Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77004

Solvent-Binding and Solvation Effects on the Electrode Reactions of Tetraphenylporphyrin Carbonyl Complexes of Ruthenium(II)

K. M. KADISH* and D. CHANG

Received April 20, 1982

The electron-transfer reactions of (5,10,15,20-tetraphenylporphyrin)ruthenium(II) carbonyl, (TPP)Ru(CO), was investigated in 12 nonaqueous solvents. In 10 of these solvents the complex existed in solution as (TPP)Ru(CO)(S), where S is a solvent molecule. This complex could be reversibly oxidized to yield $[(TPP)Ru(CO)(S)]^+$ or reduced to yield $[(TPP)Ru(CO)(S)]^-$. Potentials for the former reactions were related to the Kamlet and Taft β parameter while those for the latter reactions were linearly related to the solvent acceptor number. Stability constants were calculated for addition of each solvent molecule as a sixth axial ligand to (TPP)Ru(CO) in CH_2Cl_2–0.1 M TBAP. Stability constants for formation of (TPP)Ru(CO)(S) ranged from log $\beta_1 = 1.46$ for addition of nitromethane to log $\beta_1 = 4.63$ for pyridine addition. Finally, correlations were made between the stability constants and the spectral properties of each complex.

Introduction

The first descriptions of ruthenium(II) carbonyl porphyrins appeared in the literature in 1971.[1-5] Since then a number of papers have been published that involve structural[6-12] and physical-chemical[13-15] characterization of these complexes, as well as the effect of specific extraplanar ligands on the site and potential for metalloporphyrin oxidation.[16-19]

The initial electrochemistry of (TPP)Ru(CO) oxidation was reported by Brown et al. in 1973.[16] In CH_2Cl_2, (TPP)Ru(CO) can be oxidized by two successive one-electron oxidations. The first oxidation occurs at 0.82 V and corresponds to formation of a cation radical. The product of the second oxidation at 1.21 V was not assigned in the initial study. A later electrochemical study of ((*p*-X)TPP)Ru(CO) oxidations in the same solvent, however, suggested that the second oxidation was due to formation of the Ru^{III} complex $[((p\text{-X})TPP)Ru^{III}(CO)]^{2+}$.[18]

Unlike the well-defined current-voltage curves obtained in CH_2Cl_2, no well-defined reductions of (TPP)Ru(CO) are observed in nonbonding solvents. Recently, however, Rillema et al.[18] reported a reduction in Me_2SO could be observed at −1.32 V, which corresponded to anion radical formation. No second reduction was reported. This study suggested to us the possibility of looking at the reactions in other nonaqueous solvents in order to determine the effect of solvation and solvent binding on the oxidation/reduction potentials of these ruthenium porphyrin complexes. Previous solvent effects on iron and cobalt redox reactions had shown that potentials could be shifted by up to 700 mV through simple solvent binding.[20-23] No such data, however, were available for reactions of the ruthenium complexes, and it was hoped that this might be accomplished in the present study.

Specifically, our aim in this study was to investigate the redox potentials of (TPP)Ru(CO)(S) as a function of changes in complexed solvent molecule, S, and at the same time to relate any changes in potential to changes in formation constants for the addition of the sixth axial ligand. The ligand addition reactions were carried out in CH_2Cl_2–0.1 M TBAP and are represented as shown in eq 1. Determinations of log

$$(TPP)Ru(CO) + S \rightleftarrows (TPP)Ru(CO)(S) \qquad (1)$$

β_1 for reaction 1 represent the first values ever presented for formation of a six-coordinate ruthenium carbonyl complex from the five-coordinate (TPP)Ru(CO).

Experimental Section

Chemicals. Synthesis of (TPP)Ru(CO) was according to the procedure of Rillema et al.,[18] who used a modification of the method of Tsutsui.[1,2] The visible spectrum of the final product, (TPP)Ru(CO), was consistent with the literature spectrum reported previously. The supporting electrolyte, TBAP, obtained from Eastman Chemical Co., was first recrystallized from ethyl acetate and then dried in vacuo prior to use.

Ten different nonaqueous, aprotic solvents were used as ligands in this study. CH_2Cl_2, obtained from Fisher Scientific Co. as technical grade, was twice distilled from P_2O_5 and stored in the dark over activated 4-Å molecular sieves. THF, supplied by Matheson Coleman and Bell, was distilled under N_2 from $LiAlH_4$ immediately prior to use. DMF, obtained from Eastman Chemicals, was first shaken with KOH, then distilled from CaO under N_2, and stored over 4-Å molecular sieves before use. Pyridine, purchased from Fisher Scientific Co., was treated in a similar fashion. CH_3NO_2 (Baker Chemical), C_6H_5CN (Aldrich Chemical), CH_3CN (Matheson Coleman and Bell), CH_3COCH_3 (Matheson Coleman and Bell), DMA (Fisher Scientific), and Me_2SO (Eastman Chemical) were all received as reagent grade from the manufacturer and were dried over 4-Å molecular sieves prior to use.

