or ionic bonding. This allows all spin couplings (different VB structures), a particularly important effect for atoms with partially filled d configurations. For a wave function with N GVB pairs, this leads to 3^N configurations and hence three configurations for (1/2) and 81 configurations for (4/8). These calculations are dissociation-consistent: GVB-RCI(1/2) dissociates to a Hartree–Fock (HF) description of both M^+ and CH_3; GVB-RCI(4/8) dissociates to an HF description of M^+ and a GVB-RCI(3/6) description of CH_3. For the metal hydrides the GVB-RCI(1/2) calculations dissociate to HF fragments.

(3) $RCI(1/2) \times D_\sigma$. From the three RCI configurations all single and double excitations are allowed out of the metal–ligand σ bond to all virtual orbitals. This calculation allows for all correlation between the two electrons of the bond pair. It dissociates to an $HF \times S_\sigma$ description for both the metal ion and the CH_3 fragments (the single excitation is from the s or d_{z^2} orbital on the metal, depending on which is used for bonding, and from the p_z orbital on CH_3). Metal hydrides dissociate to an $HF \times S_\sigma$ description of M^+ and an HF H atom.

(4) $RCI(1/2) \times [D_\sigma + S_{M^+}]$. To the configurations of (3) we add all those formed by starting with the RCI configurations and allowing single excitations from the metal nonbonding valence orbitals (to all occupied and virtual orbitals). This calculation dissociates to an HF calculation on the ligand and an all singles CI for the metal valence orbitals.

(5) $RCI(1/2) \times [D_\sigma + S_{M^+,val}]$. This calculation is similar to (4) except that the single excitations are allowed out of all valence orbitals, not just those of the metal ion. For the metal hydrides the two calculations are the same. The metal methyls dissociate to an $HF \times S_{val}$ description on both fragments. This leads to an overcorrelation of the fragments in some cases (if single excitations on the metal lead to an energy lowering, e.g., $ZnCH_3^+$, $PdCH_3^+$, and $CdCH_3^+$) and hence to a calculated dissociation energy that may be slightly too low. This effect is not large and calculations by Carter and Goddard[22] on $RuCH_2$ involving a similar dissociation error show that the bond energy is underestimated by ~0.2 kcal/mol. We expect a similar error in our cases. As a test of the adequacy of this level of electron correlation, Carter and Goddard[26] performed a similar calculation breaking the C–H bond in CH_4. The theoretical bond dissociation energy was calculated at 110.5 kcal/mol in comparison to an experimental D_e of 112.2 ± 0.5 kcal/mol. The calculated bond dissociation energy is thus only 1.7 kcal/mol lower than the experimental value, suggesting that our comparable calculations on MCH_3^+ species should be quite adequate.

Acknowledgment. We thank the National Science Foundation (Grants CHE83-18041 and CHE84-07857) for partial support of this work.

Registry No. ScH^+, 83018-00-2; $ScCH_3^+$, 93349-11-2; CrH^+, 75641-98-4; $CrCH_3^+$, 89612-53-3; MnH^+, 75641-96-2; $MnCH_3^+$, 89612-54-4; ZnH^+, 41336-21-4; $ZnCH_3^+$, 47936-33-4; YH^+, 101200-09-3; YCH_3^+, 109585-23-1; MoH^+, 101200-12-8; $MoCH_3^+$, 109585-24-2; TcH^+, 106520-06-3; $TcCH_3^+$, 106500-86-1; PdH^+, 85625-94-1; $PdCH_3^+$, 90624-40-1; CdH^+, 41411-12-5; $CdCH_3^+$, 106520-07-4; Sc^+, 14336-93-7; Cr^+, 14067-03-9; Mn^+, 14127-69-6; Zn^+, 15176-26-8; Y^+, 14782-34-4; Mo^+, 16727-12-1; Tc^+, 20205-77-0; Pd^+, 20561-55-1; Cd^+, 14445-53-5; $CH_3^\bullet$, 2229-07-4.

