

Table III. A Comparison of Distances (Å) in I with Those in Similar Porphyrins

	this work	mean of 16 studies ¹⁰	EtChla ^{2a}	EtChlb ³	MgTPP(H ₂ O) ⁹
C _α -N	1.376 (3) ^a	1.379 (6)	1.374 (7)	1.369 (11)	1.376 (10) ^b
C _β -C _β	1.346 (4)	1.354 (10)	1.370 (17) ^c	1.365 (6) ^c	1.360 (10)
C _α -C _β	1.437 (3)	1.443 (5)	1.448 (10) ^c	1.441 (5) ^c	1.431 (10)
C _α -C _m	1.410 (3)	1.390 (11)	1.389 (10)	1.398 (5)	1.415 (10)
C _m -C _{Ph}	1.493 (4)	1.499 (5)			1.540 (10)

^a $\sigma_m = (\sum_m (l_m - l)^2 / (m - 1))^{1/2}$, where l_m is the mean bond length, l is the measured length, and m is the number of measurements. ^b If only two measurements, σ_m was taken as the mean of the two individual σ 's. ^c Based on unsaturated rings only.

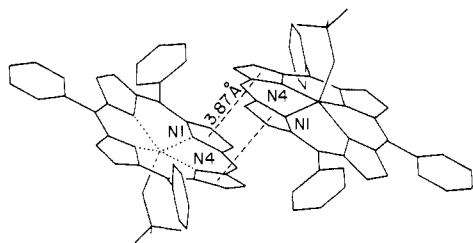


Figure 4. View of the molecular packing that illustrates the overlap of ring I with ring IV of an inversion-related molecule. Phenyl ring D attached to C20 has been removed for clarity. Another representation of this interaction with all four phenyl groups intact has been included with the supplementary material.

the uncertainty in the z coordinate of the Mg in that structure.^{9,10})

The coordination of the magnesium¹⁴ in the porphyrin pocket is somewhat asymmetric ($\sim 6\sigma$ differences in distances) with the metal pushed toward rings I and IV at lengths of 2.088 (5) and 2.080 (5) Å and away from II and III at 2.106 (5) and 2.110 (5) Å. These lie in the range found^{2,3} in chlorophyllides *a* and *b* of 2.004 (9)–2.101 (9) Å and compare with the sole Mg–N distance of 2.072 (10) Å observed⁹ in MgTPP(H₂O).

A feature of the present structure is the close molecular packing in which rings I and IV of inversion-related molecules overlap with a perpendicular separation of 3.87 (1) Å between ring centers, indicative of weak π – π interactions (Figure 4). (Weak aggregates of ZnTPP⁺⁶ and MgTPP⁺⁸ have also been postulated to exist in solution in order to rationalize electron spin resonance data.) Such close intermolecular contacts, normally considered unlikely because of steric hindrance by the phenyl groups, may account for the observed twists of those rings. They are attached to the meso carbons at significantly acute dihedral angles of 47.3 (3), 55.4 (3), 63.2 (3), and 42.1 (3)° for rings A–D, respectively. However, in at least two other nonradical porphyrins, ZnTPyP¹¹ and Fe^{III}TPP⁺ClO₄[–],¹² the meso aryl rings are far from perpendicular to the porphyrin plane.

In conclusion, these results, and those previously reported for ZnTPP⁺ClO₄[–],⁷ suggest that the porphyrin π system acts as a sink and that abstraction of an electron to yield a π cation induces no major effects on the bond distances and stereochemistry of the macrocycle (with the possible exception of the ruffling, which may accommodate the counterion). Extrapolation of these data to (bacterio)chlorophyll cation radicals in vivo suggests that the structural invariance assumed by the Franck–Condon principle¹⁵ holds true not only during the actual electron transfer but also for the initial and final

conformational states of the chromophores.¹⁶ This minimal nuclear rearrangement may thus also favor¹⁵ the rapid electron transfer observed in the primary charge separation of photosynthetic organisms.¹

In a different context, these results further indicate that the common usage of neutral-molecule coordinates for molecular orbital calculations of porphyrin radicals^{1,6} should not introduce significant errors.

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Supplementary Material Available: Listings of structure amplitudes, selected bond angles, distances and angles in the phenyl rings, some least-squares planes, anisotropic thermal parameters for the non-hydrogen atoms, fractional coordinates for the hydrogen atoms, and distances in the perchlorate bound to Mg and a view of the molecular packing with all four phenyl rings attached to both molecules (22 pages). Ordering information is given on any current masthead page.