Instrumentation. Cyclic voltammetric measurements were made by using a three-electrode system and a Princeton Applied Research Model 174A polarographic analyzer. A platinum button served as the working electrode with a platinum wire as the counterelectrode. A saturated calomel electrode (SCE), separated from the bulk of the solution by a fritted glass disk, was used as the reference electrode.

---

(1) Tsutsui, M.; Ostfeld, D.; Francis, J. N.; Hoffman, L. M. *J. Coord. Chem.* **1971**, *1*, 115.
(2) Tsutsui, M.; Ostfeld, D.; Hoffman, L. M. *J. Am. Chem. Soc.* **1971**, *93*, 1820.
(3) Chow, B. C.; Cohen, I. A. *Bioinorg. Chem.* **1971**, *1*, 57.
(4) Faller, J. W.; Sibert, J. W. *J. Organomet. Chem.* **1971**, *31*, C5.
(5) Eaton, S. S.; Eaton, G. R.; Holm, R. H. *J. Organomet. Chem.* **1971**, *32*, C52.
(6) Cullen, D.; Meyer, E., Jr.; Srivastava, T. S.; Tsutsui, M. *J. Chem. Soc., Chem. Commun.* **1972**, 584.
(7) Bonnet, J. J.; Eaton, S. S.; Eaton, G. R.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 2141.
(8) Little, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 8583.
(9) Ball, R. G.; Domazetis, G.; Dolphin, D.; James, B. R.; Trotter, J. *Inorg. Chem.* **1981**, *20*, 1556.
(10) Hopf, F. R.; O'Brien, T. P.; Scheidt, W. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 277.
(11) Schmittou, E. R.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 516.
(12) Eaton, S. S.; Eaton, G. R.; Holm, R. H. *J. Organomet. Chem.* **1972**, *39*, 179.
(13) Faller, J. W.; Chen, C. C.; Malerich, C. J. *J. Inorg. Biochem.* **1979**, *11*, 151.
(14) Eaton, S. S.; Eaton, G. R. *Inorg. Chem.* **1977**, *16*, 1, 72.
(15) Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1975**, *97*, 235.
(16) Brown, G. M.; Hopf, F. R.; Ferguson, J. A.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 5939.
(17) Brown, G. M.; Hopf, F. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 5385.
(18) Rillema, D. P.; Nagle, J. K.; Barringer, L. F., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 56.
(19) Boshi, T.; Bontempelli, G.; Mazzocchin, G. A. *Inorg. Chim. Acta* **1979**, *37*, 155.
(20) Bottomley, L. A.; Kadish, K. M. *Inorg. Chem.* **1981**, *20*, 1348.
(21) Walker, F. A.; Kadish, K. M.; Beroiz, D. *J. Am. Chem. Soc.* **1976**, *94*, 3484.
(22) Kadish, K. M.; Morrison, M. M.; Constant, L. A.; Dickens, L.; Davis, D. G. *J. Am. Chem. Soc.* **1976**, *98*, 8387.
(23) Kadish, K. M.; Bottomley, L. A.; Kelly, S.; Schaeper, D.; Shiue, L. R. *Bioelectrochem. Bioenerg.* **1981**, *8*, 832.

0020-1669/82/1321-3614$01.25/0

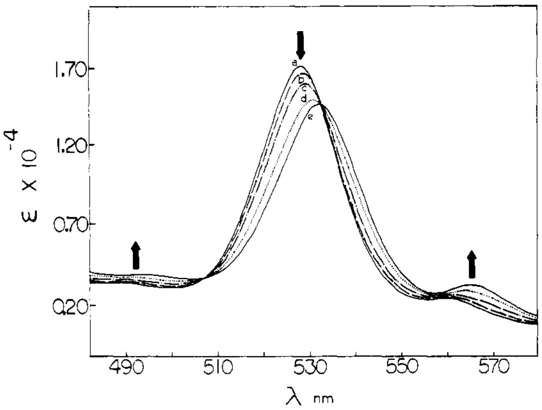


Figure 1. Spectra obtained during titration 5×10^{-5} M (TPP)Ru(CO) with pyridine in CH_2Cl_2–0.1 M TBAP. Concentration of pyridine: (a) 0; (b) 2×10^{-7} M; (c) 5×10^{-6} M; (d) 3×10^{-5} M; (e) 5×10^{-5} M.

Current–voltage curves were collected on a Houston Instruments Omnigraphic X-Y recorder at scan rates from 0.020 to 0.200 V/s. All absorption spectra were obtained at 20.0 ± 0.5 °C with a Cary Model 14 spectrophotometer using a cell of path length 1.0 cm.