Bond Energy and Other Properties of the Re–Re Quadruple Bond

David C. Smith and William A. Goddard III*

Contribution No. 7558 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. *Received February 18, 1987*

Abstract: Using generalized valence bond (GVB) methods designed for obtaining accurate bond energies, we predict an Re–Re quadruple bond strength of 85 ± 5 kcal/mol for $Re_2Cl_8^{2-}$. This is much less than early estimates of 370 kcal/mol and somewhat lower than estimates (124 to 150 kcal/mol) based on Birge–Sponer extrapolation but is in reasonable agreement with a recent thermochemical study (97 ± 12 kcal/mol). We obtain a rotational barrier of 3.0 kcal/mol and a singlet–triplet excitation energy of 3100 cm^{-1}, and we conclude that the intrinsic strength of the δ bond is 6 ± 3 kcal/mol.

Since their discovery in 1965, quadruply bonded metal dimers have provoked numerous theoretical and experimental studies. A particularly controversial issue has been the strength of the quadruple bond and, in particular, the contribution of the δ bond to the observed structure of the unbridged dimers.[1-4] We here report the results of ab initio calculations of $Re_2Cl_8^{2-}$ designed to provide accurate bond energies and torsion barriers as well as accurate shapes for the potential curves. These studies use the generalized valence bond (GVB) approach in which electron correlations are included for all eight electrons available for the quadruple bond, while solving self-consistently for all orbitals.[5,6]

We use the modified-GVB (M-GVB) approach of Goodgame and Goddard.[7] They pointed out that ab initio descriptions of multiple bonds in transition metals lead to substantial errors in the bond energy due to an inadequate treatment of the electron correlations in the ionic part of the wave function describing the bond.

$$\psi^{GVB} = \psi_{cov} + \lambda\psi_{ionic} = [\phi_l(1)\phi_r(2) + \phi_r(1)\phi_l(2)] + \lambda[\phi_l(1)\phi_l(2) + \phi_r(1)\phi_r(2)]$$

In GVB, electron correlation in the covalent part of the wave

---

[1] Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982; and references therein.

[2] Cotton, F. A.; Walton, R. A. *Struct. Bonding* **1985**, *62*, 1–49.

[3] Mathisen, K. B.; Wahlgren, U.; Pettersson, L. G. M. *Chem. Phys. Lett.* **1984**, *104*, 336–342 and references therein.

[4] Hay, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 7007–7017 and references therein.

[5] Goddard, W. A., III; Ladner, R. C. *J. Am. Chem. Soc.* **1971**, 93, 6750–6756.

[6] Bobrowicz, F. W.; Goddard, W. A., III In *Modern Theoretical Chemistry: Methods of Electronic Structure Theory*; Schaefer, H. F., III, Plenum: New York, 1977; Vol. 3, Chapter 4, pp 79–127.

0002-7863/87/1509-5580$01.50/0

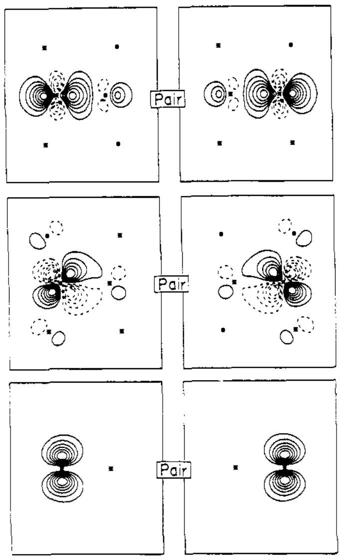

Figure 1. GVB orbitals involved in the σ, π, and δ bonds of $Re_2Cl_8^{2-}$ (reading top to bottom). Spacing between contours is 0.05 au. Negative contours are denoted by dashed lines; asterisks denote position of nuclei. The σ and π orbitals are plotted in the xz plane; the δ orbitals are plotted in a plane rotated 45° from the xz plane.

