

Inter-Metal Nitrogen Atom Transfer Reactions between Nitridochromium(V) and Chromium(III) Porphyrins

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Reactions of nitridochromium(V) porphyrins with chromium(III) porphyrins resulted in reversible, inter-metal nitrogen atom transfer between the two chromium porphyrin complexes. The progress of these reactions was followed spectrophotometrically. Kinetic analysis of the spectral data obtained over time for a variety of substituted porphyrins showed the reactions to be first order in each of the reactants and second order overall. Equilibrium constants were computed from the spectral data and ranged from 0.56 to 2.1 for the reactions between nitridochromium(V) octaethylporphyrin and a series of chlorochromium(III) tetraphenylporphyrins possessing phenyl ring substituents. Forward rate constants were determined for this reaction series and ranged from 6.8 to 1420 M⁻¹ s⁻¹. Electron-withdrawing substituents enhanced the forward rates but diminished the equilibrium constants. It is proposed that the reactions proceed by nucleophilic attack of the nitridochromium porphyrin donor on the cationic chromium(III) porphyrin nitrogen atom acceptor facilitating a net, two-electron redox process mediated by a homobimetallic μ -nitrido intermediate.

Introduction

Atom transfer reactions involve the net transfer of an atom and one or more electrons from a donor molecule to an acceptor.¹ Over the past two decades, metal-centered oxygen atom transfer reactions have been intensively studied and a consistent mechanistic picture has emerged.² Few examples of complete inter-metal oxygen atom transfer have been published.³ In most instances, such transfer is not complete; *i.e.*, the atom is shared by both the donor metal and the acceptor group. Holm has described complexes of this type as examples of partial atom transfer.¹

Complete inter-metal nitrogen atom transfer has also been documented.^{4–13} Partial and complete atom transfer products have been observed for metalloporphyrin-based nitrogen atom donor–acceptor pairs. In this paper, we demonstrate that nitridochromium(V) porphyrins engage in reversible, inter-metal nitrogen atom transfer with chromium(III) porphyrin substrates. We present an analysis of the kinetics and mechanism of this reaction.

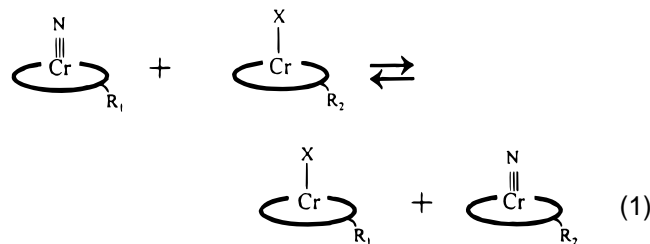
Experimental Section

H₂OEP was purchased from Aldrich Chemical Co.¹⁴ Substituted chlorochromium(III) tetraphenylporphyrins were prepared by Adler's method.^{15,16} Nitridochromium(V) porphyrins were prepared from the corresponding chlorochromium(III) porphyrins according to the pro-

cedure Buchler¹⁷ used in preparing NCr(OEP). The purity of each complex was verified by electronic and mass spectral measurements. Spectral measurements were obtained using the equipment and procedures previously described.¹⁸

Results and Discussion

The nitrogen atom transfer reaction between NCr(POR₁) and ClCr(POR₂) was monitored spectrophotometrically. Figure 1A depicts the spectra acquired with time for the reaction of 19.6 μ M NCr(OEP) and 20 μ M ClCr(TPP) in benzene. The characteristic absorption bands^{17,19} of NCr(OEP) and ClCr(TPP) decreased in intensity with the concomitant increase in the characteristic absorption bands of NCr(TPP) and ClCr(OEP). Isosbestic points were observed at 415, 446, and 470 nm. The reaction does not proceed to completion as previously observed^{6,12} for the reaction between NMn(POR) and XCr(POR). An equilibrium mixture of reactants and products is obtained within several hours:



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- (14) Abbreviations used: monovalent anion = X⁻; 1,2-dichloroethane = DCE; porphyrin dianion = POR; *meso*-tetraphenylporphyrinato dianion = TPP; substituted *meso*-tetraphenylporphyrinato dianion = T-R-PP; octaethylporphyrinato dianion = OEP.
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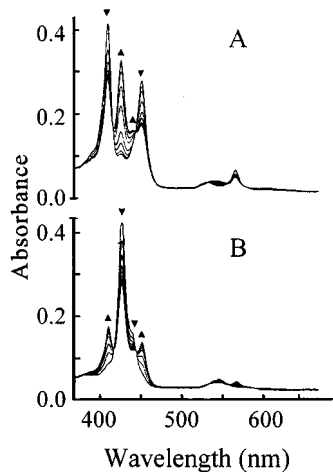


Figure 1. Electronic spectra acquired as a function of time of the reaction of (A) 19.6 μM NCr(OEP) and 20.0 μM ClCr(TPP) and (B) 24.2 μM ClCr(OEP) and 22.3 μM NCr(TPP).

The chemical reversibility of the nitrogen atom transfer was verified by reaction of NCr(TPP) with ClCr(OEP). Figure 1B illustrates the spectra acquired with time for the reaction of 22.3 μM NCr(TPP) and 24.2 μM ClCr(OEP) in benzene. The final spectrum was comparable to that obtained for the forward reaction after correction of the absorbance data for the difference in initial reactant concentrations.

Reactant and product concentrations were calculated by solving four simultaneous equations at the absorbance maximum for the Soret band of each major component in solution. Analysis of the concentration data as a function of time indicated that the data were best fit by a second-order rate law. The value of the forward rate constant for the bimolecular reaction was calculated using King's equations.²⁰ Identical rate constants were obtained when the analysis was carried out for each species involved in the reaction. The rate constants reported are the mean values from at least three separate experiments plus or minus the standard deviation of replicate determinations. The equilibrium constant for the reaction of NCr(OEP) with ClCr(TPP) was determined to be 1.4 ± 0.2 whereas the equilibrium constant for the reaction of NCr(TPP) with ClCr(OEP) was determined to be 0.56 ± 0.08 . These values are, within experimental error, inversely related. The values of the forward and backward rate constants for the reactions of NCr(OEP) with ClCr(TPP) were computed to be $94 \pm 9 \text{ M}^{-1} \text{ s}^{-1}$ and $76 \pm 8 \text{ M}^{-1} \text{ s}^{-1}$, respectively.

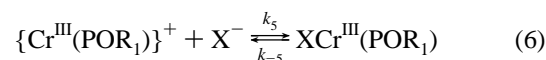
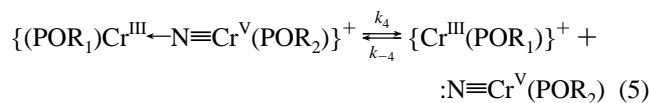
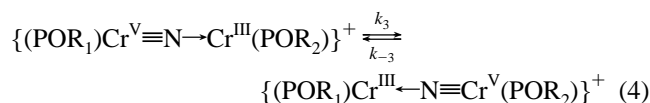
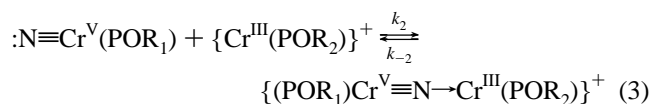
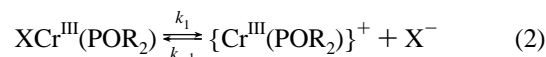
The magnitude of the forward rate constant depended upon the identity of the solvent. For example, when the reaction of NCr(OEP) with ClCr(TPP) was carried out in DCE, k_f was determined to be $440 \pm 40 \text{ M}^{-1} \text{ s}^{-1}$. This value is 4 times greater than the value measured in benzene. However, K_{eq} was 1.1 ± 1 , comparable to that determined in benzene. The increase in k_f without change in K_{eq} demands that the backward rate constant increase proportionately. The values of both k_f and K_{eq} were significantly diminished in the presence of donor solvents. For example, in the presence of a 2-fold excess of pyridine, no reaction between NCr(OEP) and ClCr(TPP) or between NCr(TPP) and ClCr(OEP) was observed. Under these conditions, six-coordinate chromium(III) porphyrin complexes are formed.²¹

The identity of the anion bound to the chromium(III) porphyrin nitrogen atom acceptor had a marked effect on k_f .