Methods of Calculation. Stability constants for addition of each nitrogenous base to (TPP)Ru(CO) were calculated spectrophotometrically by the computer program SQUAD,[24] which was modified for use in nonaqueous media. The concentrations of porphyrin and TBAP were kept constant at 5×10^{-5} and 0.1 M, respectively, and the ligand concentration varied from 0 to 0.4 M. Each ligand was titrated two times. For each titration, 15 different spectra were obtained. From each spectrum, 24 absorbances were taken between 510.0 and 567.5 nm at 2.5-nm intervals. From these absorbance data and a Benesi–Hildebrand plot,[25] an initial estimate of log β_1 was obtained. Since the spectral changes observed for all complexes observed in this study were small, the precision of log β_1 values calculated from the Benesi–Hildebrand plot are believed to be very poor. Thus, these log β_1 values were taken only as approximate values to use in the SQUAD computer program for more accurate processing. Details of the program as applied to metalloporphyrins have been published elsewhere.[26,27]

Table I. Absorption Maxima (nm) and Molar Absorptivities, ε, of (TPP)Ru(CO) and (TPP)Ru(CO)(S) in Selected Solvents

		peak wavelength, nm			$10^{-5}\epsilon$			
no.	solvent, S	Soret	β	α	Soret	β	α	$\epsilon_\alpha/\epsilon_\beta$
2	CH_2Cl_2	411.0	528.0	560.0	1.490	0.170	0.024	0.141
3	CH_3NO_2	411.0	530.5	562.0	1.508	0.165	0.026	0.158
4	C_6H_5CN	411.0	531.0	563.0	1.529	0.161	0.028	0.174
5	CH_3CN	411.0	531.0	563.0	1.533	0.159	0.028	0.176
6	*n*-PrCN	411.5	531.5	563.5	1.547	0.156	0.029	0.186
7	$(CH_3)_2CO$	411.0	531.0	561.5	1.513	0.163	0.026	0.160
8	THF	411.5	532.0	565.0	1.566	0.150	0.029	0.193
9	DMF	411.5	532.0	566.0	1.586	0.147	0.030	0.204
10	DMA	412.0	532.0	566.0	1.605	0.143	0.030	0.210
11	Me_2SO	412.0	532.5	566.0	1.638	0.139	0.031	0.223
12	py	412.5	532.5	566.0	1.650	0.135	0.032	0.237

Table II. Formation Constants for Addition of Solvent as a Ligand to (TPP)Ru(CO) in CH_2Cl_2–0.1 M TBAP

no.	ligand	DN[a]	log $\beta_1{}^0$
3	CH_3NO_2	2.1	1.46 ± 0.01
4	C_6H_5CN	11.9	2.78 ± 0.01
5	CH_3CN	14.1	2.86 ± 0.01
6	*n*-PrCN	16.6	3.12 ± 0.02
7	$(CH_3)_2CO$	17.0	1.55 ± 0.02
8	THF	20.0	3.38 ± 0.02
9	DMF	26.6	3.74 ± 0.01
10	DMA	27.8	3.90 ± 0.02
11	Me_2SO	29.8	4.53 ± 0.02
12	py	33.1	4.63 ± 0.01

[a] Reference 30.

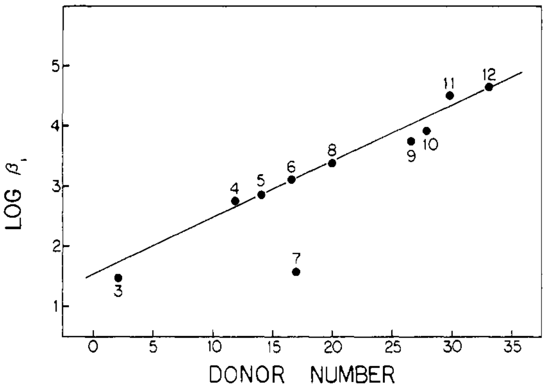


Figure 2. Plot of log β_1 for ligand addition to (TPP)Ru(CO) vs. the Gutmann donor number of the solvent. Data for this plot are found in Table II.

Results and Discussion

Ligand Addition to (TPP)Ru(CO). In the absence of a coordinating ligand, the normal (TPP)Ru(CO) absorption spectrum in CH_2Cl_2 and 0.1 M TBAP has a Soret band at $\lambda_{max} = 411$ nm, two weaker bands at $\lambda_{max} = 528$ nm and $\lambda_{max} = 560$ nm, and a shoulder at $\lambda_{max} = 490$ nm. Additions of a small amount of ligand to solutions containing 5×10^{-5} M (TPP)Ru(CO) in CH_2Cl_2–0.1 M TBAP produced red shifts in both the α and the β bands. This is shown in Figure 1 for the spectrophotometric titration of (TPP)Ru(CO) with pyridine (only the α and β bands are shown). As can be seen in this figure, the spectra began to change when only 2×10^{-7} M pyridine was added to solution (pyridine/porphyrin ratio = 0.004) and stopped changing after pyridine concentrations reached (4–5) $\times 10^{-5}$ M (pyridine/porphyrin = 0.8–1.0). Mole ratio plots were constructed of absorbance vs. the ratio (TPP)Ru(CO)/ligand and gave sharp breaks at the ratio of porphyrin to ligand of 1/1. The lack of spectral change after a 1/1 porphyrin to ligand ratio indicates that the pyridine strongly complexes with (TPP)Ru(CO) at the sixth vacant site and that a rather large stability constant can be expected. The spectrum obtained for (TPP)Ru(CO)(py) agrees with that presented in the literature. Furthermore, the presence of isosbestic points at λ = 507 and 533 nm clearly indicates the presence of only two species in solution.