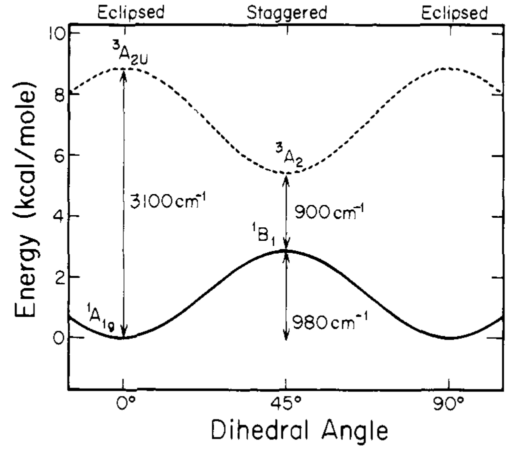

Figure 2. Energy profile for the ground state and $^3(\delta\delta^*)$ excited state of $Re_2Cl_8^{2-}$ as a function of dihedral angle. The $^3(\delta \rightarrow \delta^*)$ excitation energy was calculated for ϕ of 0° and 45°. The plot assumes a periodic energy function with the energies at ϕ of 0° and 45° as the minimum and maximum of the function for the ground state and the maximum and minimum of the function for the $^3(\delta\delta^*)$ excited state.

Table I. Comparison of Calculated and Experimental Spectroscopic Constants

	GVB–PP[a]	GVB–RCI[b]	M-GVB–RCI	exptl
bond length (Å)	2.37	2.36	2.26	2.24[c]
Re–Re force constant (mdyn/Å)	2.75	2.48	4.64	
vibrational frequency[d] (cm^{-1})	247	240	293	275[e]
bond energy (kcal/mol)	*g*	25.8	85.0	(97 ± 12)[f]
rotational barrier (kcal/mol)	−1.6	0.1	2.8	

[a] For a description of GVB–PP wave functions, see ref 6. [b] CI wave function similar to that described in Table Ia of: Moss, B. J.; Goddard, W. A., III *J. Chem. Phys.* **1975**, *63*, 3523–3531. [c] Based on X-ray diffraction study of $K_4[Re_2Cl_8]\cdot 2H_2O$; ref 9. [d] The calculated Re–Re bond length and force constants were used with an earlier determined valence force field in the vibrational analysis; ref 22. [e] Based on solid-state resonance Raman study of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$; ref 24. [f] Based on thermochemical study of $Cs_2Re_2Br_8$; ref 14. [g] Keeping a constant spin coupling, GVB–PP leads to a dissociation error of 55.5 kcal/mol.

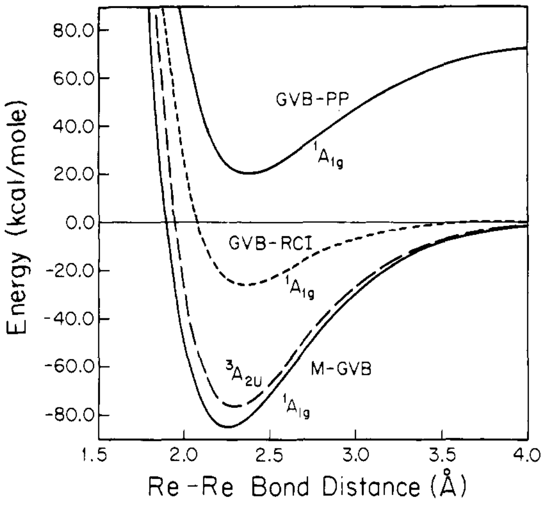

Figure 3. Calculated potential curves for $Re_2Cl_8^{2-}$.

function is well described, but the ionic terms are forced to use doubly occupied orbitals. Because of the spatial compactness of the d orbitals, there are substantial electron correlations in such doubly occupied orbitals, leading to large errors in certain atomic electron affinities and ionization potentials. In M–GVB, this correlation error of the atom is built into the atomic Coulomb integrals, but calculations are otherwise as in normal GVB.[7] The electron correlations imbedded in M–GVB would have been included in normal GVB wave functions by suitably high-level excitations (CI) and hence with M–GVB we cannot go *beyond* GVB-level calculations (since some electron correlation effects would be double corrected). M–GVB has been successfully applied in studying the sextuple bonds of Mo_2 and Cr_2, where an accurate description of bond energies (D_e) and bond distances (R_e) was obtained.[7] Thus, for Mo_2, D_e^{calcd} = 90.9 kcal/mol, D_e^{exptl} = 97 ± 5 kcal/mol, R_e^{calcd} = 1.92 Å, R_e^{exptl} = 1.93 Å; and for Cr_2, D_e^{calcd} = 42.9 kcal/mol, D_e^{exptl} = 46 ± 7 kcal/mol, R_e^{calcd} = 1.61 Å, R_e^{exptl} = 1.68 Å. The current studies involve exactly the same approach as in these earlier studies except that we now utilize effective core potentials (ECP) so that only the 15 outermost electrons (5s,5p,6s,5d) of each Re are treated explicitly; however, the potentials describe the effects of core electrons including the dominant relativistic effects.[8]