- (16) Reduced porphyrins, i.e., chlorins, bacteriochlorins, and isobacteriochlorins, exhibit a wide range of conformations because of the flexibility of the reduced pyrrole rings.^{2,3,4,17} Obviously, the present porphyrin study does not allow an assessment of the effects of oxidation on the conformations of the reduced rings of (bacterio)chlorophyll radicals.
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Electron-Transfer Reactions of Tetrakis(μ -acetato)dirhodium(II) and the Self-Exchange Rate of the Rh₂(OAc)₄⁺/Rh₂(OAc)₄ Couple

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The binuclear rhodium(II) complexes of the type Rh₂(OOCR)₄X₂ (R = alkyl; X = H₂O and various other donors) have been shown to undergo one-electron oxidation.^{1–3} The complex Rh₂(OAc)₄(OH₂)₂⁺ has the same structure⁴ as the corresponding reduced species⁵ but with significantly shorter Rh–Rh and Rh–O bonds. Photoelectron,⁶ vibrational,^{2,7} and

- (14) At the request of a reviewer, the following bond angles are presented here rather than in the supplementary material: N1–Mg–N2 = 88.3 (1)°, N1–Mg–N4 = 87.2 (2)°, N2–Mg–N3 = 86.8 (2)°, N3–Mg–N4 = 87.9 (2)°, N1–Mg–O3 = 100.3 (2)°, N2–Mg–O3 = 102.2 (2)°, N3–Mg–O3 = 104.2 (2)°, N4–Mg–O3 = 101.2 (2)°, Mg–O3–Cl = 134.5 (3)°.
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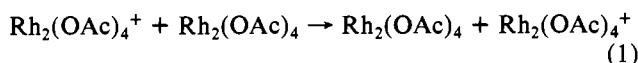
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Table I. Rate Constants of One-Electron-Transfer Reactions of $\text{Rh}_2(\text{OAc})_4^+$ and $\text{Rh}_2(\text{OAc})_4$

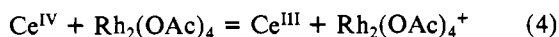
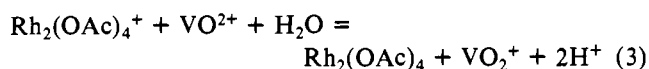
reaction	medium	$T/^\circ\text{C}^a$	concn range/mM ^b	$k/\text{M}^{-1} \text{s}^{-1}$
$\text{Rh}_2(\text{OAc})_4 + \text{Ce}^{\text{IV}}$	1 M HClO_4	25	0.5–1.5	$(6.0 \pm 0.3) \times 10^4$ ^d
		30	0.5–1.5	$(7.6 \pm 0.4) \times 10^4$
		35	0.5–1.5	$(9.6 \pm 0.4) \times 10^4$
		0.5 M H_2SO_4	5 ± 1	6.0–40.0 ^c
$\text{Rh}_2(\text{OAc})_4^+ + \text{VO}^{2+}$	1 M HClO_4	24	6.0 ^c	$(2.10 \pm 0.14) \times 10^4$
		25	8.0–50.0	$(1.98 \pm 0.02) \times 10^2$
	0.5 M HClO_4 , 0.5 M NaClO_4	25	5.0–30.0	$(1.94 \pm 0.02) \times 10^2$
		1 M HClO_4	20	0.25–1.25
$\text{Rh}_2(\text{OAc})_4^+ + \text{Fe}^{2+}$	1 M HClO_4	25	0.25–1.25	$(10.7 \pm 0.9) \times 10^4$ ^f
		30	0.25–1.25	$(12.2 \pm 1.0) \times 10^4$
		30	0.25–1.25	$(12.2 \pm 1.0) \times 10^4$
		40	0.25–1.25	$(14.4 \pm 1.2) \times 10^4$

^a ± 0.2 °C. ^b Fe, V, or Ce concentrations; $[\text{Rh}_2(\text{OAc})_4]_{\text{T}} = 0.1\text{--}0.3$ mM. ^c $[\text{Rh}_2(\text{OAc})_4]_{\text{T}} = 1.0$ mM. ^d $\Delta H^\ddagger = 8.2 \pm 1.0$ kcal mol⁻¹, $\Delta S^\ddagger = -8.7 \pm 3.3$ cal K⁻¹ mol⁻¹. ^e $\Delta H^\ddagger = 5.8 \pm 0.5$ kcal mol⁻¹, $\Delta S^\ddagger = -19.1 \pm 1.5$ cal K⁻¹ mol⁻¹. ^f $\Delta H^\ddagger = 3.9 \pm 0.6$ kcal mol⁻¹, $\Delta S^\ddagger = -21.5 \pm 2.0$ cal K⁻¹ mol⁻¹.