Addition of nine other binding solvents to (TPP)Ru(CO) showed similar spectral changes upon complexation. The absorption maxima and molar absorptivities of these (TPP)Ru(CO)(S) complexes are listed in Table I. As seen from this table, total spectral shifts upon complexation were small, ranging from 0.5 to 6 nm depending on the ligand and the peak. The fact that both the complexed and the uncomplexed species have very similar spectra makes calculation of stability constants from spectral curves difficult. Because of this, no values of stability constants have previously been published for reaction 1 by using traditional methodologies.[25]

The calculated values of log β_1 and their standard deviations from SQUAD are summarized in Table II. Also included in this table are the Gutmann donor numbers, DN, of the solvent. Solvents with high DN such as py or Me_2SO have large binding constants while those with low DN such as CH_3NO_2 or C_6H_5CN have low binding constants. A plot of log β_1 vs. DN is shown in Figure 2. As seen from this figure, a good correlation is obtained for all solvents except $(CH_3)_2CO$.

---

(24) Leggett, D. J.; McBryde, W. A. E. *Anal. Chem.* **1975**, *47*, 1065.
(25) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2073.
(26) Leggett, D. J.; Kelly, S.; Shiue, L. R.; Wu, Y. T.; Chang, D.; Kadish, K. M., submitted for publication in *J. Chem. Educ.*
(27) Kadish, K. M.; Shiue, L. R. *Inorg. Chem.*, companion paper in this issue.

Table III. Half-Wave Potentials for the Oxidation and Reduction of (TPP)Ru(CO) in Selected Solvents Containing 0.1 M TBAP

					1st oxidn		2nd oxidn		1st redn		2nd redn	
no.	solvent	DN[a]	AN[a]	β[b]	$E_{1/2}$[c]	$E_{1/2} - E_{1/2}(\mathrm{Fc})$[d]	$E_{1/2}$[c]	$E_{1/2} - E_{1/2}(\mathrm{Fc})$[d]	$E_{1/2}$[c]	$E_{1/2} - E_{1/2}(\mathrm{Fc})$[d]	$E_{1/2}$[c]	$E_{1/2} - E_{1/2}(\mathrm{Fc})$[d]
1	$EtCl_2$	0.0	16.7	0.00	0.84	0.34	1.24	0.74	*e*		*e*	
2	CH_2Cl_2	0.0	20.4	0.00	0.85	0.37	1.26	0.77	*e*		*e*	
3	CH_3NO_2	2.7	20.5	0.38	0.81	0.47	1.18	0.83	*e*		*e*	
4	C_6H_5CN	11.9	15.5	0.41	0.89	0.44	1.29	0.84	−1.49	−1.94	*e*	
5	CH_3CN	14.1	19.3	0.31	0.86	0.46	1.21	0.81	−1.46	−1.86	*e*	
6	*n*-PrCN	16.6			0.91	0.44	1.31	0.84	−1.47	−1.93	*e*	
7	$(CH_3)_2CO$	17.0	12.5	0.48	0.95	0.45	1.25	0.75	−1.47	−1.94	*e*	
8	THF	20.0	8.0	0.55	1.10	0.57	*e*		−1.46	−1.99	*e*	
9	DMF	26.6	16.0	0.69	1.03	0.51	*e*		−1.34	−1.86	*e*	
10	DMA	27.8	13.6	0.76	1.05	0.52	*e*		−1.35	−1.89	*e*	
11	Me_2SO	29.8	19.3	0.76	0.99	0.53	*e*		−1.35	−1.81	−1.78	−2.24
12	py	33.1	14.2	0.64	1.02	0.47	*e*		−1.39	−1.93	*e*	

[a] Reference 30. [b] Reference 31. [c] Volts vs. SCE. [d] Value presented is the difference (in volts) between the oxidation or reduction of (TPP)Ru(CO) in a given solvent and the ferrocene/ferrocenium couple in the same solvent. [e] Reaction not observable within solvent range.

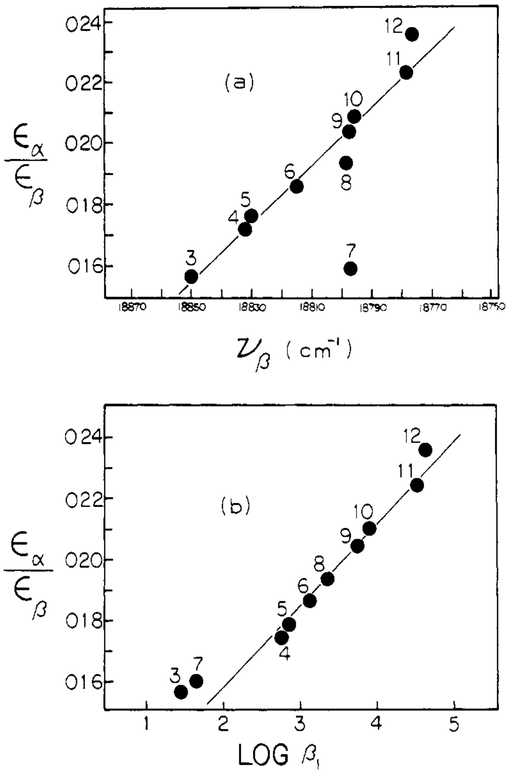


Figure 3. Plot of $\epsilon_\alpha/\epsilon_\beta$ vs. (a) the β-band frequency (ν_β) of (TPP)-Ru(CO)(L) and vs. (b) log β_1 for formation of (TPP)Ru(CO)(S) according to eq 1. The solvent numbers are identified in Table I.

