some 10 and 6 kcal/mol higher than the heats of formation calculated for these noninteracting 1,3 and 1,4 diradicals. These relationships are shown graphically for the 1,3 diradical in Scheme II. Two arguments may be made to reconcile this difference, one involving a barrier to ring closure from the diradical, the other a destabilization of the diradical relative to its noninteracting model.

Scheme II. The Enthalpy Relationship between the Noninteracting 1,3 Diradical and the Transition State for Cyclopropane Ring Opening[a]



[a] All enthalpies are given in kcal mol^{-1}. [b] J. W. Knowlton and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **43**, 113 (1949). [c] E. W. Schlag, B. S. Rabinovitch, and K. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958). [d] F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **12**, 735 (1934). [e] See ref 7, p 202. [f] Taken to be the same as for removal of first hydrogen atom; see text for discussion.

If diradicals are treated as simple two-electron systems, one would not expect destabilizing effects which are normally important only in systems where nuclei approach each other closely. Such a situation may well exist in the 1,2 diradical, formed by twisting the ethylene molecule 90°. Here the thermochemical model *underestimates* the heat of formation of the activated complex for isomerization by 5 kcal/mol.[8] Electron repulsion, "exchange" interactions, or other effects may well be poorly accounted for here by assuming a noninteracting model. However, as the diradical electrons become further separated, as in the 1,3 and 1,4 diradicals, these effects would not be expected to become more important.

Other more complex mechanisms for radical–radical interaction in diradical systems such as Hoffmann's through-bond coupling[1,5] have been discussed, but no mention of these interactions as destabilizing effects has been made.

A barrier to ring closure from the diradical, an alternative explanation for this energy difference, is discussed in detail by Benson and O'Neal.[2] These workers have shown that such ring-closure barriers are accurately transferable, without adjustment, from system to system[9] and form a convenient basis for rationalizing the competitive ring closures, bond-cleavage reactions, and bond rotations in these systems. While the origin of this barrier has never been discussed in detail, incipient ring strain provides a logical candidate. Because of the success of this treatment, and because no obvious mechanisms for raising the energy of this hypothetical species to eliminate the potential energy minimum were available, several later workers[10–12] regarded thermochemical data as support for the intermediacy of 1,3 and 1,4 diradicals trapped in shallow potential energy minima.

Quantum Calculations

Recent contributions from theoretical groups have produced pictures in direct contrast to the thermochemical model. Investigations employing such diverse methods as *ab initio* calculations,[3,4] extended Hückel theory,[5] and generalized valence bonds[6] have shown energy surfaces without minima in regions corresponding to bond-broken small ring compounds; no significant barrier to ring closure from the diradical could be found. Returning now to a comparison of the approaches to the diradical problem we note, as before, that the thermochemical analysis is reconciled with these quantum chemical calculations if the true bond-broken species in this reaction is poorly represented by the noninteracting, Benson–O'Neal model. On the other hand, if the quantum calculated surfaces which show no secondary minima are incorrect, two sources of error may be responsible. First, all presently developed calculation procedures introduce approximations which are necessary in order to deal with relatively large systems such as those under discussion. Most approximations, for example, the introduction of empirical data in the place of integral evaluation, are

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(8) R. G. Bergman, *Free Radicals*, in press.

(9) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS-21, U. S. Government Printing Office, Washington, D. C., 1970.

(10) L. M. Stephenson and J. I. Brauman, *J. Amer. Chem. Soc.*, **93**, 1988 (1971).

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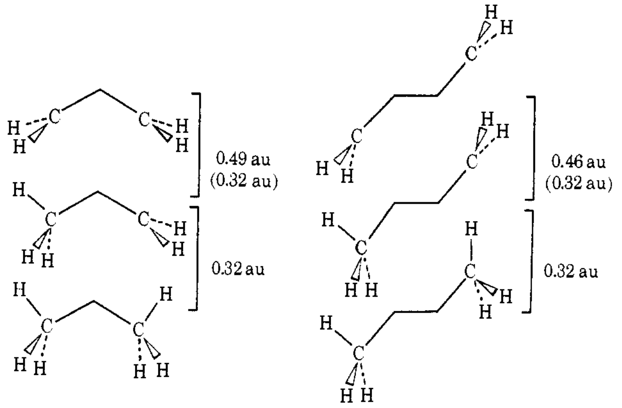
(12) J. A. Berson and J. M. Balquist, *ibid.*, **90**, 7343 (1968).