ESR⁸ spectra all indicate that the two rhodium atoms are equivalent with formal oxidation number 2.5. The couple $\text{Rh}_2(\text{OAc})_4^+/\text{Rh}_2(\text{OAc})_4$ gives reversible equilibrium potentials at the platinum electrode in aqueous media,^{1,2} and this and related couples vary from diffusion-controlled to quasi-reversible in cyclic voltammetric measurements.^{1,8–10} The rate constant for electron exchange has not been determined however; hence, we have sought to estimate the rate of the self-exchange reaction (1), in aqueous solution, from the rates



of appropriate one-electron cross reactions. Previously,¹¹ we reported the kinetics of the reaction of $\text{Rh}_2(\text{OAc})_4^+$ with Br^- ion, which involves a directly bonded intermediate $[\text{Rh}_2(\text{OAc})_4\text{Br}_2^-]$. In the present study cationic reductants were used in order to minimize complications due to inner-sphere bonding. We report kinetics of reactions 2 and 3 in perchlorate media and of reaction 4 in perchlorate and sulfate media.



Experiments

The $\text{Rh}_2(\text{OAc})_4^+$ complex was prepared in 1 M perchloric acid solution as before.¹¹ Cerium(IV) perchlorate solutions were prepared by electrolytic oxidation of cerium(III) perchlorate (K & K Laboratories, Inc.) in 1 M perchloric acid. In other experiments ammonium hexakis(nitrato)cerate(IV) was used (BDH AnalaR grade). Both were standardized by potentiometric titration (bright Pt electrode) against iron(II) ammonium sulfate. Solutions of iron(II) perchlorate were prepared, stored, and standardized as described previously.¹² Hydrated vanadyl perchlorate was prepared from vanadyl sulfate, VOSO_4 , and barium perchlorate and recrystallized from water. The solution in 1 M perchloric acid was standardized by potentiometric titration with cerium(IV).

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Table II. Data Used To Calculate the Self-Exchange Rate Constant of Reaction 1

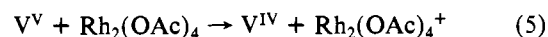
reaction	medium ^a	$\log k_{12}$ ^b	$\log K_{12}$ ^c	$\log k_{11}$	$\log f_{12}$ ^d
$\text{Ce}^{\text{IV}} + \text{Rh}_2(\text{OAc})_4$	1 M HClO_4	4.78	7.60	~0.5 ^f	-0.8
$\text{V}^{\text{V}} + \text{Rh}_2(\text{OAc})_4$	1 M HClO_4	-1.26 ^e	-3.55	~1.0 ^g	-0.2
$\text{Fe}^{\text{III}} + \text{Rh}_2(\text{OAc})_4$	1 M HClO_4	-3.09 ^e	-8.12	1.06 ^h	-0.9
$\text{Ce}^{\text{IV}} + \text{Rh}_2(\text{OAc})_4$	0.5 M H_2SO_4	4.34	3.55	0.64 ⁱ	-0.17

^a 25 °C. ^b From eq 4–6; units $\text{M}^{-1} \text{s}^{-1}$. ^c Calculated by using $E^\ominus(\text{Ce}^{\text{IV}}/\text{III}) = 1.70$ V in 1 M HClO_4 and 1.46 V in 0.5 M H_2SO_4 ,¹⁵ $E^\ominus(\text{V}^{\text{V}}/\text{IV}) = 1.034$ V in 1 M HClO_4 ,¹⁶ $E^\ominus(\text{Fe}^{3+}/2+) = 0.767$ V ($I = 1.0$ M),¹⁵ and $E^\ominus(\text{Rh}_2(\text{OAc})_4^+/\text{Rh}_2(\text{OAc})_4) = 1.25$ V.² ^d Calculated from eq 8 with $Z = 10^{10} \text{M}^{-1} \text{s}^{-1}$ and other parameters as listed. ^e From Table I, with the values of K_{12} listed in Table II. ^f Calculated from data of ref 17, by assuming a hydrogen ion dependence of the form $[\text{H}^+]^{-2}$, as was found for the $\text{Ce}^{\text{IV}}/\text{III}$ exchange in nitrate media. ^g Calculated by Rosseinsky (ref 16, p 228) from a correlation of rates of reactions $\text{A}^+ + \text{V}^{\text{IV}} = \text{A} + \text{V}^{\text{V}}$ and $\text{A}^+ + \text{Fe}^{\text{II}} = \text{A} + \text{Fe}^{\text{III}}$, where $\text{A}^+ = \text{Ag}^{\text{II}}, \text{Mn}^{\text{III}}, \text{Co}^{\text{III}}, \text{Fe}^{\text{III}}, \text{Tl}^{\text{III}}, \text{V}^{\text{V}}$, and V^{IV} . ^h $I = 0.55$ M.¹⁸ ⁱ Reference 19 (cf. ref 20, footnote 12).

