Table VIII. Summary of MM2 Calculated Steric Energies and Heats of Formation (kcal/mol)

compound	steric energy	heat of formation
oxirane (1)	9.5575	−12.58
2-methyloxirane (2)	9.8742	−22.63
cis-2,3-dimethyloxirane (3)	12.7013	−30.17
trans-2,3-dimethyloxirane (4)	10.2775	−32.60
epoxyisolongefolene (5)	46.1337	−58.70
1-(*p*-bromophenyl)-1,2-epoxycyclohexane (6)	13.6462	*a*
trans-4-*tert*-butyl-1-phenyl-1,2-epoxycyclohexane (7)	17.3730	*a*
chamigrene epoxide (8)	37.7023	−40.32
cyclohexene oxide (9)	16.3342	−32.96
cyclooctene oxide (10)	24.3703	−37.75
norbornene oxide (11)	36.7196	−12.58

[a] Heat of formation parameters for aromatics are not included in MM2.

similarity of the epoxide moieties in these three structures suggests that any systematic error would result in a consistent difference between calculation and experiment, but such consistency is not observed. We therefore concluded that the agreement between experiment and calculation for the data in Table VII did not dictate further modification of the epoxide parameters. The standard deviation is 1.50 kcal/mol, about three times larger than the errors reported by Allinger for alcohols and ethers.[22] This reflects the small number of available experimental values and suggests that some of the experimental data may be in error. The possibility that our energy minimizations had not afforded the lowest energy conformations was ruled out by running the calculations with the RIPS routine.[4] The interdependence between structural parameters and heat of formation parameters is relatively small in MM2 calculations, so it should become possible to refine the latter when additional experimental data become available. A summary of calculated heats of formation and steric energies for all structures is presented in Table VIII.

The good agreement obtained between experimental and calculated structures for a series of epoxides demonstrates that we have successfully extended the MM2 force field to include this functional class of compounds. Structural results obtained with MM2 calculations of other epoxides with these parameters should be highly reliable. Our calculated heats of formation may exhibit moderate (and possibly systematic) errors on the order of 1 kcal/mol, but relative energies for any set of related structures should again be reliable.

Acknowledgment. We thank Professor N. L. Allinger, University of Georgia, for helpful suggestions and discussions during the course of this work. We also thank Dr. David M. Ferguson, USF, for invigorating discussions and assistance with the RIPS procedure and Dr. B. D. Silverman, IBM, T. J. Watson Research Center, who provided us with a partial set of parameters that he had developed for bay-region epoxides. This work was assisted by University Computing Services at the University of South Florida, which provided technical support and extensive computing time.

Supplementary Material Available: For each compound reported, the MM2-optimized coordiantes and summary of components of the total energy (18 pages). Ordering information is given on any current masthead page.

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Cycloadditions of Cycloocta[*def*]biphenylene-1,4-dione and Other Quinones: Evidence for the Importance of Charge-Transfer Contributions to the Transition State

Charles F. Wilcox, Jr.,* Kevin R. Lassila,(1) and Corraine E. Young

Department of Chemistry, Cornell University, Ithaca, New York 14853-1301

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Cycloadditions of the title compound (5) proceed more slowly than expected for a dienophile with two activating substituents. The Hückel-based transition-state model developed by Carpenter and Wilcox indicated that the aromaticity of 5 played no significant role in its reactivity. This model also indicated that the geometrical distortions present in 5 would tend to *increase* rather than decrease its rate of cycloaddition. A correlation between the rate of reaction of 5 and several model quinones with their reduction potentials suggest that there is a significant degree of charge transfer (ca. 0.4*e*) in the transition state. Explicit consideration of charge-transfer contributions to the transition state provided an excellent fit to the experimentally observed rates.

Introduction

Polycyclic π-hydrocarbons containing multiply fused $4N$- and $(4N + 2)$-membered rings[2–5] frequently behave in ways that defy conventional chemical intuition. For example, cycloocta[*def*]biphenylene[4a,b] (1) displays thermal stability typical of an aromatic species, reactivity of a polyolefin, and a diminished diatropism consistent with increased