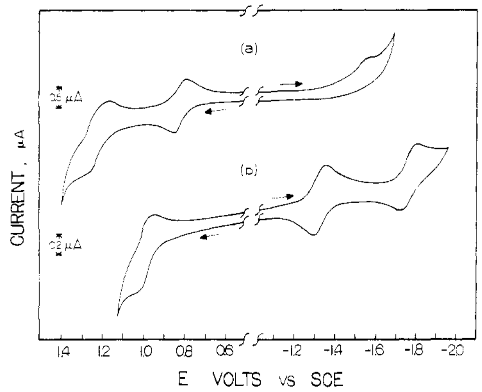


Figure 4. Cyclic voltammogram of 5 × 10^{-4} M (TPP)Ru(CO) in (a) CH_2Cl_2–0.1 M TBAP and (b) Me_2SO–0.1 M TBAP. Both were obtained at a scan rate of 0.1 V/s.

Similar deviations of $(CH_3)_2CO$ from the other solvents is seen from the spectral data in Table I. The position of the β peak position as well as the decreased ratio of the α- and β-band molar absorptivities indicates a decreased metal–ligand interaction and are consistent with a decreased value of log β_1 for complexation with this ligand. This is shown in Figure 3, which plots the ratio of $\epsilon_\alpha/\epsilon_\beta$ vs. the red shift of the β band (Figure 3a) and the same ratio vs. log β_1 for ligand addition according to reaction 1 (Figure 3b). Other correlations between ligand binding strength, spectral data, and half-wave potentials are possible. However, linearity of the plots shown in Figures 2 and 3 as well as similar linear plots of $E_{1/2}$ vs. log β_1 or $\epsilon_\alpha/\epsilon_\beta$ vs. $E_{1/2}$ clearly indicates that the same effect is observed for all complexes in this series. This effect is that ligands which donate charge to the metal also produce an increased transfer of charge to the porphyrin ring system. This increased charge affects both the spectra and the redox potentials of the metalloporphyrin. This is not a novel conclusion and has been observed for other porphyrins that are able to add one or two axial ligands to the central metal.[28,29]

Solvent Effect on the Electroreduction and Electrooxidation of (TPP)Ru(CO). Two of the problems encountered in this aspect of the study were limited solubility in several solvents and the overall limited potential range of the solvents that would enable investigation of both second oxidations and reductions. For example, in Me_2SO, two well-defined reductions of (TPP)Ru(CO)(Me_2SO) are obtained but in this same solvent the second oxidation of (TPP)Ru(CO)(Me_2SO) occurs beyond the anodic limit of the solvent. In contrast, two well-defined oxidations could be obtained in nonbonding solvents of DN <20, but a second reduction process was not observable within the cathodic potential range of these solvents.

Generally, however, the results of our solvent study showed that the best defined oxidations were obtained in nonbonding solvents such as CH_2Cl_2 while the best defined reductions could be obtained in bonding solvents such as Me_2SO or pyridine. Examples of the reduction and oxidation current–voltage curves for (TPP)Ru(CO) in Me_2SO and CH_2Cl_2 are shown in Figure 4. The ill-defined reduction in the latter solvent (Figure 4a) indicates that the process is irreversible in CH_2Cl_2. This is not true in Me_2SO, where well-defined current–voltage curves are obtained (Figure 4b). The measured potential of −1.35 V for the first reduction in Me_2SO agrees with the −1.32 V reported by Rillema et al.[18] while the second reduction at −1.78 V vs. SCE has not been previously reported.

Potentials were measured for oxidation and reduction of (TPP)Ru(CO) in $EtCl_2$ and CH_2Cl_2 and of (TPP)Ru(CO)(S)

---

(28) Gouterman, M. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, in press.

(29) Nappa, M.; Valentine, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 5075.

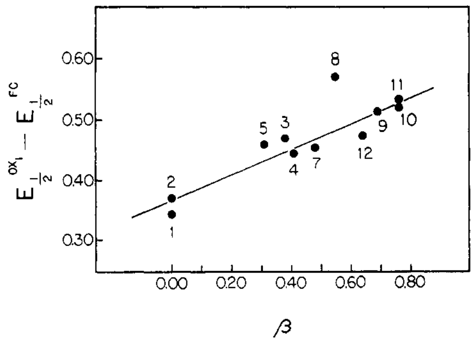


Figure 5. $E_{1/2}$ for oxidation of (TPP)Ru(CO) vs. the solvent parameter β.