Reaction rates were measured in the Aminco-Morrow stopped-flow apparatus, modified for temperature control.¹³ All measurements were taken at $\lambda = 515$ nm, where the absorbance change is due mainly to the conversion of green $\text{Rh}_2(\text{OAc})_4$ to pink-brown $\text{Rh}_2(\text{OAc})_4^+$ or vice versa. In all experiments, when cerium, iron, or vanadium was in sufficiently large excess over rhodium, pseudo-first-order kinetics were observed, and rate constants k_{obsd} were obtained by plotting $\log(A - A_\infty)$ against t , where A and A_∞ denote absorbance at time t and at equilibrium. The plots were typically linear for ca. 3 half-lives, and plots of k_{obsd} against Fe, V, or Ce concentration were linear over the ranges used, giving rate constants k as shown in Table I. Reaction 3 is zero order with respect to hydrogen ion.

Discussion

In Table II we compare the rate constants ($\log k_{12}$) for reactions 4–6 with the corresponding equilibrium constants,



$\log K_{12}$. According to the Marcus theory,¹⁴ these are related by eq 7 and 8, where the k_{11} are rate constants of the self-

$$\log k_{12} = \frac{1}{2}(\log k_{11} + \log k_{22} + \log K_{12} + \log f_{12}) \quad (7)$$

$$\log f_{12} = (\log K_{12})^2 / 4(\log k_{11} + \log k_{22} - 2 \log Z) \quad (8)$$

exchange reactions of the couples $\text{Ce}^{\text{IV}}/\text{III}$, $\text{V}^{\text{V}}/\text{IV}$, and $\text{Fe}^{\text{III}}/\text{II}$,

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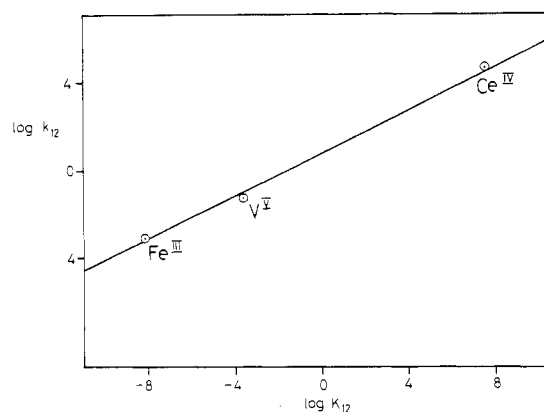


Figure 1. Plot of $\log(k_{12}/M^{-1} s^{-1})$ against $\log K_{12}$, for reactions $A^+ + Rh_2(OAc)_4 \rightarrow A + Rh_2(OAc)_4^+$, where A^+ denotes the oxidants shown. The straight line is drawn with slope 0.5.

k_{22} is the self-exchange rate constant for the couple $Rh_2(OAc)_4^+/Rh_2(OAc)_4$, and Z is the collision rate constant for uncharged reactants. Thus, for a series of reactions with the same or similar mechanisms,¹⁶ with similar values of $\log k_{11}$, and with small values of $\log f_{12}$, the plot of $\log k_{12}$ against $\log K_{12}$ is expected to be a straight line of slope 0.5, and the intercept at $\log K_{12} = 0$ is $1/2(\langle \log k_{11} \rangle + \log k_{22})$, where $\langle \log k_{11} \rangle$ is the mean of $\log k_{11}$ for the reactions in question.

For reactions 4-6, such a plot is obtained, as shown in Figure 1, with $1/2(\langle \log k_{11} \rangle + \log k_{22}) = 1.4 \pm 0.5$.

