Quenching of Triplet State Tetrakis(μ-pyrophosphito-PP′)diplatinate(II) by Nickel(II) Macrocyclic and Tris-diimine Complexes

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The excited state of tetrakis(μ-pyrophosphito-PP′)diplatinate(II), $Pt_2(pop)_4^{4-}$, has been shown to be reductively quenched by a series of Ni(II) complexes. Steady-state photolysis of $Pt_2(pop)_4^{4-}$ in the presence of $Ni(cyclam)^{2+}$ and SO_4^{2-} ions was followed by absorption spectroscopy and showed the production of the Ni(III) complex with low efficiency. The Ni(III) yield was enhanced in the presence of oxygen presumably because of scavenging of $Pt_2(pop)_4^{5-}$ from the solvent-caged {Pt₂(II,I)....Ni(III)} primary product pair resulting from electron transfer. Cage escape yields of 0.028 in N_2 saturated solution and 0.054 in aerated solutions were estimated from the data. For a series of complexes with decreasing redox potential, the rate constants for their $^3Pt_2(pop)_4^{4-}$ phosphorescence lifetime quenching decreased with driving force ΔG, consistent with Rehm−Weller behavior and leading to a reorganization energy of $\sim$60 kJ mol^{-1}. The diffusional rate constant calculated from the Debye−Smoluchowski equation was 1.6×10^{10} M^{-1} s^{-1}, in excellent agreement with the observed value of 1.6×10^{10} M^{-1} s^{-1} based on the Rehm−Weller equation. The transmission factor for the electron transfer was estimated at 10^{-4}, in the weakly adiabatic region. Although the Rehm−Weller treatment has been used successfully in reactions involving mainly uncharged organic reactants, in this investigation it leads to an unrealistic ratio for the rate constants for the diffusive separation of the charged reactants and products. An alternative interpretation of the results based on an approach by Meyer and Nagle removes this problem and the observed linear dependence of ln k_q on the square root of $E°$ (Ni(II)/Ni(III)) in the endergonic region shows that the dominant back electron transfer produces ground-state species. The analysis also leads to an estimate of the $^3Pt_2(pop)_4^{4-}/Pt_2(pop)_4^{5-}$ potential of 1.29 ± 0.05 V(vs NHE), in excellent agreement with the previous literature value of 1.34 V.

Introduction

The well-known diplatinum(II) complex $K_4Pt_2(\mu\text{-}P_2O_5H_2)_4$, more commonly referred to as “platinum pop” or $Pt_2(pop)_4^{4-}$, has become an important tool used by the inorganic photochemist. Since its discovery,[1] the unique photochemical and photophysical properties of this complex have made it very useful in the study of both oxidative[2] and reductive[3,4] photoinduced electron-transfer reactions as well as in the study[5] of excited-state atom transfer processes. Recent studies[6] have looked at the salt effects and specific cation effects in the quenching of $^3Pt_2(pop)_4^{4-}$ by a series of acidopentacyanocobalt(III) complexes and found evidence for both oxidative electron transfer and atom transfer mechanisms.

Until now, all of the examples of bimolecular reductive quenching of the excited state of $Pt_2(pop)_4^{4-}$ have been limited to reactions with organic amines, reduction being confirmed by direct spectral evidence.[4] An important example is the work of Nagle et al.[3] in which quenching by aromatic amines in methanol was used to determine a value of 1.34 V for the $^3Pt_2(pop)_4^{4-}/Pt_2(pop)_4^{5-}$ excited-state redox potential. Since a series of Ni(II) macrobicyclic complexes and tris-diimine complexes of Ni(II) spans a wide range of redox potentials on either side of this value, it was considered that they would interact with the excited state of $Pt_2(pop)_4^{4-}$ to provide the first example of reductive quenching of $^3Pt_2(pop)_4^{4-}$ in aqueous medium and by transition metal coordination complexes. We expected that such stable Ni(II) complexes would reductively quench the $Pt_2(pop)_4^{4-}$ excited state and that the macrocyclic or tris-diimine ligands would stabilize the Ni(III) quenching product long enough for it to be observed by conventional spectroscopic techniques. From the quenching behavior over the series of related Ni(II) complexes both the kinetic and thermodynamic aspects of the quenching process could be investigated. We report our findings here.

Experimental Section

Preparation of Ni(II) Complexes. The chelating ligands 1,10-phenanthroline (phen), 5-methyl-1,10-phenanthroline (5-Me-phen), 4,4′-dimethyl-1,10-phenanthroline (4,4′-Me_2-phen), 5-chloro-1,10-phenanthroline (5-Cl-phen), 5-nitro-1,10-phenanthroline (5-NO_2-phen), and 2,2′-dipyridyl (bipy), were obtained from the Aldrich Chemical Co.

