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The Reaction of Ruthenium(II) Octaethylporphyrin and Ruthenium(II) Tetraphenylporphyrin Complexes with Carbon Monoxide

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Abstract

The reactions of $Ru^{II}OEP(L)_2$ and $Ru^{II}TPP(L)_2$ with carbon monoxide, where OEP and TPP are the dianions of octaethylporphyrin and tetraphenylporphyrin, respectively, are reported for various ligands (L = dimethyl formamide, acetonitrile, aniline and substituted benzonitriles). The first-order rate constants for the loss of XC_6H_4CN from Ru^{II} OEP(XC_6H_4CN)$_2$ increase with increasing electron-withdrawing ability of X. The best Hammett σ/ρ correlation is obtained when both σ^+ and σ^- values are employed. It is concluded that sigma donation from ligand-to-metal is the major mode of bonding in ruthenium–porphyrin–benzonitrile complexes.

Introduction

The reactions of iron porphyrins with carbon monoxide and dioxygen have been studied in great detail as model systems for the binding of these small molecules to heme proteins [1, 2]. These studies have provided great strides in our understanding of heme proteins [3]. The reaction of ruthenium porphyrins with small molecules has also received considerable attention [4]. Ruthenium-substituted heme proteins have also been prepared [5–8]. We have reported our initial studies on the reaction of ruthenium myoglobin with carbon monoxide and dioxygen [8] The results are complicated by the apparent presence of isomeric proteins differing only in their axial ligation at ruthenium. The present study was undertaken in order to learn more about the mechanistic aspects of ligand exchange chemistry in ruthenium porphyrins.

Ruthenium porphyrins are generally thought to undergo ligand exchange reactions by a dissociative mechanism [4, 9]. We chose to study the following two-step reaction:

$$Ru^{II}Por(L)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru^{II}Por(L) + L \qquad (1)$$

$$Ru^{II}Por(L) + X \xrightarrow[X = CO,\, O_2]{k_x} Ru^{II}Por(X)L \qquad (2)$$

where Por = dianion of octaethylporphyrin (OEP) or dianion of tetraphenylporphyrin (TPP), L = dimethyl formamide (DMF), acetonitrile (CH_3CN), tetrahydrofuran (THF), aniline and substituted benzonitriles (XC_6H_4CN).

Results and Discussion

The ruthenium(II) bis-liganded species were formed by photolysis of $Ru^{II}Por(CO)EtOH$ [10] as approximately 10^{-6} M solutions in neat L, dimethyl acetamide/L mixtures, or toluene/L mixtures. The reactions with CO were followed by monitoring the formation of the prominent peak occurring between 540 and 550 nm in the CO-bound product. In the case of O_2 addition, the change in the Soret band at around 400 nm was followed. In each case, clean isobestic points were obtained (see Fig. 1 for example). The reactions were carried out under one atmosphere of CO or O_2 where the concentration of CO or O_2 in solution is 100–1000 times greater than the porphyrin concentration [11]. The k_{-CO} step can be ignored since the CO-bound complexes were stable in solution for several days *in vacuo*. Under these pseudo-first-order conditions, the rate law for the appearance of the CO-bound product reduces to the following:

$$d\,[Ru^{II}Por(CO)L]/dt = k_{obs}[Ru^{II}Por(CO)L] \qquad (3)$$

We used eqn. (3) to evaluate various solvent systems and ligands for further study. When the solvent was DMF, we found it difficult to obtain reproducible data. This is due to a ruthenium porphyrin catalyzed decarbonylation of DMF which produces dimethylamine and carbon monoxide. The CO generated reverses the photolysis reaction and the dimethylamine binds to the ruthenium causing non-first-order behavior. This ruthenium porphyrin catalyzed de-

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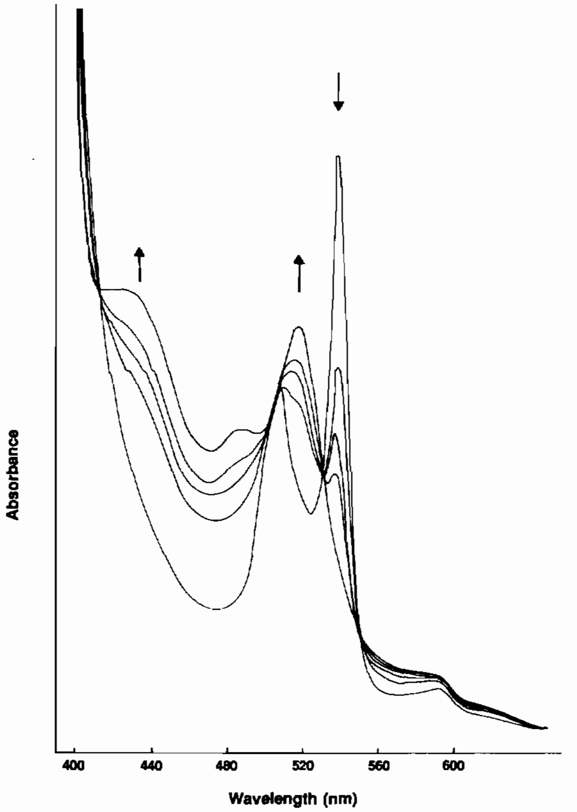