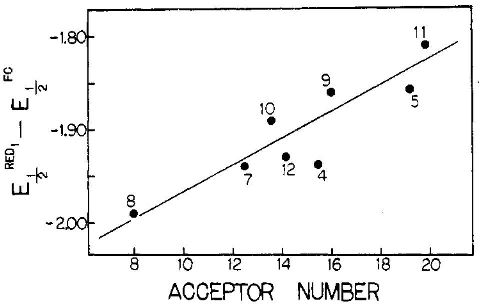


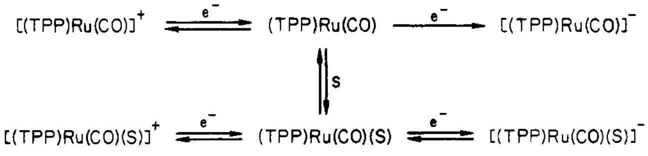
Figure 6. $E_{1/2}$ for reduction of (TPP)Ru(CO) vs. the Gutmann AN.

in 10 different bonding nonaqueous solvents. These values are listed in Table III along with the solvent donor number,[30] solvent acceptor number,[30] and β parameter of Kamlet and Taft.[31,32] Values of $E_{1/2}$ in this table have been corrected for liquid-junction potential and thus reflect the true thermodynamic potentials for the oxidation or the reduction. It is interesting to note that the first oxidation potentials roughly parallel the solvent DN while the first reductions give a good fit between $E_{1/2}$ and the AN of the solvent.

Numerous correlations have been made in the literature between half-wave potentials and DN or AN of a solvent,[30] but other scales for representing Lewis basicity of nonaqueous solvents have been developed. These include the β and π^* scale of Kamlet and Taft[31,32] and the Drago parameters E_B and C_B.[33] Recently, Kolling analyzed porphyrin electrochemical data from the literature[34] and concluded that the β and π^* scales are the more suitable choices for correlations, especially where the solvent influence on the organometallic reactants cannot be adequately represented by the bulk properties of the solvent medium.

In this study we have attempted correlations between $E_{1/2}$ and the solvent properties DN, AN, β, and π^*. For the first oxidation potential to form the π cation radical the best fit was between $E_{1/2}{}^{ox}$ and β where the correlation coefficient was 0.87 (0.95 excluding the $E_{1/2}$ in THF, which was significantly off the plot). This is shown in Figure 5. The parameter β quantifies the solvent's ability to donate an electron pair (accept a proton) and is directly related to the Gutmann DN.[31] Plots of $E_{1/2}{}^{ox}$ vs. DN gave a correlation coefficient of 0.74, which improved to 0.81 when THF was again deleted from the data. On the other hand, for the first reduction to form the π anion radical, $E_{1/2}{}^{red}$ vs. β gave a correlation coefficient

Scheme I



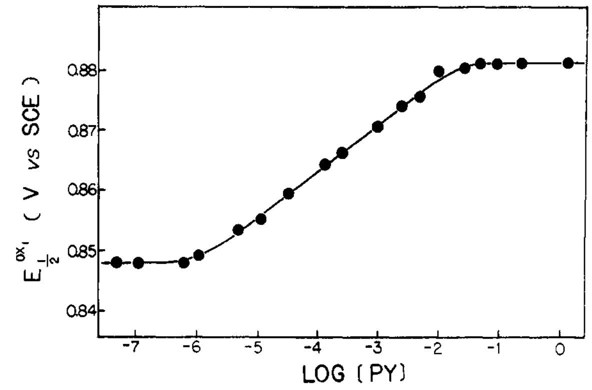


Figure 7. Half-wave potentials for oxidation of (TPP)Ru(CO) in CH_2Cl_2–0.1 M TBAP, monitored as a function of added pyridine. The ionic strength remained constant at 0.1 during the titration.

of only 0.37. For this reaction, the best fit was between $E_{1/2}{}^{ox}$ and AN (correlation coefficient 0.88). This plot is shown in Figure 6.

The recommended[34] use of π^* gave a correlation coefficient of only 0.65. Clearly, the potentials do not give an excellent fit to a single parameter, and a combination of parameters might be needed. This is discussed in detail not only for the reactions of ruthenium porphyrins but for the radical- and metal-centered reactions of porphyrin complexes containing the transition metals, Cr, Mn, Fe, and Co, as well as for porphyrin complexes of Zn, Cd, Hg, and Mg.[35]

The important piece of data from Table III is that not a great deal of variation occurs in the redox potential as a function of solvent. In the absence of information on binding constants for solvent molecules this might seem to imply a lack of solvent interaction with the Ru(II) center. Clearly, this is not the case. Because the values of log β_1 for addition of solvent to the neutral complex according to eq 1 are large (Table II) and $E_{1/2}$ shifts little with solvent (Table III), one can only conclude that similar large binding constants exist for $[(TPP)Ru(CO)(L)]^-$, [(TPP)Ru(CO)(L)], and $[(TPP)Ru(CO)(L)]^+$. This has been shown to be the case for complexes of $[(TPP)Zn(L)]^-$ and $[(TPP)Zn(L)]^+$, which differ little from those of the neutral complex with an uncharged porphyrin ring.[36]

For the specific case of the complexes examined in this study the electrode reactions involving the first oxidation and the first reduction can then be represented as shown in Scheme I.