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Table 1. Electrochemical Data and Rate Constants for the Quenching of $^3Pt(pop)_4^{4-}$ by Ni(II) Complexes: Quenching Conditions: $\mu = 0.01$ M, $T = 22 \pm 1$ °C

Ni(II) quencher	$E°$, V (vs NHE)	ref for $E°$	ΔG, eV	k_q, $M^{-1}\,s^{-1}$	$k_{q'}$, $M^{-1}\,s^{-1}$ [a]
$Ni(cyclam\text{-}diene\text{-}Me_2)^{2+}$	0.55	29	−0.97	$(1.48 \pm 0.03) \times 10^{10}$	$(3.70 \pm 0.05) \times 10^{11}$
$Ni(cyclam)^{2+}$	0.98	30	−0.54	$(1.41 \pm 0.03) \times 10^{10}$	$(1.66 \pm 0.05) \times 10^{11}$
$Ni(bicycloN_5)^{2+}$	1.03	31	−0.49	$(1.32 \pm 0.03) \times 10^{10}$	$(9.21 \pm 0.05) \times 10^{10}$
$Ni(bicycloN_4O)^{2+}$	1.17	32	−0.35	$(1.50 \pm 0.03) \times 10^{10}$	$(5.66 \pm 0.05) \times 10^{10}$
$Ni(Bz\text{-}bicycloN_5)^{2+}$	1.18	this work	−0.34	$(1.23 \pm 0.03) \times 10^{10}$	$(6.10 \pm 0.05) \times 10^{10}$
$Ni(TIM)^{2+}$	1.31	29	−0.21	$(1.07 \pm 0.02) \times 10^{10}$	$(3.50 \pm 0.04) \times 10^{10}$
$Ni(4,4'\text{-}Me_2\text{-}bipy)_3^{2+}$	1.51	7	−0.01	$(2.95 \pm 0.07) \times 10^{9}$	$(3.65 \pm 0.08) \times 10^{9}$
$Ni(phen)_3^{2+}$	1.64	7	0.12	$(1.48 \pm 0.04) \times 10^{9}$	$(1.63 \pm 0.06) \times 10^{9}$
$Ni(5\text{-}Cl\text{-}phen)_3^{2+}$	1.75	7	0.23	$(1.05 \pm 0.03) \times 10^{9}$	$(1.12 \pm 0.08) \times 10^{9}$
$Ni(5\text{-}NO_2\text{-}phen)_3^{2+}$	1.82	7	0.30	$(5.89 \pm 0.10) \times 10^{8}$	$(6.11 \pm 0.11) \times 10^{8}$

[a] Quenching rate constant corrected for diffusion.

The tris-diimine nickel(II) complex of each of these ligands was prepared in the following manner: 3.5 equivalents of the appropriate ligand (0.5 g) was dissolved in 10 mL of methanol and added to 1 equiv of $Ni(ClO_4)_2 \cdot 6H_2O$, also dissolved in 10 mL of methanol. The solution was stirred for 10 min at room temperature after which time the resulting precipitate was filtered off, washed with methanol followed by diethyl ether, and dried under vacuum. All yields were greater than 95%. These complexes were characterized by recording their UV−vis spectra in CH_3CN and comparing them to literature spectra.[7]

The macrobicyclic complexes $[Ni(bicycloN_4O)(ClO_4)]ClO_4$[8] ($bicycloN_4O$ = 17-oxa-1,5,8,12-tetraazabicyclo[10.5.2]nonadecane) and $[Ni(bicycloN_5)(ClO_4)]ClO_4$[9] ($bicycloN_5$ = 1,5,8,12,17-pentaazabicyclo-[10.5.2]nonadecane) were prepared as described previously. The ligands X-$bicycloN_5$ (=1-X-1,4,8,11,15-pentaazabicyclo[10.5.2]nonadecane) (X = formyl, benzyl, methyl) were prepared via the monoprotected 1,4,7-triazacyclononane,[10] and extrapolation of the ligands to the corresponding bicyclo systems was achieved by use of the copper(II) template synthesis outlined previously.[8] Details of the preparations will be provided elsewhere.[11]

The $K_4[Pt_2(\mu\text{-}P_2O_5)_4] \cdot 2H_2O$ was prepared as described[12] except that all stages of the preparation, purification, drying, and storage of the final product were carried out under nitrogen atmosphere to minimize oxidation**.**

