to catalyze the six-electron reductions of nitrite and sulfite to ammonia and hydrogen sulfide, respectively. A combination of experiment and theory suggests[54] that, because of the ease of oxidation of the isobacteriochlorin skeleton, π radicals play a role in the enzymatic cycles of nitrite and sulfite reductases. ESR results confirm[54b,c] the theoretical prediction[54c] that oxidation of pyridine or imidazole CO complexes of iron(II) isobacteriochlorins proceeds via the macrocycle and unambiguously establish the existence of iron π cation radicals.

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Note Added in Proof: Hoffman and co-workers[55] have obtained ^1H and ^{14}N ENDOR hyperfine splittings which further support the assignment of HRP I to a π cation. The isotopic substitution experiments suggested above for NMR are obviously equally applicable for ENDOR.

Acknowledgment. We thank the authors of ref 6, 7, 9, 44, 49, and 55 for providing us with their results prior to publication. This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, Washington, D.C., under Contract No. DE-AC02-76CH00016 at Brookhaven National Laboratory and by NSF Grant CHE 7815285 at Michigan State University.

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Communications to the Editor

Cycloreversion Reactions of Phenylated Cage Compounds Induced by Electron Transfer[1]

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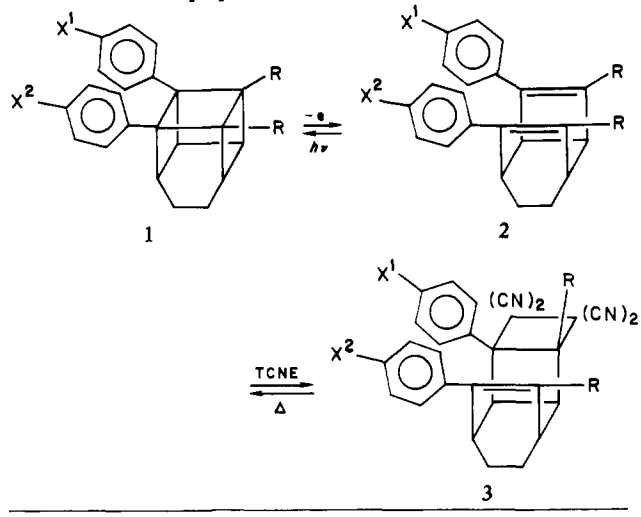
In addition to the ring-opening reactions of cage compounds catalyzed with acid[2] and metal ions,[3] photochemically and thermally induced valence isomerizations between cyclic dienes and cage compounds are well documented.[4,5] We have found that electron transfer both in the ground and excited states also can induce cycloreversion of certain cage compounds possessing phenyl groups. In this connection there are reported examples of ring-opening reactions of monocyclic phenylated cyclobutanes[6] and cyclopropanes[7] which proceed via electron-transfer reactions. However, our findings can provide a new procedure for the cycloreversion reactions of cage compounds which occur with extraordinary high efficiency.

The observed reactions are divided into three types: (1) ring opening reactions induced by electron transfer or charge transfer in the dark; (2) reactions induced by irradiation of the charge-transfer complexes; (3) reactions which occur by electron transfer between the ground state of the cage compounds and the excited state of the electron acceptors. We describe here the relationship between the types of reaction and the electron-donating or -accepting properties of substrates or electron acceptors. The mechanism of type 3 is mainly described here.

Table I. Charge-Transfer Band Maxima of 1 and 2 with TCNE in CH_2Cl_2



	R	X¹	X²	1, nm	2, nm
a	Me	OMe	OMe	700 (596)[a]	740 (627)[a]
b	Me	OME	H	630	680
c	Me	H	OMe	590	640
d	Me	H	H	538 (end)[a,b]	627 (547)[a]
e	Me	Cl	Cl		601
f	CO_2Me	H	H	420 sh	end[b]

[a] Chloranil instead of TCNE. [b] End absorption, 500-600 nm.

The charge-transfer absorption bands resulting from the interaction of bis(homocubane) derivatives **1a-f**[8] with tetracyanoethylene (TCNE) are shown in Table I, together with those of dienes **2a-f** with TCNE. Although the charge-transfer absorption band of 4-phenylhomocubane with TCNE has been reported,[9] Table I reveals that the substitution of *p*-anisyl for phenyl, especially in **1a** and **1b**, results in large red shifts of the absorption maxima. This is ascribed to a through-space[10] or through-bond

