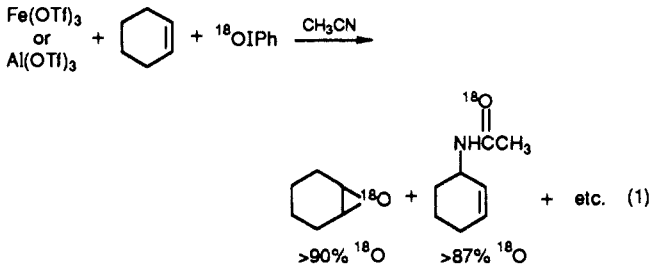
the Ritter reaction, the amide oxygen is derived from H_2O.[11] Our reactions were carried out in dry acetonitrile, however, with insufficient water to account for the product. We therefore carried out an isotopic labeling study using ^{18}OIPh to ascertain the source of oxygen. We find that the amide oxygen is derived from iodosylbenzene (reaction 1).



One additional product, 1,4-diiodobenzene, was observed in these reactions[13] (see Table I). This interesting product was found whether or not cyclohexene was present. Similar products have been found in reactions of iodonium ions.[14]

In Scheme I, we propose mechanisms that account for all of the observed products. We believe that **1a** is the first species formed when the metal complex reacts with the insoluble OIPh polymer. Related complexes have been isolated by Hill and co-workers from reactions of manganese porphyrins with iodosylbenzene.[15] Based on the work of Koser[3a] and Zefirov,[3d,f] we expect that I^{III} in **1a** will be electrophilic. We therefore propose that **1a** or **1b** reacts with the double bond of cyclohexene, forming **2**, which resembles the intermediate proposed by Koser and co-workers in their reactions.[3a] This intermediate can then react by several pathways. In pathway a, **2** rearranges to give **3**, which then forms **4** by O-I bond cleavage. Nucleophilic addition of the anion X^- and loss of PhI followed by oxygen-carbon bond formation yield epoxide. In pathway b, **2** is attacked by a nucleophile, triflate, and *cis*-1,2-cyclohexanediol ditriflate is formed by two steps of nucleophilic addition of triflate. This mechanism is further supported by the fact that the amount of *cis*-1,2-cyclohexanediol ditriflate increased when an extra source of triflate, i.e., Li(OTf), was added. In pathway c, a carbonium ion **5** is formed and then attacked by the acetonitrile solvent. This step of the reaction is analogous to the Ritter reaction. However, under the conditions of our reaction, i.e., in dry acetonitrile solvent, the oxygen originating from iodosylbenzene attacks the carbonium ion of **6** to form a six-membered-ring intermediate. Abstraction of a proton from the cyclohexane ring gives the final product, 3-acetamidocyclohexene.

In summary, all of our observations are consistent with a mechanism that does not require changes in oxidation state of the metal ion and that involves electrophilic attack of I^{III} on the olefin. We believe that this or a similar mechanism prevails in most of the non-porphyrin metal catalyzed reactions and that it should be considered as a possibility in the metalloporphyrin-catalyzed reactions as well.

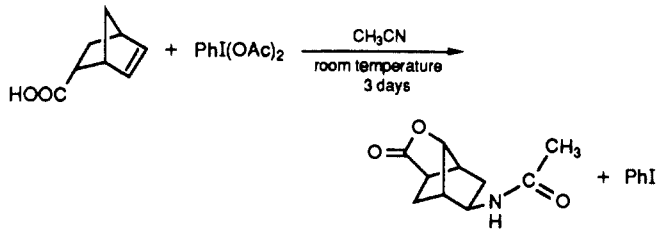
Acknowledgment. We thank Professors Joel F. Liebman and Gerald F. Koser for helpful discussions. Financial support from the National Science Foundation (J.S.V.) and the Office of Naval Research (F.D) is gratefully acknowledged.