The GVB orbitals of the singlet ground state ($^1A_{1g}$) are shown in Figure 1 where we see that four electrons in dσ, dπ_x, dπ_y, and dδ_{xy} orbitals on each Re are spin-paired to form the quadruple bond. Uncoupling the spins of the two electrons in δ orbitals leads to the lowest triplet state ($^3A_{2u}$). Rotating one $ReCl_4$ group about the bond by 45° leads (see Figure 2) to essentially identical bonding in the σ, π_x, and π_y orbitals, but the δ bond is broken with the result that the singlet and triplet states (denoted as $^1B_1$ and $^3A_2$) are nearly degenerate. Some indications of the relative strengths of these bonds are given by the overlaps in the GVB orbitals, S_σ = 0.68, S_π = 0.54, S_δ = 0.12 for the eclipsed configurations, but S_σ = 0.68, S_π = 0.53, and S_δ = 0.0 for the staggered. As the bond is stretched, the overlaps of the GVB orbitals decrease continuously to zero, leading to a smooth description of bond dissociation (molecular orbital based schemes often lead to the wrong dissociation limit, complicating predictions of bond energies).

In these calculations the geometry of each $(ReCl_4)^-$ fragment was fixed as that in the crystal,[9] and the Re–Re bond distance was optimized. An important issue here for bond energies concerns the charges. In crystals and solution, the charge of $Re_2Cl_8^{2-}$ is

---

(7) Goodgame, M. M.; Goddard, W. A., III, *Phys. Rev. Lett.* **1985**, *54*, 661–664.

(8) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299–310.

(9) Cotton, F. A.; Harris, C. B. *Inorg. Chem.* **1965**, *4*, 330–333.

Table II. Comparison of Calculated Spectroscopic Constants for the $^1A_{1g}$ and $^3A_{2u}$ States at the M-GVB-RCI Level

	$^1A_{1g}$	$^3A_{2u}$[a]	diff
bond length (Å)	2.26	2.30	+0.04
Re–Re force constant (mdyn/Å)	4.65	4.67	+0.02
vibrational frequency (cm^{-1})	293	293	0.0
bond energy (kcal/mol)	85.0	76.5	-8.5

[a] Optimization of eclipsed rotomer neglecting relaxation of $ReCl_4$ fragments from their ground-state structure.

neutralized by counter charges (e.g., K^+), and in calculating bond energies it is necessary to include the effects of these counter charges (the Coulomb energy for two charges at 2.24 Å is 150 kcal/mol!). In order to ameliorate this problem, fractional charges (leading to a net charge of 0 on each fragment) are placed at positions extrapolated from the crystallographic positions of the counterions. The charges are placed so as to maintain the overall symmetry of the system and to be invariant under a 45° rotation of the $ReCl_4^-$ units.[10] The rotational invariance allows for a comparison of the properties of the eclipsed and staggered geometries. The results for the Re–Re bond distance optimization are shown in Figure 3 and in Tables I and II.[11]