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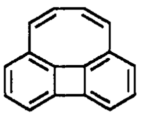
Chart I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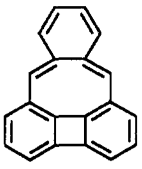
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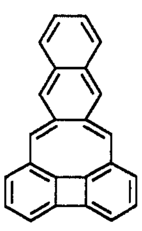
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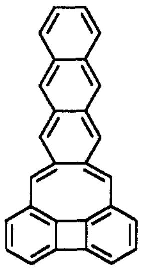
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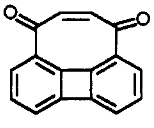
Chart II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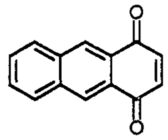
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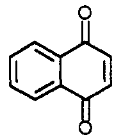
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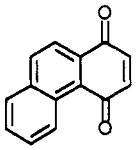
8

antiaromatic character. Dicycloocta[*defjkl*]biphenylene[5b,c] possesses formal benzene rings that are devoid of ring currents.

The polycyclic hydrocarbons 1–4 (Chart I) are of particular interest because of the bizzare effect benzannelation is predicted to have on their properties. The behavior of hydrocarbons based on cyclobutadiene,[6] benzocyclobutadiene,[7] and naphthocyclo[*b*]butadiene[8] is consistent with increased aromatic character on successive fusion of benzene rings. Evaluation of the algebraic structure counts[9] (ASC values) of 1–4, however, indicates that successive benzannelation of 1 has a quite different effect.

Benzannelation of 1 (ASC = 2) is expected to result in diminished aromatic character; 2 (ASC = 1) is predicted to be polyolefinic and less stable than 1. An additional benzenoid fusion to form 3 (ASC = 0) is expected to result in a system with a triplet Hückel ground state and, possibly, paratropic benzene rings. The trend, counterintuitively, does not continue with further benzannelation. Compound 4 (ASC = 1) is expected to be more stable than 3 and of comparable stability to 2.

Cycloaddition of cycloocta[*def*]biphenylene-1,4-dione[10] (5) with suitable furan precursors[11] would lead to materials which could be converted to the desired hydrocarbons by minor functional group manipulation. The synthesis of 5[10] has been reported recently, and preliminary studies of cycloadditions of 5 seemed to indicate that it was considerably less reactive than a number of other dienophiles with two activating substituents. For example, reaction of 1,4-diphenyl-2-butene-1,4-dione with butadiene is complete in a matter of minutes whereas reaction of 5 under identical conditions is complete only after several days.

Table I. Rate Data for Cycloadditions of 5–8

compd	$k_1{}^a$	$k_2{}^b$	k_{rel}
5	0.68 ± 0.01[c]	1.2 ± 0.1	1.0 ± 0.1
6	8.72 ± 0.05	–	12.8 ± 0.3
7	14.3 ± 0.1	16.0 ± 0.8	21.0 ± 0.5
8	31.8 ± 0.1	–	46.7 ± 0.8

[a] For reaction with 0.76 M 1,3-cyclohexadiene ($s^{-1} \times 10^{-5}$). [b] For reaction with 2.0 M 1,3-butadiene ($s^{-1} \times 10^{-5}$). [c] Uncertainties reported are standard deviations.

The sluggish reactivity of 5 was initially thought to be a result of the distorted, tub-shaped conformation of the molecule. The X-ray crystal structure of 5 indicates that the carbonyl groups are canted 17° out of the plane of the biphenylene portion of the molecule and are twisted significantly out of conjugation with the quinonoid double bond (torsional angle 43°). If 5 were forced to flatten in the transition state, the added strain could be invoked to rationalize the low reactivity. Even if the structure retained most of its puckered shape in the transition state, the diminished conjugation of the rate-enhancing electron-withdrawing groups[12] could be used to explain the anomalous rate.

The novel structure of 5, however, suggested an alternative explanation. The cycloocta ring is formally a bioxyanion-substituted cyclooctatetraene dication. Any electron transfer in the transition state would have the effect of introducing destabilizing antiaromatic cyclooctatetraene character. If electron transfer were sufficiently important, the relatively low reactivity of 5 could be explained.

We report here the results of a study of cycloadditions of 5 and a number of reference compounds as well as a study of their reduction potentials. A clear dependence of the rates on the reduction potentials is demonstrated and is interpreted in terms of a significant degree of electron transfer in the transition state.