Quenching of the Triplet State of $^3Pt_2(pop)_4^{4-}$. A fresh solution of $Pt_2(pop)_4^{4-}$ was prepared by dissolving in 0.01 M $HClO_4$ sufficient complex to give an absorbance of about 1 in a 1 cm path at 370 nm (about 2×10^{-5} M). This solution was purged with nitrogen until the lifetime reached a constant upper limit, τ^0. This varied in the range 7.0−9.5 μs depending on the age of the sample and the solution composition. The quencher, also dissolved in 0.01 M $HClO_4$, was delivered into the $Pt_2(pop)_4^{4-}$ solution in 7−12 aliquots, 5−20 μL in volume, and each lifetime was determined at 22 ± 1 °C using an average value of five measurements. Excitation was with a 20 ns pulse using a nitrogen laser exciting a solution of quinine sulfate to shift the irradiation to 370 nm as described in the literature.[6] The quenching rate constants, k_q, for the quenching reaction of $^3Pt_2(pop)_4^{4-}$ with each of the nickel complexes were obtained from the slopes of Stern−Volmer plots of τ^0/τ versus quencher concentration.

Steady-State Analysis. Solution mixtures containing 1×10^{-4} M $[Ni(cyclam)](ClO_4)_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) and $\sim 3 \times 10^{-5}$ M $K_4[Pt_2(pop)_4]$ in 0.1 M Na_2SO_4 were irradiated with 365 nm light from an HBO 100 W mercury lamp with a Corning CS7-60 filter and monochromator, and 5 cm of water as an infrared absorber. The lamp intensity was determined by ferrioxalate actinometry (typically 2×10^{-8} einstein s^{-1}). Degassed solutions were irradiated with nitrogen bubbling in 1 cm rectangular glass spectrophotometer cells held in a thermostated cell compartment at 22.0 ± 0.1 °C. UV/vis spectra were run on a Cary 5 UV−vis spectrophotometer. Spectroscopic data were transferred to a Macintosh IIci for evaluation using Igor Pro 3.0 (Wavemetrics) in order to determine difference spectra resulting from steady-state photolysis.

Flash Photolysis. Nanosecond flash photolysis was carried out using a Spectra Physics Quanta-Ray GCR-11 Nd:YAG laser (355 nm). Solutions containing enough $Pt_2(pop)_4^{4-}$ to give an absorbance of 0.6−0.8 at 370 nm and 1×10^{-4} M in $[Ni(cyclam)](ClO_4)_2$ quencher were made up in 1×10^{-3} M $HClO_4$ and irradiated in 7.0 by 7.0 mm I.D. Suprasil quartz cells. Nitrogen was bubbled through the solutions, except during the measurement period. Transient absorption measurements were obtained with right angle geometry using an Oriel/Osram 150 W Xe lamp, and a Digichrom 240 computer-controlled monochromator. Detection was by a Hamamatsu R928 photomultiplier and Tektronix 520A digital oscilloscope. The system is controlled by a Mac IIsi computer program written using Labview 3.0.

Results

Stern−Volmer Quenching of $^3Pt_2(pop)_4^{4-}$ by Ni(II) Complexes. In a thoroughly degassed solution, and in the absence of any quencher, the lifetime of a fresh solution of a fresh sample of $Pt_2(pop)_4^{4-}$ was found to be about 9 μs, which is in good agreement with literature.[13−15] The addition to 3.0 mL of $Pt_2(pop)_4^{4-}$ solution of several successive 5−20 μL aliquots of Ni(II)-complex ($\sim 1 \times 10^{-3}$ M in 0.01 M $HClO_4$) was found to cause a steady decrease in the measured lifetime. Stern−Volmer analysis of the lifetime data gave linear plots which provided values for the second-order rate constants, k_q, for the quenching of the excited state of $Pt_2(pop)_4^{4-}$ by each of the ten Ni(II) complexes. The rate constants were found to be in the range 10^{10} to 10^8 $M^{-1}\,s^{-1}$, and are tabulated in Table 1 along with electrochemical data for the compounds. The bimolecular rate constant k_q decreased with increasing redox potential $E°$ of the Ni(II) complex in a manner that provides strong evidence for a reductive electron-transfer quenching mechanism.

UV−Vis Analysis/Reductive Electron-Transfer Mechanism. To identify the quenching products and establish the mechanism of the quenching reaction, changes in the UV−vis absorption spectrum were monitored under conditions of constant irradiation. Sulfate stabilizes Ni(III) species through complex formation,[16] and it was thought that its addition in these experiments would stabilize the Ni(III) quenching product long enough for it to be observed. *Note that sulfate was added only*