Fig. 1. Photolysis *in vacuo* of 10^{-6} M $Ru^{II}OEP(CO)(EtOH)$ and 0.02 M C_6H_5CN in DMA using sixteen 3600 Å bulbs in a Rayonet Photochemical Reactor. Each trace represents 3–5 s of irradiation time.

carbonylation has been reported to be an efficient method to decarbonylate aldehydes [12] and thus it is not surprising that it occurs, albeit less efficiently, with DMF. Nevertheless, we were able to obtain some data with DMF as both the solvent and the ligand:

Porphyrin	CO/O_2	Temperature (°)	K_{obs} (min^{-1})
$Ru^{II}OEP(DMF)_2$	CO	0 °	0.178 ± 0.015
$Ru^{II}OEP(DMF)_2$	CO	25 °	0.440 ± 0.025
$Ru^{II}OEP(DMF)_2$	O_2	0 °	0.164 ± 0.020

These data demonstrate that with $Ru^{II}OEP(DMF)_2$ at 0 ℃ the addition of both CO and O_2 proceeds by the dissociative mechanism shown in eqns. (1) and (2) and the rate-determining step in each case is the loss of DMF. We could not obtain reproducible data with O_2 addition at 25 ℃. This is probably due to outer-sphere electron transfer competing with the dissociative mechanism [13]. When imidazole, 1-methylimidazole or 2-methylimidazole were used as ligands in DMF, the $Ru^{II}OEP(Im)_2$ species reacted rapidly with O_2 to give a Ru(III) species, but $Ru^{II}OEP(Im)_2$ would not react with CO over long periods of time. Thus, in the case of $Ru^{II}OEP(Im)_2$, reaction with O_2 occurs via an outer-sphere electron transfer reaction to give initially $Ru^{III}OEP(Im)_2$.

When THF is used as both solvent and ligand, the k_{obs} rate constants for $Ru^{II}OEP(THF)_2$ at 20 ℃ are 0.075 min^{-1} ± 0.012 in the case of O_2 addition and 0.085 min^{-1} ± 0.010 in the case of CO addition. This indicates again that CO and O_2 addition both occur via a dissociative mechanism and that in each case the loss of THF is rate-determining. In THF the outer-sphere electron transfer reaction does not occur with oxygen, indicating that this reaction with DMF and imidazole probably occurs through the axial ligands and not through the porphyrin ring.

With acetonitrile as both ligand and solvent, the reaction rates are 50 to 100 times slower than with DMF or THF, indicating that nitriles bind much more strongly to $Ru^{II}OEP$. The activation energy for CO addition to $Ru^{II}OEP(CH_3CN)_2$ was calculated from rate measurements at 36 ℃ (0.0288 min^{-1}), 40 ℃ (0.0415 min^{-1}) and 45 ℃ (0.0650 min^{-1}) to be 17.25 kcal/mol. $Ru^{II}OEP(CH_3CN)_2$ reacts slower than $Ru^{II}TPP(CH_3CN)_2$. For example, the TPP species gives a k_{obs} value for CO addition at 25 ℃ of 0.0332 min^{-1} ± 0.0012, while the OEP species gives a k_{obs} value at 36 ℃ of 0.0288 min^{-1} ± 0.0010. Although these rate differences are small, they are in the opposite direction from that expected. The porphyrin core of OEP is considerably more basic than that of TPP [14]. We would expect that increasing the basicity of the porphyrin nitrogens would lead to increased rates of ligand exchange as observed by Eaton and Eaton [15] for t-butylpyridine exchange in $Ru^{II}OEP$ and $Ru^{II}TPP$ complexes. Stynes *et al.* [16] also observed lower activation enthalpies for the loss of t-butylpyridine from $Ru^{II}OEP(CO)$(t-bupy) than from $Ru^{II}TPP(CO)$(t-bupy). Our results could indicate that back-bonding from metal to ligand is important; however, our data from benzonitrile studies show that back-bonding is not important (*vide infra*) in benzonitrole and thus we would not expect it to be important with acetonitrile. Again, the k_{obs} values for CO addition are identical, within experimental error, to the values for O_2 addition. Thus, outer-sphere electron transfer to oxygen does not occur with acetonitrile as the ligand either.