In the absence of a sixth axial ligand the reduction of (TPP)Ru(CO) is irreversible but the oxidation gives well-defined current–voltage curves. This corresponds to the top pathway in the scheme. In contrast, addition of a sixth axial ligand to yield (TPP)Ru(CO)(S) gives rise to well-defined current–voltage curves for both the oxidation and reduction, and electron transfer is via the lower pathway in the scheme. The shift of potential from 0.37 V (vs. Fc^+/Fc) in CH_2Cl_2 to 0.47 V (vs. Fc^+/Fc) in neat pyridine reflects the greater relative stability of (TPP)Ru(CO)(py) over [(TPP)Ru-

---

(30) Gutmann, V., "The Donor-Acceptor Approach to Molecular Interactions"; Plenum Press: New York, 1978.

(31) Taft, R. W.; Pienta, N. J.; Kamlet, M. J.; Arnett, E. M. *J. Org. Chem.* **1981**, *46*, 661.

(32) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1980**, *13*, 485.

(33) Drago, R. S.; Kroeger, M. K.; Stahlbush, J. R. *Inorg. Chem.* **1981**, *20*, 306.

(34) Kolling, O. *Anal. Chem.* **1982**, *54*, 260.

(35) Kelly, S.; Shiue, L. R.; Malinski, T.; Chang, D.; Kadish, K., manuscript in preparation.

(36) Kadish, K. M.; Shiue, L. R.; Rhodes, R. K.; Bottomley, L. A. *Inorg. Chem.* **1981**, *20*, 1274.

$[(TPP)Ru(CO)(py)]^+$ as compared to (TPP)Ru(CO) over $[(TPP)Ru(CO)]^+$.

It should be noted, however, that the 100-mV difference in potential refers to differences between neat solvents and that addition of smaller quantities of pyridine to CH_2Cl_2 or $EtCl_2$ (which forms (TPP)Ru(CO)(py)) produced only slight shifts of potential from those of the five-coordinate species. This is shown clearly in Figure 7, which illustrates half-wave potentials monitored during the titration of (TPP)Ru(CO) with py in CH_2Cl_2–0.1 M TBAP.

There is no significance to the slope $\Delta E_{1/2}/\Delta \log (\mathrm{py})$ between log [py] = –6 and –2, and this only indicates a transition region upon pyridine binding. The flat region above 10^{-2} M py, however, indicates that py is not lost upon oxidation of (TPP)Ru(CO)(py). If a loss of ligand occurred in this region, a predicted 60 mV/log [L] slope would be obtained. The 30-mV difference in potentials between (TPP)Ru(CO) and (TPP)Ru(CO)(py) half-wave potentials reflects the almost identical stability constants of (TPP)Ru(CO)(py) and $[(TPP)Ru(CO)(py)]^+$. In fact, calculation of log β_1 for the addition of py to $[(TPP)Ru(CO)]^+$ using the data in this figure and equations derived in previous publications[36,37] leads to a value of log $\beta_1^+ = 4.10$ for reaction 2.[38] This value may be

$$[(TPP)Ru(CO)]^+ + py \rightleftarrows [(TPP)Ru(CO)(py)]^+ \quad (2)$$

compared to a log $\beta_1 = 4.63$ for addition of pyridine to the neutral complex according to eq 1.[38]

In summary, we have shown that solvent molecules will strongly bind to (TPP)Ru(CO) at the single vacant axial position to form (TPP)Ru(CO)(S) and that, upon oxidation or reduction of this species, a six-coordinate anion or cation radical of Ru(II) may be produced. We have also measured the first stability constants for ligand addition to (TPP)Ru(CO) and shown that the magnitude of this constant is directly related to the Gutmann donor number of the solvent. Finally, we have measured, for the first time, a formation constant for addition of a donor ligand to $[(TPP)Ru(CO)]^+$. This aspect of the study is most important in attempting to "tune" redox potentials of these types of systems, where it is possible to convert between a metal-centered and a ring-centered oxidation as a function of the bound axial ligand. This will be the subject of a future communication.

Acknowledgment. The support of the National Science Foundation (Grant CHE-7921536) is gratefully acknowledged. We also wish to acknowledge the help of Professor D. J. Leggett in analyzing the spectral data via SQUAD.