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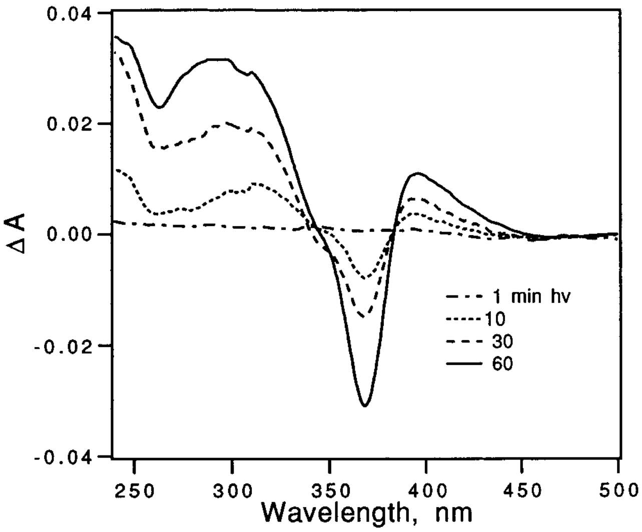

Figure 1. Absorbance changes during steady irradiation of $Pt_2(pop)_4^{4-}$ with $Ni(cyclam)^{2+}$ in 0.1 M sodium sulfate/0.010 M perchloric acid solution with nitrogen stirring. Irradiation wavelength 370 nm.

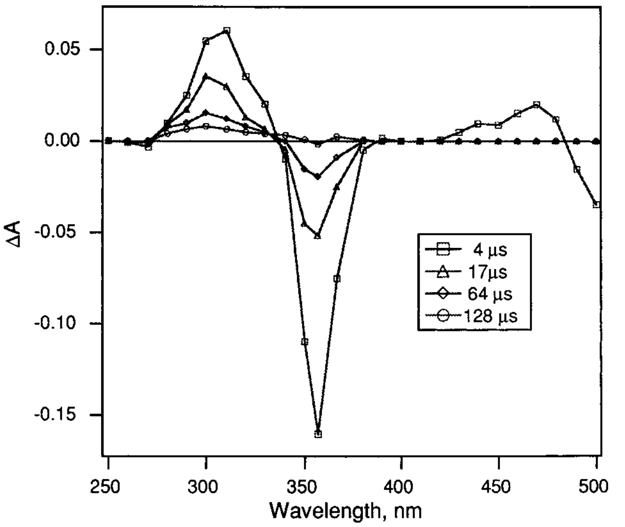

Figure 2. Transient absorption spectra for a solution of $Pt_2(pop)_4^{4-}$ with $Ni(cyclam)^{2+}$ in 0.1 M sodium sulfate/0.010 M perchloric acid solution (deaerated). Excitation; 30 mJ at 355 nm.

in these experiments and was absent in all the quenching studies. A thoroughly deaerated aqueous solution containing $[Ni(cyclam)](ClO_4)_2$ ($\sim 1 \times 10^{-4}$ M) and $Pt_2(pop)_4^{4-}$ ($A_{370} \sim 1$, 1×10^{-5} M) in 0.01 M $HClO_4$ and 0.1 M Na_2SO_4 was irradiated at $\lambda = 370$ nm for varying lengths of time. After each time interval, the UV–vis spectrum was immediately recorded. Figure 1 shows the result for photolysis of a nitrogen degassed solution. It is seen that the permanent bleaching of the $Pt_2(pop)_4^{4-}$ absorption band at 370 nm corresponded with the growth of a new band at 295 nm. The electronic spectra for $Ni(cyclam)(SO_4)^+$ in acetonitrile, obtained from literature,[17] shows two bands, one at 370 nm ($\epsilon = 6000\ M^{-1}\ cm^{-1}$) and the other at 295 nm ($\epsilon = 11\,000\ M^{-1}\ cm^{-1}$). Therefore, the band observed to develop at 295 nm was assigned to the formation of the quenching product $Ni(cyclam)SO_4^+$. This supports the conclusion that the quenching mechanism involves reductive quenching of the excited state of $Pt_2(pop)_4^{4-}$ by $Ni(cyclam)^{2+}$.

The reactant Ni(II) complex is shown in eq 1 as an ion pair,

$$Ni(cyclam)^{2+}\cdots SO_4^{2-} + {}^3Pt_2(pop)_4^{4-} \rightarrow Ni(cyclam)SO_4^{+} + Pt_2(pop)_4^{5-} \quad (1)$$

but there is literature evidence[18] for equilibria involving square planar and octahedral complexes in this system. This complexity may be one of the reasons why we did not find a good quantitative relationship between the loss of the platinum dimer and the Ni(III) complex produced. When the identical quenching reaction between ${}^3Pt_2(pop)_4^{4-}$ and $Ni(cyclam)^{2+}$ was carried out in oxygenated solutions, the change in absorbance at 295 nm (ΔA_{295}) was enhanced. The value of ΔA_{295} after 60 min of irradiation was found to be 0.032 in deareated solution versus 0.055 in the aerated solution. This indicates that there is nearly a 2-fold increase in the yield of the $Ni(cyclam)SO_4^+$ quenching product when oxygen is present in the solution. One likely explanation for this result is that the residual oxygen scavenges the reduced product, $Pt_2(pop)_4^{5-}$, thus preventing it from reacting in a back electron transfer step to re-form $Ni(cyclam)^{2+}\cdots SO_4^{2-}$ and increasing the yield of the Ni(III) quenching product which is able to escape from the solvent-caged species. Assuming that no bulk recombination occurs, the quantum yield of product formation $\Phi_{product}$ can be expressed as