We have found that dimethylacetamide (DMA) does not readily undergo the decarbonylation observed with DMF and it does not bind very strongly to ruthenium porphyrins. It is thus an ideal solvent for ligand-binding studies. Assuming the mechanism shown in eqns. (1) and (2), a large excess of CO over $Ru^{II}Por(L)_2$ and steady-state kinetics for $Ru^{II}Por(L)$, the following equations can be derived:

$$k_{obs} = k_1 k_{CO}[CO]/(k_{-1}[L] + k_{CO}[CO])$$

$$1/k_{obs} = k_{-1}[L]/\{k_1 k_{CO}[CO]\} + 1/k_1$$

Thus, a plot of $1/k_{obs}$ *vs.* [L] gives a straight line with an intercept equal to $1/k_1$. In this manner we have measured k_1 for a series of substituted benzonitriles. The benzonitrile concentrations were adjusted so that only the $Ru^{II}OEP(XC_6H_4CN)_2$ species was present. The results are shown in Table I. The rate constant for the loss of substituted benzonitrile increases as the substituent becomes more electron withdrawing, while the weakly electron donating *p*-methyl slightly decreases the off-rate. The strongly donating *p*-methoxy does not follow this pattern, which probably indicates a change in mechanism for this strongly donating substituent [17]. Thus, we have not included the *p*-methoxy rate constant in the treatment of the data which follows.

Hammett σ/ρ plots were obtained using the k_1 values in order to determine the electronic substituent effects. The use of σ gives a correlation coefficient (R) of 0.96 while σ^+ gives $R = 0.97$ and σ^- gives $R = 0.98$. However, we obtain the best fit ($R = 0.99$) when both σ^+ (*p*-methyl and *p*-chloro) and σ^- (*p*-acetyl) values are used. This plot is shown in Fig. 2. The plot gives a rho value of +0.64, indicating that the loss of benzonitrile is facilitated by electron-withdrawing groups. This result is consistent with σ-donation from ligand to metal as the dominant bonding mode for benzonitrile-substituted ruthenium octaethylporphyrin. As electron donation from the phenyl ring to the nitrogen increases, the nitrogen–ruthenium bond becomes stronger and the k_1 value decreases. Metal-to-ligand π-back-bonding does not appear to be important with benzonitroles. If back-bonding were important, electron-withdrawing groups would enhance the ligand bonding resulting in non-linear σ/ρ plots. Vuik *et al.* [18] also observed that ligand exchange kinetics in ruthenium porphyrins are less sensitive to the π-acidity of the axial ligands than might have been expected.

TABLE I. Rate Constants (min^{-1}) for the reaction of Ru(II)-$OEPL_2$ with Carbon Monoxide in Dimethylacetamide at 25 °C[a,b]

L	k_{obs} (conc.)	k_1
Benzonitrile	0.144 (0.05 M) 0.071 (0.10 M) 0.045 (0.20 M)	0.352
p-Tolunitrile	0.156 (0.05 M) 0.112 (0.10 M) 0.073 (0.20 M)	0.249
p-Methoxybenzonitrile	0.255 (0.05 M) 0.156 (0.10 M) 0.083 (0.20 M)	0.907
m-Methoxybenzonitrile	0.198 (0.05 M) 0.115 (0.10 M) 0.067 (0.20 M)	0.516
p-Chlorobenzonitrile	0.292 (0.05 M) 0.112 (0.10 M) 0.088 (0.20 M)	0.455
p-Acetylbenzonitrile	0.466 (0.05 M) 0.304 (0.10 M) 0.163 (0.20 M)	1.370

[a] The variation in separate runs is ±5% or less. [b] The $Ru^{II}OEP(L)_2$ concentration is 10^{-6} M.

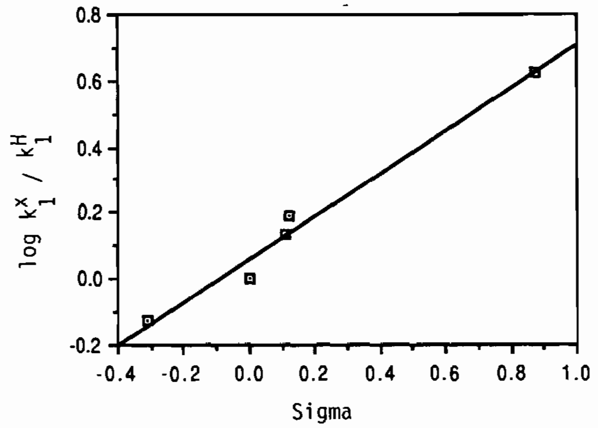
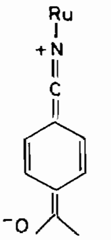


Fig. 2. Hammett σ/ρ plot of k_1 values for $Ru^{II}OEP(XC_6H_4CN)_2$ using σ^+ for *p*-methyl and *p*-chloro, σ for *m*-methoxy and σ^- for *p*-acetyl; $\rho = +0.63$; $R = 0.99$.