made in such a way as to generate accurate results for classically bonded structures. Diradicals with terminal carbon atoms separated from each other well beyond normal bond distances may contain interactions for which present methods are poorly calibrated; these factors and others may lead to consistent overestimations of diradical energies in quantum chemical procedures. A second possible source of error might reside in the calculation of the transition state energy. Once again, the quantum chemical methods might be inaccurately calibrated, if, as the thermochemical method suggests, a rather peculiar combination of ring strain and bond energy seems to be involved in the reaction coordinate associated with ring closure.

In an effort to understand the difference in the two approaches, we have attempted to mimic the thermochemical analysis by computing the binding energy loss associated with successive removal of hydrogen atoms from the ends of hydrocarbon chains. This analysis allows us to test the thermochemical approach with a quantum chemical method, while avoiding the problems associated with calculations on small ring compounds. Thus the energy required to produce the diradical species is derived by a prodedure which does not involve the cyclic compound. The INDO variation of the method due to Pople and coworkers[13] was employed and gave the results in Chart I. The binding energies show quite clearly that removal of the second hydrogen atom, to produce the triplet 1,3 and 1,4 diradicals, requires the same energy input as that for removal of the first. With Hartree–Fock methods, such as CN-INDO, the triplet diradical energy is likely to be more reliable than the singlet diradical energy, since the triplet species forces electrons into separate spatial orbitals, and avoids the problems associated with overemphasis of dipolar structures in singlet species. Thus our triplet diradical calculations offer support for the underlying assumptions in the Benson–O'Neal model.

Chart I. INDO Calculations of Thermochemical Diradicals[a]



[a] The differences in binding energy associated with removal of the terminal hydrogen atoms in hydrocarbon chains are shown. Values corresponding to conversion of the monoradical to *triplet* diradicals are given in parentheses. Idealized geometry is employed with the carbon planes bisecting HCH angles in the 1,3 and 1,4 diradicals. Rotation of the terminal methylenes into the carbon plane leads to even larger differences between mono- and diradical.

Previous quantum calculations of the energy surfaces for cyclopropane and cyclobutane ring-opening reactions have dealt, of course, with the singlet manifold. While these calculations have displayed varying degrees of success in matching experimental activation energies, all have shown energy surfaces without significant minima in the region of bond-broken small ring compounds. Novel interpretations of the nature of the 1,3 and 1,4 diradical have been made, using the often stated assumption that these calculations lead to qualitatively (if not quantitatively) reliable results.

Our calculated binding energies for the singlet species show that at least part, if not all, of the discrepancy between thermochemical and quantum chemical views occurs in the calculation and estimation of diradical energies, since removal of the second hydrogen atom to form singlet diradicals is calculated by the INDO method to be significantly more difficult than removal of the first. Thus, the MO method employed here describes a singlet diradical with significant electronic *destabilization*. This may, in fact, be the case for all calculations performed to date on the potential surfaces for cyclobutane or cyclopropane ring opening. That is, any calculation which gives the experimental activation energy correctly for cyclopropane[14] or cyclobutane ring-opening reactions and which also depicts the potential energy surface as possessing no secondary minima, must of necessity be describing a diradical species higher in energy (by 6–10 kcal/mol) than the appropriate noninteracting species, the Benson–O'Neal model.

Summary

We conclude that either all quantum chemical methods so far applied to this problem are incapable of handling the interactions in diradicals, or that 1,3 and 1,4 diradicals are actually destabilized relative to noninteracting models by 10 and 6 kcal/mol, respectively. With simple molecular orbital methods, the error might well reside in the calculations, particularly in view of the well-known tendency of these methods to describe the dissociation process in terms of high energy ionic pairs. On the other hand, Goddard's generalized valence bond method[6] and the configuration interaction procedures of Salem[4] eliminate some of these difficulties, while still giving rise to diradical energy surfaces without minima.