The bond energy for the Re–Re quadruple bond calculated at the M-GVB level is 85.0 kcal/mol, the first ab initio estimate of the energy of a quadruple metal–metal bond. Similar calculations on Mo_2 and Cr_2 lead to bond energies within 5 kcal/mol of experiment, and we believe that similar accuracy can be expected in the Re–Re quadruple bond studies, leading to D_e-$(\mathrm{Re}\overset{4}{-}\mathrm{Re}) = 85 \pm 5$ kcal/mol. A more conservative estimate of the uncertainty, perhaps, ±10 kcal/mol, would be warranted given the lack of comparable theoretical and experimental studies on other systems. Experimental values for the bond energy of the quadruple bond have been quite difficult to obtain. Early estimates have ranged as high as 370 kcal/mol.[1] Birge–Sponer extrapolations using the harmonic stretching frequency and the anharmonicity constant determined from resonance Raman measurements suggest an Re–Re bond energy of 152 ± 19 kcal/mol for $Re_2Cl_8^{2-}$ and 139 ± 24 kcal/mol for $Re_2Br_8^{2-}$.[12] Such Birge–Sponer extrapolations for multiple bonds are fraught with peril and could easily lead to errors of 50–70 kcal/mol.[13] A more reliable thermochemical study places the Re–Re bond energy for $Cs_2Re_2Br_8$ at 97 ± 12 kcal/mol,[14] this estimate depending on empirically based assumptions in order to estimate the Re–Br bond energy. Given the various experimental uncertainties, we believe that the theoretical value of 85 kcal/mol is the best current estimate of the bond energy. Early extended Hückel calculations placed the quadruple bond in $Re_2Cl_8^{2-}$ at 370 kcal/mol.[1] Recent theoretical work with the Hartree–Fock–Slater transition-state method has estimated the Re–Re triple bond energy in $Re_2Cl_4(PH_3)_4$ to be 134 kcal/mol.[15] Generally, these latter methods lead to an overestimate of the bond energy by 1 to 2 eV,[16] suggesting $D_e \approx 90$ to 110 kcal/mol, in line with the GVB results.

Given a total bond energy of 85 kcal/mol, the question is how strong is the δ-bond? One way to establish this is by the singlet–triplet gap at the eclipsed geometry (calculated at 3100 cm^{-1} = 0.38 eV = 8.8 kcal/mol), suggesting a δ bond strength of 4.5–9.0 kcal/mol (this estimate ignores spin-coupling with the other orbitals of the bond). A second approach is to use the rotational barrier at the ground-state equilibrium bond distance. The energy difference between the eclipsed and staggered geometries involves opposing energy contributions. Rotating from eclipsed to staggered changes the overlap, i.e., the δ bond goes to zero so that bonding is lost. Simultaneously electrostatic and steric interactions between Cl's bonded to opposite Re's are relieved. With this competitive effect in the total energy, one can only obtain bounds to the pure δ contribution to the bonding. The calculations give a direct barrier of 3.0 kcal/mol,[17a] a lower bound on the strength of the δ bond. The calculated barrier for the triplet state (favoring staggered) of 3.0 kcal/mol[17b] should be an upper limit on the steric barrier, suggesting an upper limit on the δ bond of 6.0 kcal/mol. From the above analysis, a reasonable estimate of the δ bond strength is 6 ± 3 kcal/mol, which is weak compared with σ and π bonds but sufficiently large to explain the ubiquity of the eclipsed geometry for d^4–d^4 metal dimers.

There are not experimental estimates of the δ bond strength; however, from dynamic NMR studies of meso-substituted molybdenum porphyrin dimers, the activation energy for rotation about the quadruple metal–metal bond has been estimated to be 10.1 ± 0.5 kcal/mol.[18] This is larger than the value calculated for $Re_2Cl_8^{2-}$, perhaps because steric interactions (which reduce the barrier) are smaller in the porphyrin. From measured $\delta \rightarrow \delta^*$ splittings in odd-electron complexes [e.g., $Mo_2(SO_4)_4^{3-}$ and $Tc_2Cl_8^{3-}$], Trogler and Gray have estimated the δ bond energy to be 9–10 kcal/mol.[19]

Early self-consistent-field (SCF) calculations found the ground state of the staggered conformation to be a triplet, about 60 kcal/mol lower than the singlet ground state of the eclipsed geometry. Addition of CI reduced the difference between eclipsed and staggered geometries to 4 kcal/mol, yet still favored the triplet state of the staggered conformation.[20] Other recent ab initio calculations find the ground state for the eclipsed and staggered geometries to be a singlet with essentially no barrier between the two rotomers.[21]