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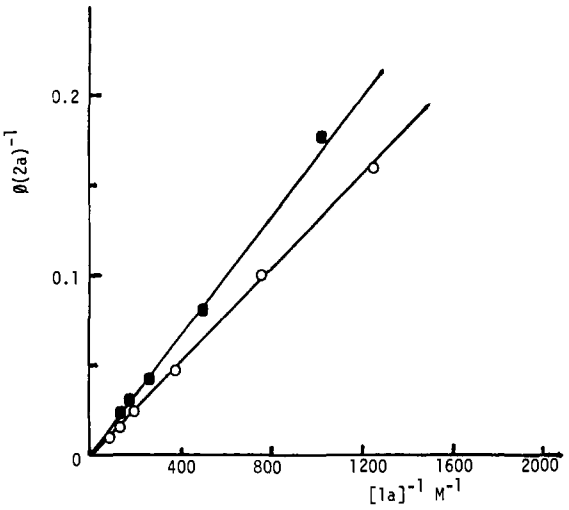

Figure 1. Plots of $[\Phi(\mathbf{2a})]^{-1}$ vs. $[\mathbf{1a}]^{-1}$. Acetonitrile solutions containing 9,10-phenanthraquinone, 4.1×10^{-5} M, 412 ± 10 nm irradiation (●), and *p*-benzoquinone, 8.0×10^{-4} M, 436 ± 10 nm irradiation (○), at 23 °C.

interaction which is maximized in the bis-arylated cage compounds because of good overlap of the π orbitals of two parallel aryl groups with the σ orbitals of the C_1–C_2 bond.[11]

When a methylene chloride solution of a 1:1 mixture of **1a** and TCNE was stirred at room temperature for 2 h, a 1:1 adduct **3a**, mp 153–155 °C, was obtained in 70% yield.[12] Under the same conditions, diene **2a** added to TCNE to give **3a** in 84% yield. Other *p*-anisyl derivatives **1b** and **1c** similarly react with TCNE to give dienes **2b** and **2c**, but only **2b** affords adduct **3b**, mp 167–169 °C.[13] The structural assignments of **3a** and **3b** are based on spectral properties[14] as well as the chemical evidence that heating of the adducts in refluxing benzene regenerates **2a** and **2b**. The fact that **2a** and **2b**, containing the cyclobutene ring with the anisyl group, add to TCNE also allows a structural discrimination between the two isomeric dienes **2b** and **2c** and between the two isomeric cage compounds **1b** and **1c**.

As shown in Table I, this bis-arylated cage compound also exhibits charge-transfer absorption bands with quinones such as *p*-chloranil and 2,6-dichloro-*p*-benzoquinone. When a methylene chloride or acetonitrile solution of *p*-anisyl derivative **1a**, **1b**, or **1c** and one of the above quinones was allowed to stand at room temperatures, the cycloreversion reactions giving dienes were observed without the formation of the [2 + 2] adduct. These cycloreversion reactions of **1a–c** are classified as type 1 reactions. The diphenyl derivative **1d** showed no cycloreversion reactions on treatment with TCNE, *p*-chloranil, or 2,6-dichloro-*p*-benzoquinone in the dark. However, irradiation of a methylene chloride solution of **1d** and TCNE or *p*-chloranil by using a Na lamp (590 nm) for 1 h produced diene **2d** in almost quantitative yields. These ring-opening reactions of **1d** belong to type 2 reactions. The quantum yield for the type 2 reaction of **1d** and TCNE ([**1d**] and [TCNE] = 3.20×10^{-2} M) was about 5 at 468 ± 10 nm at room temperatures.[15] The fact that the quantum yield is more than unity suggests that a chain reaction should be involved in type 2 reactions.

Table II. Reduction Potential and Excited Triplet Energy of Sensitizers

sensitizer	$E^{red}_{1/2}$, V[a]	$E^{*red}_{1/2}$, V[a]	E_T, kcal/mol	reaction
anthracene	-1.94	-0.10	42.7[c]	no
acetophenone	-1.99	1.22	74.1[c]	slow
benzophenone	-1.72	1.28	69.2[c]	no
benzil	-1.04[b]	1.31[b]	54.3[c]	no
9,10-phenanthraquinone	-0.6	1.52	48.8[d]	yes
p-benzoquinone	-0.48	1.82	53[d]	yes
9,10-anthraquinone	-0.83	1.89	62.7[d]	yes

[a] $E^{*red}_{1/2} = E^{red}_{1/2}$ + sensitizer triplet energy; sensitizer ground-state reduction potentials (vs. SCE, DMF) are complied in ref 17. [b] Value in Me_2SO complied in ref 17. [c] Values complied in S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973. [d] Values complied in S. Patai, "The Chemistry of Functional Groups. The chemistry of the quinonoid compounds", Interscience, New York, 1974.