The implication of diradical destabilization is a unique and surprising implication of the quantum mechanical calculations. We know of no linear systems, (aside from the ethylene example mentioned earlier) which are *destabilized* relative to a noninteracting model. Breslow[15] has reported experimental evidence for conjugative destabilization in cyclic π systems, but at the present time we can offer no obvious mechanism by which a diradical could be subject to "linear antiaromaticity."

Present understanding of short-chain-length diradicals does not allow us to make a clear choice between the thermochemical and quantum chemical views. Despite the large number of calculations of potential energy surfaces which depict the 1,3 and 1,4 diradicals as existing on energy surfaces without minima, however, no substantial experimental basis exists which eliminates the potential energy minimum suggested by Benson and O'Neal.

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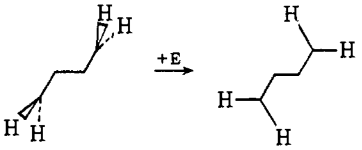
(13) A readable and critical analysis of this method appears in J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(14) Which, indeed, Goddard's method accomplishes, without adjustment.

(15) *Cf.* R. Breslow, R. Grubbs, and S. Murahashi, *J. Amer. Chem. Soc.*, **92**, 4139 (1970), and references contained.

It is the primary purpose of this paper to point out the consequences associated with a combination of these two apparently conflicting views of diradicals. An *exact* quantum mechanical treatment of the three carbon problem (see Scheme II) would be expected to reproduce the heats of formation for propane, the propyl radical, cyclopropane, and the transition state for ring opening of cyclopropane as shown, since these enthalpies are experimental quantities, with neither accuracy nor interpretation of the numbers seriously in doubt. If such an exact treatment persisted in showing no secondary minima in the region of bond broken small ring compounds then, by definition, a higher bond dissociation enthalpy for the second C–H bond relative to the first, again with reference to the right-hand portion of Scheme II, would be required. Such a difference in C–H bond energies does exist within the framework of the INDO calculations presented here, and may well be a feature of other current methods.

The origin of this difference is particularly difficult to pinpoint in the present case. As can be seen from the geometries employed for the calculations (see Chart I), both the 1,3 diradical and the 1,4 diradical in the extended trans conformation require more energy to remove the second C–H than for the first in reaching the singlet diradical. Direct overlap interactions between diradical electrons cannot be the basis for this difference in C–H bond energies in the extended trans 1,4 diradical. Hoffmann has pointed out that such through-space interaction is also not important in the 1,3 diradical, and thus is equally unlikely as a basis for the C–H bond energy difference here. Although the *through-bond coupling* described by Hoffmann[16] might seem to be an attractive candidate, we are discouraged from invoking this effect to explain our results. We pointed out in the previous paper in this series[1] that rotation of the terminal methylene groups about the C–C bonds involved a large energy input relative to model systems. Thus, the geometry which maximized through bond coupling (left structure, above) minimized the energy of the system. Such an effect cannot be, simultaneously, a candidate for raising the overall energy of the system. It also seems unlikely that the simple inductive effect of the $CH_2\cdot$ group in the propyl or butyl radical could be sufficient to account for the 6–10 kcal/mol increase in bond energy which is required to reconcile thermochemical and quantum views. Consequently, we believe that the calculations presented here simply reveal the inability of the INDO method to deal accurately with diradicals, a effect which may be general for all methods so far applied to this problem.



The energetics of the ring-opening reactions of small ring compounds is a currently very attractive area for tests of quantum mechanical methods. Since all presently utilized methods show no secondary minima as implied by the Benson–O'Neal treatment, we suggest that the methods are also likely to show differences in C–H bond energies when attempting to mimic the thermochemical analysis. An understanding of these energy differences will, we believe, provide an important key to the differences between the thermochemical and quantum chemical approaches and suggests an interesting area for analysis by advanced methods.

Acknowledgment. Financial support from a Dreyfus Teacher-Scholar Grant, the Alfred P. Sloan Foundation, and the National Science Foundation (GP-27532) is gratefully acknowledged.

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(16) R. Hoffmann, *Accounts Chem. Res.*, 3, 1 (1971).