$$\Phi_{product} = \Phi_{isc}\, \eta_q\, \eta_{ce} \quad (2)$$

where is Φ_{isc} the intersystem crossing quantum yield, η_q is the quenching efficiency, and η_{ce} is the cage escape efficiency. For the reaction of $Pt_2(pop)_4^{4-}$ ($\sim 1 \times 10^{-5}$ M) and $Ni(cyclam)^{2+}\cdots SO_4^{2-}$ ($\sim 1 \times 10^{-4}$ M), $\Phi_{product}$ was determined to be 2.8×10^{-4} in deaerated solution (0.01 M $HClO_4$) and 5.3×10^{-4} in aerated solution. According to the literature,[19] the main $Pt_2(pop)_4^{4-}$ absorption is ${}^1A_{1g} \rightarrow {}^1A_{2u}$ followed by intersystem crossing to the corresponding triplet state ${}^3A_{2u}$ with a yield approaching unity, i.e., $\Phi_{isc} = 1.0$. The cage escape efficiency η_{ce} may therefore be calculated using the relationship

$$\eta_{ce} = \frac{\Phi_{product}}{\Phi_{isc}\eta_q} = \Phi_{product}\left(\frac{1 + k_q\tau^0[Q]}{k_q\tau^0[Q]}\right) \quad (3)$$

The cage escape efficiency η_{ce} was calculated to be 0.028 in the absence of oxygen, and 0.054 in the presence of oxygen. A cage escape efficiency of less than 1.0 can be attributed to the competing processes of back electron transfer between the caged primary products, with or without quenching to the ground state. The low cage escape efficiencies found for this reaction are undoubtedly a reflection of efficient back electron transfer within the $\{Pt_2(II/I)\cdots Ni(III)\}$ caged species.

Flash Photolysis Study. Laser flash photolysis with transient absorption detection was used in attempts to provide further details about the net chemical reaction. The transient absorption changes shown in Figure 2 were observed after a 30 mJ, 355 nm laser flash excitation of $Pt_2(pop)_4^{4-}$ containing sufficient $Ni(cyclam)^{2+}$ to quench the emission lifetime by about 30% ($\sim 4 \times 10^{-5}$ M) in 0.1 M Na_2SO_4 and 0.010 M $HClO_4$ degassed aqueous media. Immediately after the laser flash, a decrease in the ground-state concentration of $Pt_2(pop)_4^{4-}$ resulted in bleaching of the absorbance at 370 nm and the appearance of two peaks at 325 and 460 nm. These absorbances can be assigned[14] to the ${}^3Pt_2(pop)_4^{4-}$ ${}^3A_{2u}$ triplet excited state. After 17 μs, ΔA at 460 nm had returned to zero indicating that the triplet ${}^3Pt_2(pop)_4^{4-}$ complex has disappeared. On this time scale there

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remains a transient absorbance signal with an absorbance maximum at 310 nm. This absorbance has been assigned to the oxidized platinum species $Pt_2(pop)_4^{3-}$.[14] Absorbance changes due to the expected quenching products $Ni(cyclam)SO_4^+$ (λ = 295, 370 nm) and $Pt_2(pop)_4^{5-}$ (λ = 420 nm) were not detected under these conditions. The formation of the oxidized species $Pt_2(pop)_4^{3-}$ is consistent with a report[20] that $Pt_2(pop)_4^{4-}$ readily undergoes photoionization leading to the formation of $Pt_2(pop)_4^{3-}$ and solvated electrons (e^-_{solv}). At a pulse energy of 30 mJ, photoionization is clearly the dominant process. Under the acidic conditions used, e^-_{aq} would rapidly produce hydrogen atom (H) which, like e^-_{aq}, is also a strong reductant.

The interference caused by the photoionization of $Pt_2(pop)_4^{4-}$ is a major difficulty in these flash photolysis experiments. There are two possible ways to alleviate this problem. The better option would be to change the excitation wavelength from 355 nm to a region, for example 385 nm, where $^3Pt_2(pop)_4^{4-}$ does not absorb as strongly, but unfortunately this was not an option with the equipment available. The other option is to reduce the pulse energy used. By monitoring the ratio of $^3Pt_2(pop)_4^{4-}$ to $Pt_2(pop)_4^{3-}$ formation as a function of laser pulse energy, it was determined that a laser pulse energy of <2 mJ would have to be used to minimize problems arising from the photoionization of $Pt_2(pop)_4.^{4-}$ Unfortunately with a pulse energy this low, transient absorption experiments were not practical owing to the low molar absorptivities of the products $Ni(cyclam)(SO_4)^+$ and $Pt_2(pop)_4^{5-}$.