Results and Discussion

Kinetics. Pseudo-first-order rate constants for the disappearance of 5–8 were determined spectrophotometrically in the presence of a thousandfold excess of cyclohexadiene in mixed xylenes at 100 °C. With quinones 5 and 7 the pseudo-first-order kinetics for cycloaddition with excess butadiene were also measured. The measured rate constants are reported in Table I.[13]

The reference quinones were selected, in part, because they provided a reasonably constant steric environment that would leave electronic effects unobscured. In addition, solvation differences between the systems should be minimal. They also had the practical advantage of being readily accessible.[14,15]

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(13) (a) A rate constant of 42.9 × 10^{-5} s^{-1} was determined for the reaction of 1,4-benzoquinone with cyclohexadiene. By use of the correlation given in eq 2, an *F*-test indicated that this rate is significantly lower than one consistent with the correlation. It would be unwise to reject the point on this basis alone, but other evidence suggests that the observed reaction is that of 5,8,9,10-tetrahydronaphthoquinone with cyclohexadiene. Data from ref 13b was used to calculate a rate of ca. 5600 × 10^{-5} s^{-1} ($t_{1/2}$ = 12 s) for reaction of benzoquinone under our reaction conditions, indicating that reaction of benzoquinone with the diene was completed during the equilibration period in the spectrometer. (b) Balbolov, E.; Kurtev, K. *React. Kinet. Catal. Lett.* **1987**, *34*, 377–81.

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Our initial qualitative observation of decreased reactivity for **5** is clearly demonstrated by the data. Even the least reactive benzenoid quinone reacts nearly 13 times faster than **5**.

Electronic Considerations. Carpenter and Wilcox[16] have developed a simple Hückel-based model for correlating the effect of unsaturated hydrocarbon substituents on the rates of pericyclic and biradical reactions. With this model, reaction rates for five different classes of reactions covering a range of activation energies of more than 50 kcal/mol could be fit to a single correlation line with a standard deviation in log k of 0.3. The model as formulated is restricted to hydrocarbon reactions and cannot be applied unambiguously to the pericyclic reactions studied here. However, the results are so clear that the extension to carbonyl compounds seems justified.

If the quinones **5**–**8** are treated as hydrocarbons (i.e., the carbonyl oxygens are replaced by CH_2 groups), the model predicts that the expected range in rates for the set of five quinodimethanes would be less than a factor of two. Moreover, the calculated rates vary in a direction opposite to that observed experimentally. If the α values of carbons corresponding to the carbonyl oxygens are decreased to -1.0 or -2.0 β units to mimic the influence of increased electronegativity, the picture hardly changes. The conclusion is that the aromaticity of the quinone has almost no effect on its ability to react with a given diene.

This conclusion is in marked contrast to Diels–Alder additions in which the structural variation resides in the diene component. These latter reactions are particularly sensitive to the difference in aromaticities of the diene and the corresponding transition state. For example, the predicted rate ratio for the addition of *o*-xylylene to benzoquinone vs addition of butadiene to benzoquinone is 350.

The lack of structural effect in the present series is readily understood in terms of the ASC approach.[9] Because the quinones are cross-conjugated and there are no Kekulê structures that interchange the bonds of the preexisting aromatic ring with the developing benzenoid transition state, the difference in ASC values for ground and transition states all have a constant value of 2.0 independent of structure. Put simply, the ASC model predicts that to a first approximation all of the quinones should react at the same rate and that delocalization effects will not account for the low reaction rate of quinone **5**.

Geometric Considerations. In the above analysis quinone **5** was treated as a planar species when in fact the X-ray structure shows the eight-membered ring to be a half tub. Although this geometric distortion in **5** might be conceived as the source of its low reactivity, the Carpenter–Wilcox model suggests the opposite. In performing the calculations, deviations from planarity in **5** were accounted for by reducing the resonance integrals of the appropriate bonds according to the relation $b = b_0 \cos \theta$ where θ is the torsional angle between the orbitals[17] as determined from the X-ray structure.[10] The calculated enthalpies of activation hardly change, and surprisingly, decreased conjugation with the carbonyl groups results in an increase in the calculated rate of reaction. It appears that increased interaction of the reacting double bond with the flanking carbonyl group destabilizes the transition state more than the ground state, resulting in the surprising prediction that ring deformations should result in an increase and not a decrease in reaction rate.

Table II. Reduction Potentials and LUMO Energies for 5–8

compd	$E_{1/2}{}^{a}$	E_{LUMO}
5	-0.90	-3.151^{b}
6	-0.75^{c}	-3.549
7	-0.71^{c}	-3.712
8	-0.66^{d}	-3.885

[a] *V* vs SCE. [b] eV. [c] Reference 21. [d] Reference 22.