With weak electron acceptors such as *p*-benzoquinone, 9,10-anthraquinone, 9,10-phenanthraquinone, *s*-trinitrobenzene, and *p*-dicyanobenzene, neither cage compounds **1a–d** nor dienes **2a–d** exhibit any charge-transfer absorption band. However, when an acetonitrile solution of **1a** or **1d** containing *p*-benzoquinone or 9,10-phenanthraquinone was irradiated with light of longer wavelength than 400 nm for a short time (1–15 min), diene **2a** or **2d** was obtained in good yields (70–90%). These reactions belong to type 3, and occur very efficiently with increasing quantum yields as the concentration of **1a** or **1d** is increased. Surprisingly the limiting quantum yields of the reactions were found to be infinite, as shown in Figure 1, suggesting the occurrence of a chain reaction. The reactions were quenched with piperylene. In addition, the luminescence of 9,10-anthraquinone[18] was quenched by **1a** with the rate $k_q = 1.4 \times 10^8$ M^{-1} s^{-1}.

In order to establish the limitation of type 3 reactions, the photosensitized reactions of **1a** were carried out in the presence of other sensitizers such as benzophenone, acetophenone, benzil, and anthracene. Although a slow conversion to **2a** took place when acetophenone was used,[19] other sensitizers did not lead to the reaction. As shown in Table II, the reactions depend on the reduction potentials but not the triplet energies of the sensitizers, except for acetophenone. Thus, a classical energy-transfer mechanism is less likely than an electron-transfer mechanism. In connection with this, the oxidation potentials of cage and diene compounds were polarographically measured and the $E^{ox}_{1/2}$ values of 1.09 and 1.41 V (vs. SCE) for **1a** and **1d** and 1.09 and 1.40 V for **2a** and **2d** were obtained.[20] Comparison of these potential values with the reduction potentials ($E^{red}_{1/2}$ in Table II) of the electron acceptors[17] along with the fact that the type 3 reaction of **1a** was quenched with triethylamine ($E^{ox}_{1/2} = 0.82$ V vs. SCE) should support the electron-transfer mechanism.

On the basis of these findings, we propose a reaction mechanism for the type 3 reactions which involves a chain process. The

$$\mathrm{Q} \xrightarrow{h\nu} \mathrm{Q}^* \quad (1)$$

$$\mathrm{Q}^* + \mathbf{1} \rightarrow \mathrm{Q}^{-}\cdot + \mathbf{1}^{+}\cdot \quad (2)$$

$$\mathbf{1}^{+}\cdot \rightarrow \mathbf{2}^{+}\cdot \quad (3)$$

$$\mathbf{2}^{+}\cdot + \mathbf{1} \rightleftharpoons \mathbf{2} + \mathbf{1}^{+}\cdot \quad (4)$$

$$\mathbf{2}^{+}\cdot \text{ or } \mathbf{1}^{+}\cdot + \mathrm{Q}^{-}\cdot \rightarrow \mathbf{2} \text{ or } \mathbf{1} + \mathrm{Q} \quad (5)$$

(11) E. Osawa, A. Kanematsu, et al., *J. Am. Chem. Soc.*, in press.
(12) Satisfactory elemental analyses were also obtained for **3**.
(13) Among many examples of the [2 + 2] cycloaddition reactions between electron-rich olefins and TCNE, there is an example of hindered alkoxy styrenes which fails to add with TCNE. Cf. J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **84**, 2210 (1962).
(14) Spectral data of **3a** are as follows: λ_{max} (CH_3CN) 248 nm (log ε 4.28); ν_{max} (KBr) 2230 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.37–1.85 (m, 5 H), 1.82 (s, 3 H), 1.89 (s, 3 H), 2.61 (m, 1 H), 3.15 (m, 2 H), 3.57 (s, 3 H), 3.72 (s, 3 H), 6.33–7.17 (m, 8 H); *m/e* 372 (100%), 128 (61%).
(15) Even if the exact quantum yield value could not be determined because of the change of the charge-transfer absorption band between cage compound and TCNE according to the progress of reaction, it is considered that this value at 5% conversion is approximately correct, since the low conversion of the cage compound causes minor change of the charge-transfer absorption band.
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initiation step consists of excitation of the quinone and generation of the radical cation $1^{+}\cdot$ by electron transfer from the cage compounds. The ring cleavage process of the radical cation $1^{+}\cdot$ giving the radical cation $2^{+}\cdot$, followed by a subsequent electron transfer from **1** to $2^{+}\cdot$, comprises the propagation steps. Then, the radical cation $1^{+}\cdot$ reenters the chain cycle. Reaction 4 can be considered to be reversible, because there is no gap in the oxidation potentials between **1** and **2**. However, reaction 3 involving the bond cleavage reaction releases much strain energy and cannot be reversible. Thus, the propagation sequence is promoted. The termination step involves a quenching reaction of the radical cations $1^{+}\cdot$ and $2^{+}\cdot$ with the radical anion $Q^{-}\cdot$. The absence of sensitizer radical ion from the propagation sequence probably allows the long chain lengths observed.