(11) The Ritter reaction is the formation of an amide by the addition of a nitrile to a wide variety of compounds capable of forming carbonium ions, e.g.,

$$(CH_3)_3C^+ + :N{\equiv}CCH_3 \xrightarrow{H_2O} (CH_3)_3CNHCOCH_3$$

See: Krimen, L. I.; Cota, D. J. In *Organic Reactions*; Wiley Inc.: New York, 1969; Vol. 17, pp 213.

(12) We have found similar amide products in reactions of iodobenzene diacetate with olefins, e.g.,



See ref 6b.

(13) Trace amounts of 1,2-diiodobenzene were also detected. The same reaction in the absence of cyclohexene gave the same amount of 1,4-diiodobenzene. The control reaction of iodosylbenzene in acetonitrile in the presence of iodobenzene gave approximately 0.05 mM 1,4-diiodobenzene.

(14) For example,

$$2C_6H_5I{=}O \xrightarrow{H_2SO_4} (IC_6H_4I^+C_6H_5)HSO_4^- + H_2O$$

$$IC_6H_4I^+C_6H_5 + Cl^- \rightarrow C_6H_5I + IC_6H_4I + C_6H_5Cl + IC_6H_4Cl$$

Koser, G. F. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds., John Wiley & Sons Ltd.: Chichester, 1983; Chapter 25, pp 1265-1351.

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Effect of a Polarizable Medium on the Charge-Transfer States of the Photosynthetic Reaction Center from *Rhodopseudomonas viridis*

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Photosynthetic electron transfer is arguably the most important series of chemical transformations for life on this planet.[1-3] In recent years the structure of the reaction centers (RC) from the photosynthetic bacteria *Rhodopseudomonas viridis* and *Rhodobacter sphaeroides* have been presented.[4-7] On the basis of these structures, several mechanisms have been proposed to explain the primary electron-transfer event[8-10] with as yet no consensus.

We report here INDO/S[11-13] calculations of the excited states of a model of the RC of *Rps. viridis* in both the absence and presence of a polarizable medium.[14] For our calculations we model the RC as the bacteriochlorophyll b (BChlb) dimer (P) and the auxiliary BChlb (B_L, B_M), and bacteriopheophytin b (H_L, H_M) chromophores (L and M branches, respectively). Also included are the four histidine amino acid side chains that coordinate with the fifth position of the Mg atoms of the BChl's. The phytol tails of the chromophores are truncated.

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Table I. INDO/S Calculated Energies and Dipole Moment Differences with the Ground State for Qy1 and CT States from the RC Model

	gas-phase calcn		solvent calcn[b]	
state	energy, cm^{-1}	$\Delta\mu$[a]	energy, cm^{-1}	$\Delta\mu$
Qy1	11550	4.6	11460	4.6
$B_L \rightarrow H_L$	17305	48.1	13947	47.1
$B_M \rightarrow H_M$	17765	48.1	14405	47.1
$P \rightarrow H_L$	19728	78.9	12608	75.0
$P \rightarrow B_L$	19836	49.9	16597	46.1
$P \rightarrow B_M$	20192	55.5	16713	48.4
$P \rightarrow H_M$	20588	76.9	13496	74.8

[a] The calculated dipole moment of the excited state − the calculated dipole moment of the ground state (units are debyes). [b] $\epsilon = 2.023$, $\eta = 1.4266$, and $a_0 = 10.6$ Å (see text).

To model the protein as a solvent, we use the self-consistent reaction field (SCRF) method.[15,16] Here we introduce a correction to the excited states which assumes that the solvent can electronically polarize in response to the solute's excited-state electronic distribution. We model the protein as a solvent with the bulk properties of cyclohexane (dielectric constant 2.023, refractive index 1.4266) and a cavity radius of 10.6 Å.[17]

The results of the self-consistent field (SCF) show that the molecular orbitals (MOs) are largely localized to specific chromophores. The MOs of P are localized over both BChlb monomers of P and demonstrate the supermolecule nature of the dimer.[18] The highest lying occupied orbital is localized on P, and the lowest unoccupied orbital is localized on H_L. This order of MOs by itself suggests flow of charge upon excitation in the observed direction along the L branch.