The M-GVB calculations lead to an Re–Re bond distance of 2.26 Å, in excellent agreement with the experimental value of 2.24 Å. This is consistent with the results on Mo_2 where M-GVB leads to an error of -0.01 Å.[7] We calculate a metal–metal stretching force constant of 4.6 mdyn/Å, and using a valence force field,[22] we obtain a metal–metal stretching frequency of 293 cm^{-1}.[23] This can be compared with the vibrational frequency for $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ (determined from resonance Raman) of 275 cm^{-1}.[24]

Summarizing, our calculations (i) provide the first prediction based on ab initio studies of an eclipsed ground state for a

---

[10] An average metal–ion distance of 4.3 Å was maintained (determined from the X-ray diffraction data). Charges of +0.125 were placed in the same plane as defined by the four Cl's of each $ReCl_4$ unit. The charges were placed at 22.5° off of the Re–Cl vector. The validity of this approach is supported by the small effect on excitation energies and rotational barriers where use of the counterions (i) increases the $^3(\delta \rightarrow \delta^*)$ excitation energy by 10 cm^{-1} for the eclipsed conformation and less than 10 cm^{-1} for the staggered conformation and (ii) decreases the rotational barrier by 0.5 kcal/mol.

[11] The calculations lead to a slight barrier in the potential curves as the neutral $ReCl_4$ fragments are brought together. This barrier is 0.45 kcal/mol (at 4.18 Å) for GVB-RCI and 0.13 kcal/mol (at 4.92 Å) for M-GVB. This occurs because the nonplanar $ReCl_4$ fragments are kept at a fixed nonplanar geometry as the fragments are separated, leading to a small dipole moment and hence a slight repulsive interaction at large R.

[12] Trogler, W. C.; Cowman, C. D.; Gray, H. B.; Cotton, F. A. *J. Am. Chem. Soc.* **1977**, *99*, 2993–2996.

[13] Gaydon, A. G. *Dissociation Energies and Spectra of Diatomic Molecules*; Chapman and Hall: London, 1968; see Chapter 5.

[14] Morss, L. R.; Porcja, R. J.; Nicoletti, J. W.; San Filippo, J.; Jenkins, H. D. B. *J. Am. Chem. Soc.* **1980**, *102*, 1923–1927.

[15] Ziegler, T. *J. Am. Chem. Soc.* **1984**, *106*, 5901–5908.

[16] Messmer, R. P. *J. Vac. Sci. Technol. A.* **1984**, *2*, 899–904.

[17] (a) The ground-state rotational barrier calculated for $Re_2Cl_8^{2-}$ is 3.3 kcal/mol, while the ground-state rotational barrier calculated for $Re_2Cl_8^{2-}$ with counterions is 2.8 kcal/mol. (b) The triplet barrier calculated for $Re_2Cl_8^{2-}$ is 3.0 kcal/mol, while the triplet barrier calculated for $Re_2Cl_8^{2-}$ with counterions is 3.4 kcal/mol.

[18] Collman, J. P.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 2592–2596.

[19] Trogler, W. C.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 232–239.

[20] Bernard, M. *J. Am. Chem. Soc.* **1978**, *100*, 2354–2362.

[21] (a) At the GVB-CI level there is less than 1 kcal/mol difference between the staggered and eclipsed forms of $Re_2Cl_8^{2-}$; see ref 4. (b) The staggered form of $Mo_2Cl_8^{4-}$ was found to be 3 kcal/mol *more* stable than the eclipsed form at the CAS-SCF level: Strömberg, A.; Pettersson, L. G. M.; Wahlgren, U. *Chem. Phys. Lett.* **1985**, *118*, 389–394.

[22] Bratton, W. K.; Cotton, F. A.; Debeau, M.; Walton, R. A. *J. Coord. Chem.* **1971**, *1*, 121–131.

[23] Details and further analysis of the force field calculations will be published later. These calculations were carried out with BIOGRAF/IV (from Biodesign, Inc.).

[24] Clark, R. J. H.; Stead, M. J. *Inorg. Chem.* **1983**, *22*, 1214–1220.