The detailed mechanism for the type 1 and 2 reactions is still ambiguous, but the key step must be electron transfer from the cage compounds to the electron acceptors in both cases. Since the type 2 reaction also involves a chain process, there seems no essential differentiation between the type 2 and 3 reactions. When the electron-transfer reaction occurs thermally from the cage compounds to TCNE or quinone, type 1 reaction might result. On the other hand, if the reaction requires excitation of charge-transfer complexes or sensitizers, type 2 and 3 reactions will occur.

More recently, we have discovered that the type 3 reactions of **1d** also take place with quantum yields over unity when dye sensitizers such as triphenylpyrylium and trityl salts[21] or semiconductors such as ZnO and CdS were used.[22] Thus, it could be concluded that electron-releasing properties of the cage compounds which are ascribed to their strain energies and oxidation potentials might be important factors for the cycloreversion reactions which are induced to occur by electron transfer.

Acknowledgment. Financial support was provided from the Ministry of Education, Science and Culture.

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Statistical State Solvation Sites

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The structural organization of solvent molecules around a dissolved solute in solution has been discussed extensively in the recent literature in terms of solvation sites. In aqueous solutions, solvation sites are the regions in which water molecules are likely to be found in the vicinity of a dissolved molecular solute. The solvation site concept can be extended straightforwardly to molecular solutions in general.

Up to this point, solvation sites have been equivalenced with local minima in the solute–solvent potential energy hypersurface, as advanced by Pullman, Pullman, and co-workers.[1] Calculations of solvation sites based on molecular quantum mechanics have been reported for diverse biological molecules and used to discuss aqueous hydration and solvent effects on biomolecular conformational structure. The Pullman approach has generated useful insight into aqueous solvation processes but can be improved upon by including solvent–solvent interactions, temperature effects, and consideration of the statistical weight of solvation sites in the N-particle molecular assembly.[2] We offer here a new definition of solvation sites expressed on the statistical state of an N-molecule system at a given temperature in which all of the above critical points are accommodated. The procedure is illustrated by the determination of solvation sites for *trans*-glyoxal from an analysis of computer simulation results on the dilute aqueous solution, $[(HCO)_2]_{aq}$, at 25 °C.

All information about the structure of molecular solutions is in principle contained in the generic molecular distribution functions for the system, and information on solvation sites follows in principle from the analysis of these functions in the region of the first solvation shell of a solute. A general procedure for the analysis of the local solution environment of a dissolved solute from molecular distribution functions has recently been proposed from this laboratory.[3] Here the solvent molecules in the various N-molecule configurations of the system are assigned to the closest or most proximal solute atom (the proximity criterion). The subsequent analysis is organized in the general framework of quasicomponent distribution function theory.[4] By use of this approach the primary and higher order solvation of each solute atom is determined. The spatial extent of the first coordination shell of the solute can be well defined from the solute–solvent radial distribution for primary solvation. The probability density distribution for solvent molecules in the first shell can thus be determined, and the spatial probability distribution of solvent molecules in the immediate vicinity of the solute can be displayed. The further resolution of this density according to solute atoms or functional groups can be achieved by using the proximity criterion, and the analysis of these results leads to the determination of solvation sites. These sites are defined on the statistical state of the system with N-molecule interactions, temperature factors, and statistical weights taken into account and are henceforth called "statistical state solvation sites". Alternative uses of probability density maps to analyze simulation results on aqueous solutions have been described by Hagler et al.[5] and Romano and Clementi.[6]

To examine the viability of the statistical state solvation site concept, we have carried out a liquid state (T, V, N) ensemble Monte Carlo computer simulation on $[(HCO)_2]_{aq}$, represented by 1 glyoxal molecule and 215 water molecules under periodic boundary conditions at 25 °C. Ensemble averages in the calculation of properties and in the structural analyses were formed from $1000K$ configurations after equilibration, chosen on the basis of the Metropolis method. General aspects of the calculations and related recent results are reviewed in ref 7 and 8 and literature cited therein.

The primary coordination number of glyoxal in $[(CHO)_2]_{aq}$ was found to be 17.77 water molecules. The 90% probability density distribution of these molecules was determined and displayed by using computer graphics by means of the program PSI/77 by Jorgensen.[9] The results are collected in the composite Figure 1.

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