Correlation with Reduction Potentials. A possible explanation for the low reactivity of **5** consistent with the above results is that electron transfer from the diene to the quinone plays an important role in the transition state.[18] This interpretation is qualitatively compelling because charge transfer would increase cyclic delocalization about the eight-membered ring. The resulting destabilization of the transition state would explain the low reactivity of **5** and is consistent with a higher calculated reaction rate upon geometric distortion.

In order to quantify this interpretation, we measured the reduction potential of quinone **5** in DMF by cyclic voltammetry[19] and correlated it with the known potentials of the other quinones (Table II). The reduction potentials were then related to the reaction rates of the quinones.

Quinone **5** was found to be considerably more difficult to reduce than the benzenoid quinones, which is consistent with the expectation that the reduction potential should be linearly related to the change in delocalization energy upon reduction.[20]

A plot of the first reduction potentials vs the Pariser–Parr–Pople LUMO energies calculated using the PPP model contained in Allinger's MMPM program[23] gives an excellent linear correlation. The relationship is shown in eq 1. The standard deviation in the slope of 0.050, and the correlation coefficient is 0.99. The low magnitude of the slope demonstrates the leveling effect of solvent for a process forming a charged species.

$$E_{1/2} = -0.328E_{\text{LUMO}} - 1.929 \tag{1}$$

In order to determine the relative importance of electron transfer in the present Diels–Alder transition states, the correlation between ln k_{rel} and $(23.07/RT)E_{1/2}$ was determined. The scaling factor of $23.07/RT$ was included so that the slope of the line would have the physical significance of the fraction of charge transfer in the transition state.

The relative rate constants of the quinones were corrected for symmetry (**5**, 1; **6**, 2; **7**, 2; **8**, 2) to remove nonethalpic contributions to the rate data. The fit is given in eq 2.

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(22) (a) Estimated from a plot of $E_{1/2}$ values available in ref 20b which were obtained in aqueous solution vs values in ref 20. The data set included compounds **6**, **7**, 1,4-benzoquinone, and 9,10-anthraquinone. Regression analysis gave the line defined by $E_{1/2} = 0.82E_{1/2}{}^{H_2O} - 1.10$. The standard deviation in the slope and correlation coefficient were 0.04 and 0.998, respectively. From ref 20b, $E_{1/2}{}^{H_2O} = 0.53V$ giving a value $E_{1/2} = -0.66 \pm 0.03$. (b) Reference 19a.

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$$\ln k_{\rm rel} = 0.415(23.07/RT)E_{1/2} + 11.59 \qquad (2)$$

The low standard deviation in the slope (0.015) and the nearly ideal correlation coefficient (0.999) indicate that the reduction potential of the quinone and the activation barrier are closely related. The fraction of charge transfer is large and indicates that the relative reactivities of quinones **5**–**8** can be described by a combination of (a) statistical factors and (b) significant charge transfer from the diene to the quinone in the transition state. In these Diels–Alder reactions, the ASC results presented earlier indicated that the change in aromatic stabilization in going from the ground to the transition state is essentially constant. Presumably, the charge-transfer contribution is also present in Diels–Alder additions in which the structural variation resides in the diene component. However, in these cases, the charge-transfer component is obscured by the large change in the aromatic contribution.

A Simple Model To Rationalize the Rates of Cycloadditions of Quinones. The above analysis is completely empirical, and it is of some interest to demonstrate the theoretical basis for such a fit. The wave function for the transition state for these reactions can be approximated as the sum of the wave function for the ground-state components and that for the charge-transfer state.

$$\psi_{\rm TS} = \psi_{\rm GS} + \psi_{\rm CT} \qquad (3)$$

$$\begin{vmatrix} A - (E_{\rm TS} - E_{\rm GS}) & B \\ B & E_{\rm CT} - (E_{\rm TS} - E_{\rm GS}) \end{vmatrix} = 0 \qquad (4)$$