J. Am. Chem. Soc. **1987**, *109*, 5583–5586

quadruply bonded metal dimer, (ii) predict an Re–Re quadruple bond energy of 85 ± 5 kcal/mol—the first direct estimate of the strength of this prototypical quadruple bond, and (iii) suggest that the δ bond energy is 6 ± 3 kcal/mol.

Acknowledgment. We acknowledge Dr. Siddharth Dasgupta for his contributions in the vibrational analysis. This work was partially supported by grants from the Sun Co. and from National Science Foundation (No. CHE83-18041).

Ligand-Aided Photoreduction of Iron–Porphyrin Complexes Probed by Resonance Raman Spectroscopy

Y. Ozaki,[1a] K. Iriyama,[1a] H. Ogoshi,[1b] and T. Kitagawa*[1c]

Contribution from the Division of Biochemistry, The Jikei University School of Medicine, Nishi-shinbashi, Minato-ku, Tokyo, 105 Japan, Department of Chemistry and Chemical Engineering, The Technological University of Nagaoka, Nagaoka, 949-54 Japan, and Institute for Molecular Science, Okazaki National Research Institutes, Myodaiji, Okazaki, 444 Japan.

Received June 30, 1986

Abstract: Photoreduction has been observed for the first time for an iron porphyrin with a biologically relevant axial ligand by using resonance Raman (RR) spectroscopy (for Fe^{III}(OEP)(2-MeIm), OEP = octaethylporphyrin and 2-MeIm = 2-methylimidazole). The action spectrum for the photoreduction obtained by visible absorption spectra exhibited a broad maximum around 420–460 nm, which was appreciably shifted from the Soret band of Fe^{III}(OEP)(2-MeIm) at 395 nm. Similar photoreduction was observed for Fe^{III}(OEP)(1,2-Me$_2$Im) (1,2-Me$_2$Im = 1,2-dimethylimidazole) but not for Fe^{III}(OEP)L$_2$ (L = imidazole and 1-methylimidazole) and Fe^{III}(OEP)X (X = F, Cl, Br, I, and ClO$_4$). The coincidence of the RR spectrum of the photoreduced species with that of the ferrous porphyrin rules out the possibility of ring reduction to a porphyrin anion radical or chlorin. The dependence of the photoreduction on the concentration of 2-MeIm suggested that the ligand-free Fe^{II}(OEP) is a likely intermediate and thus that the light-induced charge transfer from the axial ligand to the iron ion is the primary process of photoreduction.

In the resonance Raman (RR) studies of some hemeproteins, occurrence of photoreduction has been noticed upon laser irradiation at selected wavelengths,[2–8] but nothing is known about its mechanism and electron donors. Apart from those studies, the photoreduction has been explored for several metalloporphyrins from the view of photochemistry,[9–15] although no Raman study has been included. To gain an insight into the photoreduction mechanism of hemeproteins, we investigated iron porphyrin complexes with a biologically relevant axial ligand by using RR spectroscopy. The use of this technique might allow us to infer an intermediate molecular species involved in the photoreduction on the basis of the accumulated knowledge about the RR spectra of iron porphyrins.[16,17] Here we report RR evidence for photoreduction of 2-methylimidazole (2-MeIm) and 1,2-dimethylimidazole (1,2-Me$_2$Im) complexes of iron–octaethylporphyrin [Fe^{III}(OEP)] and point out the formation of the four-coordinate ferrous complex as an intermediate.

Experimental Procedures

Fe^{III}(OEP)X (X = F, Cl, Br, I, and ClO$_4$) were synthesized with the methods described elsewhere.[18,19] 2-MeIm was recrystallized just before use, and its ^{1}H NMR spectrum showed that it did not contain any detectable impurity. The procedures for preparing the alkyl-imidazole complexes of Fe^{III}(OEP)X and Fe^{II}(OEP)(2-MeIm) were described previously.[20] As a solvent dichloromethane (CH$_2$Cl$_2$) of spectroscopic grade (Wako, Osaka) was used without further purification. All solutions were degassed unless otherwise stated and kept at 10 °C during the Raman measurements.