Of the three self-exchange values, $k_{11}(Fe^{III/II})$ is the best established (Table II). For the cerium couple, the estimate $\log k_{11}(Ce^{IV/III}) \sim 0.5$ involves an extrapolation from 6 M $HClO_4$ to the present medium (Table II, footnote *f*). As regards the $V^{V/IV}$ couple, Rosseinsky¹⁶ found a correlation of rates of reactions of V^{IV} and Fe^{II} with a wide range of oxidants, and after excluding noncationic oxidants, which could bind strongly to the reductants, he deduced $\log k_{11}(V^{V/IV}) = 1.0$ in 1.0 M $HClO_4$. Thus the assumption of similar k_{11} values in our three reactions seems justified, and taking $\langle \log k_{11} \rangle = 0.8$, we propose $\log k_{22} = 1.2 \pm 1.0$, for the couple $Rh_2(OAc)_4^+/Rh_2(OAc)_4$, at 25 °C in 1.0 M $HClO_4$. The $\log f_{12}$ terms (Table II) are small enough not to disturb this result. The value of k_{22} is in the range expected for a redox couple that requires appreciable relaxation of bonds in the inner coordination sphere.²¹ On going from $[Rh_2(OAc)_4(OH_2)_2]^+$ to $[Rh_2(OAc)_4(OH_2)_2]$, the M-M distance increases by 3.0%, the M-OH₂ distance by 4.0%, and the mean M-O(carboxyl) distance by 1.2%.^{4,5} (Compare the increase of 7.0% in the Fe-O distance between $Fe(OH_2)_6^{3+}$ and $Fe(OH_2)_6^{2+}$.)

The reaction $Ce^{IV} + Rh_2(OAc)_4$ is slower in 0.5 M H_2SO_4 than in 1 M $HClO_4$ by a factor of only about 3. The non-bridging ligand effect²³ of sulfate ion would lead to a factor of about 250 (based on eq 7 and the equilibrium constants shown in Table II). The predominant form of Ce^{IV} in the sulfate medium is $Ce(SO_4)_3^{2-}$,²⁴ and the effective 80-fold enhancement in rate is presumably due to bridging by sulfate ion, from Ce to the axial site of the $Rh_2(OAc)_4^+$ ion. In the reaction $Ce^{IV} + Fe^{II}(aq)$, where bridging is also possible, the effective enhancement is greater still, the rate in 0.5 M H_2SO_4

being higher than that in 1 M $HClO_4$.²⁵

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Registry No. $Rh_2(OAc)_4^+$, 83681-59-8; $Rh_2(OAc)_4$, 15956-28-2; Ce, 7440-45-1; Fe, 7439-89-6; V, 7440-62-2.

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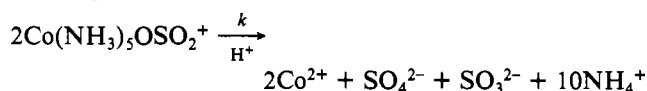
Mechanistic Information from the Effect of Pressure on the Intramolecular Electron-Transfer Reaction of O-Bonded (Sulfito)pentaamminecobalt(III) in Aqueous Solution

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Received June 1, 1982

Recent studies from this laboratory¹⁻³ have reported significant effects of pressure on some typical electron-transfer reactions involving Co(III) complexes in a nonaqueous medium. Similar results have been reported elsewhere^{4,5} for these and closely related reactions in an aqueous medium. These results exhibit interesting tendencies that could form a good basis for discriminating between various possible electron-transfer mechanisms. A detailed understanding of the effects is rather difficult at present due to lack of data on a sufficient number of representative systems. The recent addition of a high-pressure stopped-flow unit⁶ to our instrumentation has significantly expanded the range of systems that can now be studied.

In some earlier work,⁷ the kinetics and mechanism of the formation and acid-catalyzed decomposition reactions of O-bonded (sulfito)pentaamminecobalt(III) were studied in great detail. These reactions involve fast uptake and loss of SO_2 , respectively, during which no Co-O bond breakage occurs.⁸ The $Co(NH_3)_5OSO_2^+$ species undergoes a subsequent fairly rapid intramolecular redox reaction⁷ according to the overall process



for which $k = (1.4 \pm 0.3) \times 10^{-2} s^{-1}$ at 25 °C. We have now studied the pressure dependence of this reaction and found an extraordinary high positive volume of activation.

Experimental Section

$Co(NH_3)_5OSO_2^+$ was prepared in solution by treating a solution of $[Co(NH_3)_5OH_2](ClO_4)_3^{7,9}$ with $Na_2S_2O_5$ at pH ~ 6 , maintained by using a McIlvaine citric acid-phosphate buffer system.¹⁰ This

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