Discussion

Reductive Electron-Transfer Quenching of $^3Pt_2(pop)_4^{4-}$. Determination of quenching mechanisms can be difficult when energy transfer processes and electron transfer are both energetically possible. In this study we were fortunate in obtaining direct chemical evidence for the net photoredox products expected for reductive electron-transfer quenching of $^3Pt_2(pop)_4^{4-}$. In addition there is, see Table 1, a clear relationship between the magnitude of the Ni(II)/Ni(III) redox potential and the quenching rate constant that is strongly indicative of reductive electron transfer quenching. Unfortunately our efforts to directly observe the primary products of this electron transfer in flash photolysis experiments were defeated by the intense excited-state absorption and consequent photoionization of $Pt_2(pop)_4^{4-}$. Nevertheless, the reductive electron-transfer mechanism is further supported by an analysis of the data using the traditional Rehm−Weller approach.

Rehm−Weller Behavior. For this system, the steps involved in the bimolecular reductive quenching of the excited state of $Pt_2(pop)_4^{4-}$ (D) by the Ni(II) complexes (Q) can be summarized as

$$D^* + Q \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} \{D^*.....Q\} \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} \{D^-.....Q^+\} \underset{k'_d}{\overset{k'_{-d}}{\rightleftharpoons}} D^- + Q^+ \quad (4)$$

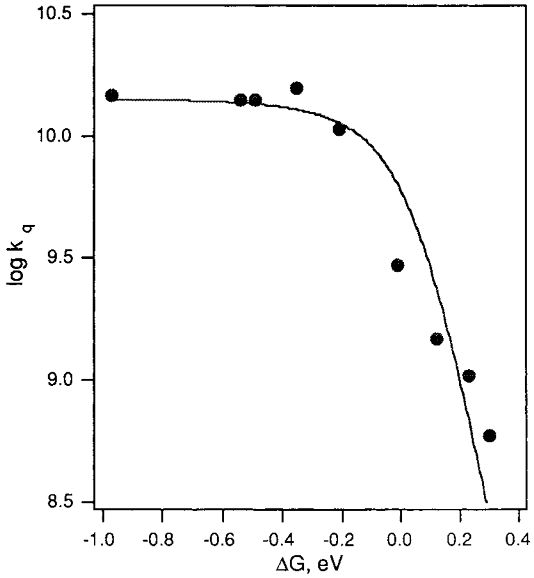

Figure 3. Rehm−Weller behavior. Plot of log k_q vs driving force ΔG.

Here k_d, k'_d, k_{-d}, and k'_{-d} are the rate constants for diffusion and dissociation of the precursor and successor complex, and k_e and k_{-e} are the rate constants for the forward and back electron-transfer steps within the encounter complex. A kinetic analysis of this scheme leads to the familiar expression

$$k_q = \frac{k_d}{1 + \dfrac{k_{-d}}{k_e^\circ e^{-\Delta G^\ddagger/RT}} + \dfrac{k_{-d}}{k'_{-d}} e^{\Delta G/RT}} \quad (5)$$

which relates the observed quenching rate constant k_q to the activation barrier ($\Delta G^\ddagger$) and the free energy change (ΔG) of the reaction. The frequency factor $k_e^\circ = \kappa k T/h$, where κ is the transmission coefficient.

The free energy change (ΔG) of the overall electron-transfer reaction can be estimated from the standard potentials of the two redox couples involved, together with terms for the Coulombic interactions of the reactants and products.[21]

$$\Delta G = E(Q^+/Q) - E(^*D/D^-) + W_p - W_r \quad (6)$$

Here the value W_r is the electrostatic work term for bringing the charged reactants together in the precursor complex, and W_p is the corresponding work term for the successor complex. These work terms are often neglected, particularly in cases where one of the reactants is uncharged. For the reaction studied here, however, involving 2+ and 4− reactants and 3+ and 5− products, the contribution of the work terms must be included.