Registry No. (TPP)Ru(CO), 32073-84-0; (TPP)Ru(CO)(CH_3NO_2), 82614-53-7; (TPP)Ru(CO)(C_6H_5CN), 82614-54-8; (TPP)Ru(CO)(CH_3CN), 82621-16-7; (TPP)Ru(CO)(*n*-PrCN), 82614-55-9; (TPP)Ru(CO)($(CH_3)_2CO$), 82614-56-0; (TPP)Ru(CO)(THF), 82614-57-1; (TPP)Ru(CO)(DMF), 82614-58-2; (TPP)Ru(CO)(DMA), 82614-59-3; (TPP)Ru(CO)(Me_2SO), 82621-20-3; (TPP)Ru(CO)(py), 41751-82-0; $(TPP)Ru(CO)(CH_3NO_2)^+$, 82614-60-6; $(TPP)Ru(CO)(C_6H_5CN)^+$, 82614-61-7; $(TPP)Ru(CO)(CH_3CN)^+$, 82614-62-8; $(TPP)Ru(CO)(n\text{-}PrCN)^+$, 82614-63-9; $(TPP)Ru(CO)((CH_3)_2CO)^+$, 82614-64-0; $(TPP)Ru(CO)(THF)^+$, 82614-65-1; $(TPP)Ru(CO)(DMF)^+$, 82614-66-2; $(TPP)Ru(CO)(DMA)^+$, 82614-67-3; $(TPP)Ru(CO)(Me_2SO)^+$, 82614-68-4; $(TPP)Ru(CO)(py)^+$, 43070-17-3; $(TPP)Ru(CO)(C_6H_5CN)^-$, 82614-69-5; $(TPP)Ru(CO)(CH_3CN)^-$, 82614-70-8; $(TPP)Ru(CO)(n\text{-}PrCN)^-$, 82614-71-9; $(TPP)Ru(CO)((CH_3)_2CO)^-$, 82614-72-0; $(TPP)Ru(CO)(THF)^-$, 82614-73-1; $(TPP)Ru(CO)(DMF)^-$, 82614-74-2; $(TPP)Ru(CO)(DMA)^-$, 82614-75-3; $(TPP)Ru(CO)(Me_2SO)^-$, 82614-76-4; $(TPP)Ru(CO)(py)^-$, 82621-21-4.

---

[37] Kadish, K. M.; Bottomley, L. A. *Inorg. Chem.* **1980**, *19*, 832.

[38] Kadish, K. M.; Leggett, D. J.; Chang, D. *Inorg. Chem.*, companion paper in this issue.

Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77004

Investigation of the Electrochemical Reactivity and Axial Ligand Binding Reactions of Tetraphenylporphyrin Carbonyl Complexes of Ruthenium(II)

K. M. KADISH,* D. J. LEGGETT, and D. CHANG

Received March 5, 1982

Stability constants for nitrogenous base addition to (TPP)Ru(CO) and $[(TPP)Ru(CO)]^+$ were calculated. Spectrophotometric methods were utilized for stability constant determinations of the five-coordinate neutral complex while a combination of spectrophotometric and electrochemical techniques was utilized to calculate values for ligand addition to the cation radical. Twenty different nitrogenous bases were investigated. For (TPP)Ru(CO)(L) values of log β_1 ranged from 3.62 to 5.63 and generally increased as a function of the ligand pK_a. Values of log β_1 for formation of $[(TPP)Ru(CO)(L)]^+$ ranged from 2.40 to 6.63 and also increased with the ligand pK_a. Comparisons were made between the measured values of log β_1 and reversible potentials for the electrode reaction $(TPP)Ru(CO)(L) \rightleftarrows [(TPP)Ru(CO)(L)]^+$.

Introduction

The electrochemical oxidation of ruthenium(II) porphyrins such as (P)Ru(CO), (P)Ru(CO)(L), and $(P)Ru(L)_2$ has been reported in nonaqueous media where P = OEP^{2-}, $Etio^{2-}$, and TPP^{2-} and L = py, CH_3CN, and THF.[1,2] When CO is one of the extraplanar ligands, the initial site of oxidation is at the conjugated porphyrin ring, yielding a π cation radical. In contrast, when ruthenium(II) is decarbonylated, the site of initial oxidation is at the central metal ion, yielding the corresponding Ru(III) complex.[1,2] The difference in potentials between these two reactions is approximately 600 mV with the decarbonylated complex being the most easily oxidized. For example, $(TPP)Ru(py)_2$ is oxidized to $[(TPP)Ru^{III}(py)_2]^+$ at 0.21 V in CH_2Cl_2 while $[(TPP)Ru^{II}(CO)(py)]^+$ is produced from (TPP)Ru(CO)(py) at 0.81 V in the same solvent. Both the carbonyl and non-carbonyl complexes undergo a second oxidation at potentials greater than 1.1 V, with the product of $[(TPP)Ru^{II}(CO)(py)]^+$ oxidations being assigned as abstraction from the metal center.[3]

This example of how axially coordinated ligands can change not only the half-wave potentials but also the site of porphyrin oxidation is remarkable and is clearly related to the stabilizing

---

[1] Brown, G. M.; Hopf, F. R.; Ferguson, J. A.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 5939.

[2] Brown, G. M.; Hopf, F. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 5385.

[3] Rillema, D. P.; Nagle, J. K.; Barringer, L. F., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 56.

0020-1669/82/1321-3618$01.25/0