For the configuration interaction (CI) calculation, the MO active space was chosen to balance the number of MOs on symmetry-related chromophores on both the L and M branches. This CI included all single excited configurations from the 40 highest occupied MOs into the 42 lowest virtual MOs giving 1681 configurations.[19]

In both gas-phase and solvent calculations we find that the two lowest energy transitions correspond to excitations involving P. These states are labeled Qy1 and Qy2 on the basis of a study of Mg-bacteriochlorin dimers[18,20] and correspond to $P_{(-)}$ and $P_{(+)}$ states observed experimentally.[21,22] The energy (oscillator strengths) for Qy1 and Qy2 in the gas-phase calculation are 11550 cm^{-1} (1.1702) and 12848.6 cm^{-1} (0.6646), respectively. In the solvent calculation these two states are 11461 cm^{-1} (1.1826) and 12818 cm^{-1} (0.5860), respectively.[23]

States that are dominated (>98%) by transitions between chromophores, we label as CT states. The energies for some of these states and the difference in their state dipole moments with the ground state are given for both the gas-phase and solvent calculations in Table I, and their energy ordering relative to Qy1 is shown in Figure 1. The large values of $\Delta\mu$ are consistent with the CT character of these states. States involving CT from P to either H_L or H_M have the largest $\Delta\mu$ consistent with the larger charge-separation distance. The asymmetry of the RC model is

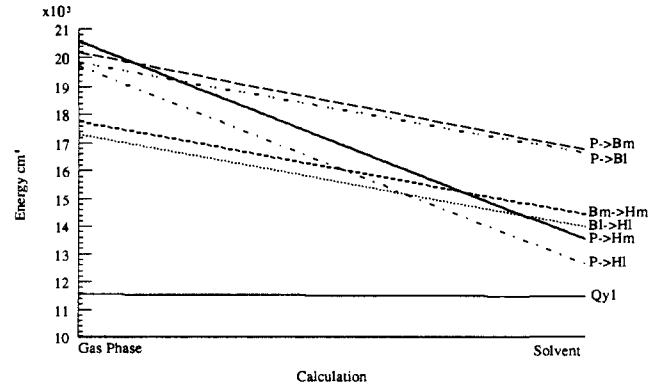

Figure 1. Energies of CT states and Qy1 in the absence and presence of solvent. The abscissa is arbitrary, the two end points representing the gas-phase calculation ($\epsilon = 1$) and the protein surroundings ($\epsilon = 2$).

apparent in the relative ordering of analogous CT states involving the L and M branch chromophores. For both the gas-phase and solvent calculations, analogous transitions energetically favor the L vs the M branch. In both the RC calculations and calculations on H_L and H_M done separately, we observe that the HOMO–LUMO gap is smaller for H_L and the LUMO energy of H_L lies below that of H_M. Thus we calculate the Qy band of H_L lower in energy than H_M (810 and 775 nm, respectively). This compares to the experimental values reported by Breton being roughly 805 and 790 nm for the Qy bands of H_L and H_M, respectively, in the RC at 10 K.[22] The HOMO of the RC is localized on P while the LUMO is localized on H_L and the LUMO + 1 is localized on H_M. This, in part, explains the asymmetry of the L vs the M branch that placed the $P \rightarrow H_L$ CT transition roughly 850 cm^{-1} lower in energy than for $P \rightarrow H_M$ (Table I). Consideration of specific amino acids close to H_L or H_M could effect this ordering. The center to center distances for P–H_L and P–H_M are 17.79 and 17.75 Å, respectively (based on the average of the macrocycle nitrogens). Thus we find that $P \rightarrow H_L$ has a larger change in state dipole moment than the $P \rightarrow H_M$ transition based on the geometry of the RC. This asymmetry in $\Delta\mu$ is further enhanced by the ground-state charge asymmetry in P which placed the center of charge further away from H_L vs H_M.