The values of ΔG for the reactions between $^3Pt_2(pop)_4^{4-}$ and each of the Ni(II) quenchers were determined using the estimated $^3Pt_2(pop)_4^{4-}/Pt_2(pop)_4^{5-}$ redox couple (1.34 V versus NHE)[3], the Ni(III)/(II) redox couples, and the calculated work terms for reactants and products. In the latter calculations, the radius of $Pt_2(pop)_4^{4-}$ was taken as 0.43 nm based on a Chem-3D space-filling model, while the crystallographic data[8] for $Ni(bicycloN_4O)^{2+}$, led to an estimate of 0.28 nm which was used for the Ni complexes. The derived estimates of the work terms were $W_{11}(Pt^{4-*/5-}) = 0.42$ eV, $W_{22}(Ni^{2+/3+}) = 0.20$ eV, $W_R(Pt^{4-*}/Ni^{2+}) = -0.21$ eV, and $W_P(Pt^{5-}/Ni^{3+}) = -0.39$ eV. The resultant plot of log k_q versus ΔG, shown in Figure 3, shows classic Rehm−Weller behavior. In the plots of Figures 3 and 4, $Ni(bicycloN_4O)^{2+}$ was omitted as it was essentially identical with $Ni(bicycloN_5)^{2+}$. Over the range of ΔG values studied for

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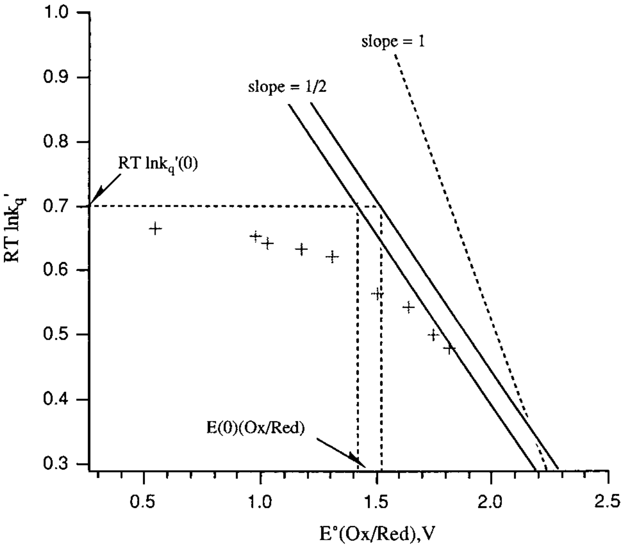

Figure 4. Estimation of excited-state redox potential for $Pt_2(pop)_4^{4-}$. Plot of $RT \ln k_q'$ vs $E°$(Ni(III)/Ni(II)).

this series of Ni(II) quenchers, no evidence for the Marcus inverted region was observed.

To extract kinetic parameters, a computer modeling program (Igor Pro 3.0 software, Wavemetrics) was used to fit the Figure 3 plot of log k_q versus ΔG to a Rehm−Weller function in four parameters, a_1, a_2, a_3, and a_4:

$$k_q = 1 + \frac{a_1}{1 + (a_2 e^{\Delta G^{\ddagger}/RT}) + a_4 e^{\Delta G/RT}} \tag{7}$$

with $\Delta G^{\ddagger}$ of eq 7 defined in terms of the variable a_3 by the function[22]

$$\Delta G^{\ddagger} = \Delta G + \frac{a_3}{\ln 2} \ln\left\{1 + \exp\left[\frac{-\Delta G \ln 2}{a_3}\right]\right\} \tag{8}$$

Comparisons using eqs 5, 7, and 8 show that parameters a_1 to a_4 correspond to the values k_d, $k_{-d}/k_e°$, $\Delta G^{\ddagger}(0)$, and k_{-d}/k'_{-d}, respectively. In attempting to fit the experimental data to these equations, it was found that an unconstrained model was ineffective. Exploration of the reasons for this showed that it arose because of the paucity of nickel complexes available whose redox potentials and hence data points fall in the region of maximum curvature, the region which defines the $\Delta G^{\ddagger}(0)$ value. However, the values of a_1 and a_4 were well defined at 1.6×10^{10} M^{-1} s^{-1} and 0.1, respectively. By constraining a_1 and a_4 to these values, a fit of the data gave minimum χ^2 value for $a_2 = 2 \times 10^{-4}$ and $a_3 = 0.54$ eV. The reorganizational energy would then be four times this, that is in excess of 2 eV. On the other hand, values of $a_2 = 0.1$ and $a_3 = 0.16$ eV give almost as good a fit, shown as the solid line in Figure 3. We consider the corresponding reorganizational energy of 0.60 eV or 60 kJ mol^{-1} to be more reasonable.

For comparison purposes, the diffusion-controlled rate constants k_d, k_{-d}, k'_d, and k'_{-d} defined in eq 4 were calculated using the Debye−Smoluchowski and Debye−Eigen equations for the diffusion of charged particles. This treatment has been outlined by Chiorboli and co-workers[23] who give the relevant equations in cgs units, and by Kirk and Cai[24] in SI units. The calculated value of 1.6×10^{10} M^{-1} s^{-1} for the diffusional rate constant k_d is in excellent agreement with the value of a_1 obtained from the fit to the quenching data. The frequency factor $k_e°$ can then be estimated as 2.2×10^9 s^{-1} by combining the ratio $k_{-d}/k_e° = 0.1$ and the calculated value $k_{-d} = 2.23 \times 10^8$ M^{-1} s^{-1}. This results in an estimate of the transmission coefficient of $\kappa \sim 10^{-4}$. Such a value falls within the weakly adiabatic domain for electron transfer and can be the result of either electronic factors resulting from poor overlap of the donor and acceptor orbitals, or nuclear factors which arise from changes in the coordination geometries of the reactants associated with the transfer of the electron. For this series of electron-transfer reactions between the nickel quenchers and $^3Pt_2(pop)_4^{4-}$, a small value for κ may indicate that a tunneling mechanism for electron transfer is important.