The correlation of reaction rates with both σ^+ and σ^- is very unusual as most Hammett plots either correlate with σ^+ or σ^- but not both. A number of Hammett σ/ρ plots involving reactions of ruthenium porphyrins have appeared. For example, Kadish *et al.* [19] and others have correlated electrochemical oxidation and reduction potentials for RuTPP with either σ or σ^+ values, while Rillema *et al.* [20] have correlated CO addition to RuTPP with σ. However, none of these studies used strongly electron-withdrawing groups which would have σ^- values. The correlation with both σ^+ and σ^- can be explained in terms of resonance structures **A** and **B**. Resonance structure **A** will weaken the ligand–metal bond (hence σ^- correlation) while resonance structure **B** will strengthen the ligand–metal bond (hence σ^+ correlation).



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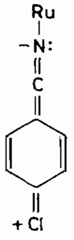

B

A number of reports have appeared dealing with ligand exchange in ruthenium porphyrins. Rillema *et al.* [20] have reported a negative rho value for the second-order addition of CO to Ru^{II}(X-TPP)-

$(DMF)_2$. Electron-withdrawing groups on the phenyl rings decrease the basicity of the porphyrin nitrogens. This strengthens the ruthenium–DMF bonding resulting in a slower rate of CO addition. Eaton and Eaton [15] also observed a negative rho value for 4-t-butylpyridine exchange in Ru^{II}(X-TPP)(CO)(t-butylpyr). Again, the electron-withdrawing groups on the phenyl rings decrease the basicity of the porphyrin nitrogens which strengthens the pyridine-to-ruthenium bond causing slower exchange. Our results are consistent with these studies in that electron-withdrawing groups on the ligand weaken the metal–ligand bond and thus increase the ligand off-rate.

We have also studied CO addition to $Ru^{II}OEP(XC_6H_4NH_2)_2$ in DMF where the value of k_1 for aniline is 0.70 min^{-1} ± 0.05 at 25 °C. This is twice as large as the k_1 value found for benzonitrile; however, DMA was used as solvent for the benzonitrile studies. We were not able to obtain reproducible data for substituted anilines at concentrations greater than 0.02 M and thus we could not determine k_1 for these compounds. However, k_{obs} for substituted anilines (0.02 M) increases as the substituent on the phenyl ring becomes more electron-withdrawing. This parallels the results obtained with substituted benzonitriles.

The solvent dependence of these ligand off-rates was briefly studied by comparing the reaction of CO with $Ru^{II}OEP(C_6H_5CN)_2$ in both DMA and toluene. In DMA $k_1 = 0.352$ min^{-1} while in toluene $k_1 = 0.470$ min^{-1}. The solvent effect is relatively small although loss of benzonitrile does occur slightly faster in the less polar solvent.

Experimental

DMA and DMF were stirred over BaO and distilled from $CuSO_4$ at reduced pressure prior to use. Acetonitrile, THF and toluene were purified by distillation from CaH_2. Aniline was dried over CaH_2 and distilled at reduced pressure prior to use. The substituted benzonitriles were purified by distillation or recrystillization.

Ru^{II}OEP(CO)(EtOH) and Ru^{II}TPP(CO)(EtOH) were prepared by refluxing equal weight mixtures of the porphyrin and $(Ru)_3(CO)_{12}$ in toluene [15.] The $Ru^{II}Por(L)_2$ solutions were prepared by photolysis of degased solutions (10^{-6} M) of Ru^{II}Por(CO)(EtOH) in the appropriate solvent system using a Rayonet Photochemical reactor equipped with sixteen 3600 Å bulbs. The kinetic runs were initiated by bubbling CO into a thermostated reaction cell for 30 s followed by monitoring the change in absorbance with time. The data were analyzed in terms of the first-order rate law: $\ln 1/n = kt$ where $n = (A_\infty - A_{obs})/(A_\infty - A_0)$; A_0 = initial absorbance, A_∞ = final absorbance and A_{obs} = absorbance at any time t. These ln plots were linear over at least three half-lives. The variation in separate runs was usually ±5% or less.

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