The reaction of NCr(OEP) with (SCN)Cr(TPP) in benzene proceeded with a k_f of $230 \pm 21 \text{ M}^{-1} \text{ s}^{-1}$. In contrast, the reaction of NCr(OEP) with FCr(TPP) occurred very slowly; *i.e.*, equilibrium was not established after 24 h. This trend parallels the trend observed for the nitrogen atom transfer between NMn-(POR) and XCr(POR) in that the forward rate constant decreases with increasing anion field strength.^{6,12} Interestingly, the equilibrium distribution did not significantly vary with counterion identity. For example, K_{eq} for the reaction NCr(OEP) and XCr(TPP) was 1.4 ± 0.2 when $X = \text{Cl}^-$ and 1.4 ± 0.2 when $X = \text{SCN}^-$.

The rate of the reaction between NCr(OEP) with ClCr(TPP) was very dependent upon the concentration of added chloride (in the form of $n\text{-Bu}_4\text{NCl}$). No appreciable reactivity was observed over a 24 h period when the $[n\text{-Bu}_4\text{NCl}]/[\text{ClCr(TPP)}]$ ratio exceeded 2. Kelly and Kadish²² have published conductivity data which infer that the extent of ionization of chromium(III) porphyrins differs markedly with anion ligand field strength. Their evidence indicates that $\sim 40\%$ of $(\text{ClO}_4)\text{Cr(TPP)}$ is ion-paired in CH_2Cl_2 or DCE compared to only 2% for ClCr(TPP). This fact and the marked dependence of the rate of reaction between NCr(OEP) and ClCr(TPP) on added $n\text{-Bu}_4\text{NCl}$ suggest that the dissociated, four-coordinate $\{\text{Cr(TPP)}\}^+$ is the nitrogen atom acceptor. The dependence of the reaction rate on both solvent and anion identity provides additional support for this hypothesis. Ionization of the coordinately and covalently bound anion should be favored in solvents of higher dielectric constant, since this property measures the inherent ability of the solvent to separate charges. The forward rate constant observed in DCE ($\epsilon = 10.35$) was 4 times greater than that observed in benzene ($\epsilon = 2.27$). Similarly, weakly bound anions should make better leaving groups and promote the formation of the cationic nitrogen atom acceptor.

On the basis of these observations, we propose the following mechanism for nitrogen atom transfer from nitridochromium(V) porphyrins to chromium(III) porphyrins:



The first step is formation of the nitrogen atom acceptor by conversion of the coordinate-covalent $(\text{POR}_1)\text{Cr}^{\text{III}}\text{-Cl}$ complex to the ion-paired cationic chromium(III) porphyrin. The second step involves nucleophilic attack by the nitride on the cationic chromium(III) porphyrin, producing a positively charged homobimetallic μ -nitrido intermediate. The cationic μ -nitrido intermediate then undergoes an intramolecular, bridging nitrogen atom mediated, two-electron transfer and dissociates to form

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NCr(POR₂) and {Cr(POR₁)}⁺. The latter species is in equilibrium with its corresponding coordinate–covalent complex (POR₁)Cr^{III}–Cl.

We have been unable to detect the cationic μ -nitrido intermediate spectrally or electrochemically and thus conclude that it is present only in low concentration. However, there is substantial evidence in support of this proposed species. First, the presence of a competing axial ligand, *e.g.* pyridine, prohibited nitrogen atom transfer. Nitrogenous bases readily bind to the chromium(III) center, forming either X(L)Cr(POR) or {(L)₂Cr(POR)}⁺X[–], but do not bind to the vacant axial position of NCr(POR).^{16,23} Second, the reaction rate is dramatically reduced when *n*-Bu₄NCl is added. If one assumes that the second step is rate determining and applies the steady-state approximation, the following kinetic expression for the observed forward rate constant can be derived:

$$k_f = \frac{k_1 k_2}{k_{-1} [X]} \quad (7)$$

The observed decrease in rate in the presence of added chloride is consistent with this expression and provides credibility to the assumptions. Third, no reaction was observed when NCr(OEP) was treated with ClCr(T-2,4,6-(MeO)₃-PP) in either benzene or DCE. Porphyrins possessing substituents at the 2,6-positions of the phenyl rings have been shown to inhibit formation of μ -oxo²⁴ and μ -nitrido²⁵ iron porphyrin complexes. Thus, unreactivity of ClCr(T-2,4,6-(MeO)₃-PP) suggests the existence of a binuclear intermediate. Fourth, a cationic heterobimetallic μ -nitrido complex formed by reaction of NRe(POR) with ClCr(POR) has been characterized and provides precedent for the proposed dinuclear intermediate.¹¹ This mechanism is consistent with those proposed for all known intermetal, two-electron nitrogen, oxygen, and halide atom transfer reactions.¹⁰

Additional support for this mechanism arises from an investigation of the impact of phenyl ring substituents on the values of k_f and K_{eq} . The reaction between NCr(OEP) and a series of ClCr(T-4-R-PP) complexes was studied in benzene. The values of K_{eq} and k_f were determined and are given in Table 1. A linear relationship was found between $\log(K_{eq})$ and the Hammett–Taft substituent constant σ_p , suggesting a uniform mechanism throughout the series of nitrogen atom acceptors. A ρ value of -0.20 was determined; this value indicates that

Table 1. Equilibrium and Forward Rate Constants for the Reaction of NCr(OEP) with ClCr(*p*-R-TPP) in Benzene

donor	acceptor	K_{eq}	k_f (M ⁻¹ s ⁻¹)
NCr(OEP)	ClCr(T-4-PhCH ₂ O-PP)	2.1 ± 0.2	6.8 ± 0.6
	ClCr(T-4-MeO-PP)	1.6 ± 0.2	16 ± 2
	ClCr(T-4-Me-PP)	1.5 ± 0.2	60 ± 6
	ClCr(TPP)	1.4 ± 0.2	94 ± 9
	ClCr(T-4-F-PP)	0.70 ± 0.10	120 ± 12
	ClCr(T-4-Cl-PP)	0.50 ± 0.06	470 ± 50
NCr(TPP)	ClCr(T-4-F ₃ C-PP)	0.37 ± 0.04	1420 ± 100
	ClCr(OEP)	0.56 ± 0.08	76 ± 8

electron-donating substituents on the chromium(III) acceptor shift the equilibrium to the right. Similarly, a linear relationship between $\log(k_{f,R}/k_{f,H})$ and σ_p was also observed. A ρ value of $+0.72$ indicates that the rate of reaction is enhanced by electron-withdrawing substituents on the chromium(III) acceptor. The latter trend demonstrates that the reaction rate is significantly enhanced by increasing the electrophilic character of the acceptor and is consistent with the notion of nucleophilic attack. The trend in k_f with phenyl ring substituent compares with the trend observed for the reaction of NMn(POR) donors with substituted chromium(III) porphyrin acceptors. The trend observed for K_{eq} with phenyl ring substituent may seem inconsistent with the trend observed for k_f . However, since K_{eq} is the ratio of the forward and backward rate constants, the trend in K_{eq} reflects the difference in the effect of phenyl ring substituent on k_f relative to k_b . For example, the values of k_f and k_b for the reaction between NCr(OEP) and ClCr(T-4-PhCH₂O-PP) were 6.8 ± 0.6 and 3.2 ± 0.6, respectively. In comparison, the corresponding values of k_f and k_b for the reaction between NCr(OEP) and ClCr(T-4-F₃C-PP) were 1420 ± 100 and 3840 ± 100, respectively. Note that the forward rate constant for the reaction of NCr(OEP) with ClCr(T-4-F₃C-PP) was 210 times greater than that for the reaction with ClCr(T-4-PhCH₂O-PP) whereas the backward rate constant was 1200 times greater. Thus, electron-withdrawing groups on the porphyrin phenyl rings enhanced the rate of both the forward and the backward reactions. However, the effect of the substituent on the rate of the backward reaction was about 6 times that on the rate of the forward reaction. We suggest that the trend in k_b reflects the relative affinity of the chromium(III) center for formation of a coordinate–covalent bond with anionic axial ligands. Present efforts involve exploration of the scope of this reaction with other metallomacrocyclic nitrogen atom donor–acceptor pairs.

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