For the gas-phase calculation the energy separation between Qy1 and the CT states ranges from about 6000 to 9000 cm^{-1}. We would expect for a pseudoactivationless primary electron transfer[9] that the relevant CT states would be accessible to the lowest excited state by a much smaller energy gap. Also the calculation gives $B_L \rightarrow H_L$ as the lowest accessible CT state, being almost 2400 cm^{-1} lower in energy than $P \rightarrow H_L$ and $P \rightarrow B_L$. Even assuming that the energies of these CT states are strongly affected by small geometric changes, it is difficult to envision that these changes would reorder the CT states and place them energetically close to Qy1. Thus the "gas-phase" calculation suggests a role for the auxiliary BChlb that does not agree with current experimental results.[24]

The solvent calculation exhibits dramatic changes relative to the gas-phase calculation. The CT states are all significantly lowered in energy, and their relative ordering is changed. We calculate that $P \rightarrow H_L$ is now within about 1200 cm^{-1} of Qy1. Also CT from P to the H chromophores is lower in energy than from P to the B chromophores. This concurs with the lack of an experimentally observed intermediate involving either B^+ or B^- in picosecond and subpicosecond experiments.[24,25] The splitting between $P \rightarrow H_L$ and $P \rightarrow B_L$ is about 4000 cm^{-1} whereas the splitting between $P \rightarrow H_L$ and $B_L \rightarrow H_L$ is about 1300 cm^{-1}.

Of considerable interest are the reasons for electron transfer along the L side vs the M side, a feature that these calculations reproduce on the basis of differences from C_2 symmetry alone. We need not include the effect of specific residues[26] for this

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calculated asymmetry, but of course, the geometric conformation that we have assumed for the reaction center of *R. viridis is* influenced by the protein and all its polar groups.[27] No doubt specific interactions can change the observed kinetics, but we might speculate that the primary influence of these specific interactions arises from changes in the geometry of the reaction center, itself. Considering only thermodynamics, a difference in energy of 890 cm^{-1} between $P \rightarrow H_L$ and $P \rightarrow H_M$ excitations translates into a factor of 70:1 favoring the L side at room temperature, to be compared with experimental values of about 100:1 to 200:1.[28-30]

These calculations do not specifically include the nearby hydrogen bonding or aromatic amino acid residues that may be important in electron transfer.[31] Also this simple solvent model is correct only through first order in the CI. We do not attempt to demonstrate highly accurate agreement with experiment. Rather we wish to show that consideration of the protein as a polarizable medium can play a significant role in lowering the energies of the $P \rightarrow H_{L,M}$ CT states relative $P \rightarrow B_{L,M}$, placing them vibrationally accessible to the lowest excited state of the RC. Our calculations also demonstrate the preference for CT along the L branch as well as supplying a rationale for the absence of an active participation of the auxiliary BChl.[32]

Acknowledgment. This work was supported in part through a grant from the Office of Naval Research (N00014-90-J-1608).

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An Unprecedented and Reversible Cobalt-to-Carbon Alkyl Bond Rearrangement in the Coenzyme B_{12} Model Complex $C_6H_5CH_2Co^{III}[C_2(DO)(DOH)pn]I$