The energy of the transition state relative to the ground state, $E_{\rm TS} - E_{\rm GS}$, can be obtained by solution of the corresponding 2 × 2 secular determinant shown above. In this determinant, the A term is the electronic energy change on forming the transition state and includes any repulsion energy added when the ground-state components are brought together. From the null result of the Wilcox–Carpenter model and the similar steric environments for the different reactants, the A term will be essentially constant. The B term represents the interaction element between the two terms in the wave function and will be assumed to be a constant characteristic of the transition states for the cycloaddition. The $E_{\rm CT}$ term represents the structure-dependent charge-transfer energy. If the electrostatic contributions are assumed to be essentially equal, then $E_{\rm CT}$ will be simply $C + E_{\rm LUMO}$. Solution of the determinant gives the expression for $E_{\rm TS} - EG_{\rm S}$ shown in eq 5. This equation can be solved directly or linearized (limit of small B/A) to give the approximate expression shown in eq 6, where a and b are complex combinations of A, B, and C. From a plot of the statistically corrected ln k vs the PPP values for $E_{\rm LUMO}$ the parameters of eq 7 were obtained. The standard deviation of the values for ln k are 0.20 and the correlation coefficient is 0.998.

$$E_{\rm TS} - E_{\rm GS} = \frac{A + C + E_{\rm LUMO} + \{(A - C - E_{\rm LUMO})^2 + 4B^2\}^{1/2}}{2} \qquad (5)$$

$$\ln k = aE_{\rm LUMO} + b \qquad (6)$$

$$\ln k = -4.26E_{\rm LUMO} - 13.37 \qquad (7)$$

Conclusions

The observation that **5** reacts relatively slowly in cycloaddition reactions cannot be explained on the basis of its aromaticity nor by its distorted geometry. ASC theory suggests that these cycloadditions should be remarkably insensitive to the aromaticity of the starting material. Moreover, calculations suggest that distortion of the system should *increase* rather than *decrease* the reaction rate.

The excellent correlation between the activation energy of these reactions and the reduction potentials of the quinones suggested the presence of a significant degree of charge transfer in the transition state. This empirical analysis can be justified by a simple theoretical model, which considers charge-transfer contributions to the transition state.

Experimental Section

Materials. Naphthoquinone was obtained commercially and purified by sublimation followed by recrystallization from acetone in the manner recommended by Fieser.[24] 1,4-Phenanthraquinone was prepared by reaction of styrene with 1,4-benzoquinone in refluxing xylene according to the method of Rosen and Weber.[14] 1,4-Anthraquinone[15] was prepared by reduction of 1,4-dihydroxyanthraquinone with NaBH.

Tetra-*n*-butyl perchlorate (TBAP) was recrystallized three times from ethyl acetate and dried in vacuo at 80 °C for three days. Dimethylformamide (DMF) used in the electrochemical experiment was dried over 4-Å molecular sieves.

Spectrophotometric Determination of Rate Constants. A stock solution of 1,3-cyclohexadiene (6.42 g/100 mL solution in mixed xylenes) was prepared and stored at −20 °C. This solution was used in all kinetic measurements.

In a typical kinetic run ca. 3 mL of this solution was introduced into a 1.0-cm quartz cuvette, which was placed in a Hewlett-Packard Model 8450A diode array UV–visible spectrometer equipped with a constant-temperature cell holder maintained at 100 °C by an external circulating bath. The spectrometer was referenced with respect to the diene solution, and then a small amount of quinone was added until the absorbance at the wavelength of interest was between 1 and 2. The wavelengths used were 1,4-anthraquinone (406 nm), 1,4-naphthoquinone (330 nm), and 1,4-phenanthraquinone (414 nm). If the absorbance above was greater than 2, the solution was diluted with the diene solution.

After a brief equilibration period, absorbances at the wavelengths listed were measured at 5–60-min intervals for at least 3 half-lives. The rate constants were determined from the slope of plots of ln $(A_{\rm t} - A_{\rm inf})$ vs t where $A_{\rm t}$ is the absorbance at the wavelength of interest at time t and $A_{\rm inf}$ is an absorbance after the reaction had progressed at least 5 half-lives. In all cases the plots displayed excellent linearity.

Cyclic Voltammetry of 5. The reduction potentials of **5** were determined by using a Princeton Applied Research Model 173 potentiostat/galvanostat in conjunction with a Model 175 Universal programmer. A standard 25-mL three-compartment electrochemical cell with platinum working and counter electrodes and saturated calomel reference electrode (SCE) was used. DMF and TBAP were used as solvent and supporting electrolyte, respectively.

The cyclic voltammogram of **5** displayed a well-defined peak with a half-wave potentials of −0.95 V and a less well defined peak at −1.29 V (vs SCE). The difference in peak potentials on the cathodic and anodic peaks indicated that, at a sweep rate of 150 mV/s, the first reduction ($E_{\rm p}$ = 80 mV) was reversible ($\Delta E_{\rm p}$ = 330 mV) while the second was irreversible.

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