Raman spectra were measured with a JEOL-400D Raman spectrometer equipped with an RCA-31034a photomultiplier. The excitation sources used are Kr$^+$ (Spectra Physics, Model 164), He/Cd (Kinmon Electrics, Model CDR80MGE), and Ar$^+$ (NEC, Model GLG3200) lasers. Raman shifts were calibrated with indene, and errors of peak frequencies would be less than 1 cm^{-1} for well defined bands. Conventional absorption spectra were recorded with a Hitachi 124S spectrophotometer.

To determine an action spectrum of photoreduction, the degassed solution of Fe^{III}(OEP)(2-MeIm) was placed in a water bath at 20 °C and illuminated by a projector lamp for 5 min in the presence of short cut filters including Y-48, Y-46, Y-44, L-42, L-40, and L-38 (Hoya Corp.). For every measurement a fresh sample from the same stock solution was prepared and their absorption spectra were observed. Since the short cut filter specified by λ_1 allows light with the wavelength longer than λ_1 to pass, the difference between the spectra observed in the presence of the filters, λ_1 and λ_2, which is designated by $S(\lambda_1 - \lambda_2)$, represents the effect of the illumination of light with the wavelengths between λ_1 and λ_2. For

---

* Author to whom correspondences should be addressed.

(1) (a) The Jikei University School of Medicine. (b) Technological University of Nagaoka. (c) Institute for Molecular Science.

(2) Kitagawa, T.; Orii, Y., *J. Biochem. (Tokyo)* **1978**, *84*, 1245.

(3) Adar, F.; Yonetani, T. *Biochim. Biophys. Acta*, **1978**, *502*, 80.

(4) Salmeen, I.; Rimai, L.; Babcock, G. T. *Biochemistry* **1978**, *17*, 800.

(5) Ogura, T.; Sone, N.; Tagawa, K.; Kitagawa, T. *Biochemistry*, **1984**, *23*, 2826.

(6) Kitagawa, T.; Nagai, K. *Nature (London)* **1979**, *281*, 503.

(7) Kitagawa, T.; Chihara, S.; Fushitani, K.; Morimoto, H. *J. Am. Chem. Soc.* **1984**, *106*, 1860.

(8) Yoshikawa, S.; Mochizuki, H.; Chihara, S.; Hagihara, B.; Kitagawa, T. *Biochim. Biophys. Acta*, **1984**, *786*, 267.

(9) Harriman, A.; Porter, G. *J. Chem. Soc., Faraday Trans.* **1979**, *75*, 1543.

(10) Bartocci, C.; Scandola, F.; Ferri, A.; Carassiti, V., *J. Am. Chem. Soc.* **1980**, *102*, 7067.

(11) Bizet, C.; Morliere, P.; Brault, D.; Delgado, O.; Bazin, M.; Santus, R. *Photochem. Photobiol.* **1981**, *34*, 315.

(12) Bartocci, C.; Maldotti, A.; Traverso, O.; Bignozzi, C. A.; Carassiti, V. *Polyhedron* **1983**, *2*, 97.

(13) Maldotti, A.; Bartocci, C.; Amadelli, R.; Carassiti, V. *Inorg. Chem. Acta* **1983**, *74*, 275.

(14) Hoshino, M.; Konishi, S.; Imamura, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1713.

(15) Imamura, T.; Jin, T.; Suzuki, T.; Fujimoto, M. *Chem. Lett.* **1985**, 847.

(16) Kitagawa, T.; Ozaki, Y. In *Structure and Bonding* **1987**, *64*, 71.

(17) Spiro, T. G. In *Iron Porphyrins*; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, 1983; Vol. 2, p 91.

(18) Ogoshi, H.; Watanabe, E.; Yoshida, Z.; Kincaid, J.; Nakamoto, K. *J. Am. Chem. Soc.* **1973**, *95*, 2845.

(19) Ogoshi, H.; Sugimoto, H.; Yoshida, Z. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3414.

(20) Ozaki, Y.; Iriyama, K.; Ogoshi, H.; Ochiai, T.; Kitagawa, T. *J. Phys. Chem.* **1986**, *90*, 6105.

0002-7863/87/1509-5583$01.50/0