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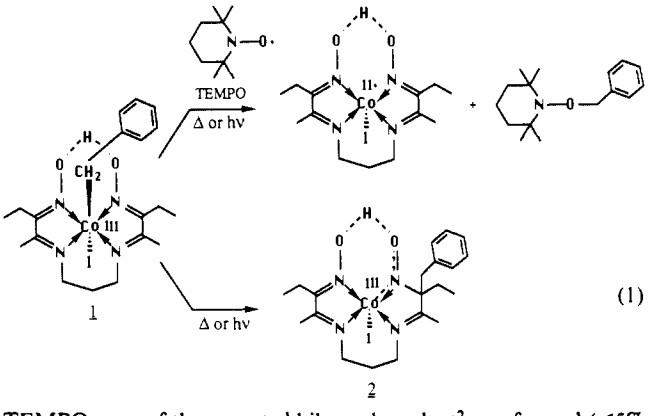
Previously,[2] in developing the now widely used[3-5] nitroxide radical-trapping method for studying cobalt–carbon[3,4] and other metal–carbon[3,5] bond homolyses, we examined the thermolysis of the orange-brown benzyl coenzyme B_{12} model complex[6] $C_6H_5CH_2Co^{III}[C_2(DO)(DOH)pn]I$ (**1**), both with and without the nitroxide TEMPO, eq 1. Surprisingly, in the absence of



(1)

TEMPO none of the expected bibenzyl product[2] was formed (<5% by NMR).[2c] Instead, a curious blood-red product, **2** (λ_{max} = 525 nm), is produced that initially appeared to be similar to paramagnetic, red $Co^{II}[C_2(DO)(DOH)pn]I$ (λ_{max} = 522 nm). However, ^1H NMR (vide infra) indicates that **2** is in fact diamagnetic and *still contains the benzyl group in what is a low-symmetry* (C_1) *structural isomer of* **1**.

Herein we report the required clean, high-yield photochemical synthesis of **2**, the first definitive characterization of **2** (by X-ray

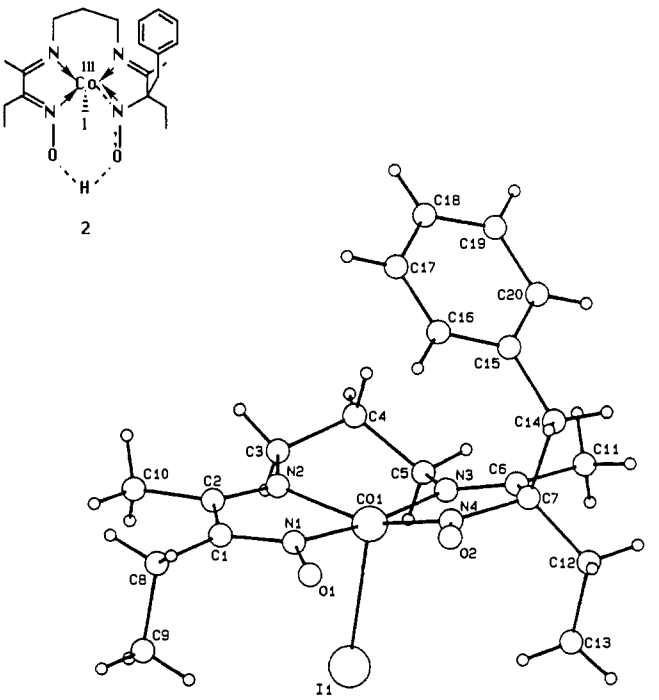


Figure 1. X-ray crystallographically determined molecular structure of the cobalt-to-carbon alkyl migration product **2**, (*SP*-5-15)-[2-[[3-[[2-(hydroxyamino)-1-methyl-2-(phenylmethyl)butylidene]amino]propyl]imino]-3-pentanone oximato(2-)-*N*,*N*′,*N*″,*N*‴]iodocobalt(III).

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(3) (a) The nitroxide method has subsequently proven to be the method of choice for B_{12} alkyls[3b-d] [including coenzyme B_{12} itself,[4a,b] AdoCbi$^+$ (base-free B_{12}),[4c] MeB_{12},[4d] and neopentyl-B_{12}[4e]] as well as non-B_{12} systems.[5] (b) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 5197-5202. Blau, R. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 3530-3533. (c) Geno, M. K.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1238-1240. Geno, M. K.; Halpern, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1052-1053. (d) Gamelkoorn, H. J.; de Bolster, M. W. G.; Bait, S. *Inorg. Chem.*, submitted for publication.
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