The value obtained for the fourth parameter, $k_{-d}/k'_{-d} = 0.09$, seems unrealistic. The two reacting complexes will have similar sizes before and after electron transfer, but the charge product changes from $-4 \times 2 = -8$ before transfer to $-5 \times 3 = -15$ after. The expectation is therefore that k'_{-d} should be smaller, not larger, than k_{-d}. The assumption of the Rehm−Weller treatment based on eq 4 is that the electron transfer is quasi-reversible, in the sense that reverse electron transfer restores the excited state of the platinum dimer. It is also possible, and perhaps more likely, that back electron transfer gives ground-state species; in this alternative situation, the parameter a_4 is then a composite function of several rate constants, which resolves the anomaly noted above. A full comparison of these two kinetic situations has been presented[25] and we can now confront our data with this more general analysis of the kinetics. This gives us some information on the relative likelihoods of the competing back electron-transfer processes and also allows us to obtain an independent value for the $^3Pt_2(pop)_4^{4-}/Pt_2(pop)_4^{5-}$ excited-state potential.

Kinetic Analysis and Estimation of the $^3Pt_2(pop)_4^{4-}/Pt_2(pop)_4^{5-}$ Excited-State Reduction Potential. The kinetic scheme corresponds to that shown in eq 4 with the addition of back electron transfer to produce ground-state species

$$\{D^-.....Q^+\} \xrightarrow{k'_g} D + Q \tag{9}$$

Steady-state analysis of this scheme, together with the assumption[26] that $\Delta G \ll 2\lambda$, shows that when back electron transfer to ground-state species dominates, a plot of $RT \ln k'_q$ versus the redox potential for the quencher species, E(Ox/Red), should be linear with slope $^1/_2$. In contrast, when back electron transfer to excited-state D* dominates, such a plot should have slope 1. The same analysis[25] provides a means for estimating the potential for the excited-state redox couple, later applied[3] to estimate the redox potential of the $^3Pt_2(pop)_4^{4-}/Pt_2(pop)_4^{5-}$ couple. The present series of quenching reactions between $Pt_2(pop)_4^{4-}$ and the Ni(II) complexes has been used to provide a second determination for this excited-state redox couple.

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[26] Figure 3 shows that ΔG_{et} ranges from −1.0 to 0.3 V while $2\lambda \sim 1.2$ V.

The quenching rate constants, k_q, must first be corrected for diffusional effects since

$$\frac{1}{k_q} = \frac{1}{k_q'} + \frac{1}{k_d} \qquad (10)$$

To calculate the corrected rate constants k_q', the value $k_d = 1.54 \times 10^{10}\ M^{-1}\ s^{-1}$, obtained from the computer fitting to our experimental data, was used. The use of a constant k_d value across the series assumes that the diffusional rate constant is determined mainly by the solvent properties and charge effects and is relatively independent of the small differences in size and shape of the Ni(II) complexes. The corrected rate constants are listed in the last column of Table 1.

The plot of ln k_q' versus E(Ox/Red) values for this series of Ni(II) quenchers, Figure 4, shows that the data points appear to be reaching an asymptotic limit at higher Ni(III/II) redox potentials but unfortunately this linear portion of the plot could not be developed further owing to a lack of Ni(II) complexes having E(Ox/Red) values >1.82 V. Also these high potentials approach the limit at which water oxidation will begin to interfere. The data are sufficient to indicate, however, that this region is better fit by a straight line with a slope in the range close to 1/2 (shown in Figure 4 by the two solid straight lines chosen to bracket the range of feasible asymptotes), than by a line with slope = 1 (shown by the dotted line). This indicates that this series of quenching reactions is most consistent with a dominant back electron transfer to form ground-state $Pt_2(pop)_4^{4-}$.

A potential, E(0)(Ox/Red), may be defined for a hypothetical quencher for which $\Delta G = 0$. This E(0)(Ox/Red) value may be interpolated from the plot of RT ln k_q' vs E(Ox/Red) if an independent estimate of $k_q'(0)$, the corrected rate constant for the quenching reaction between the hypothetical quencher and $Pt_2(pop)_4^{4-}$, can be made. It follows that once RT ln $k_q'(0)$ is known, the value of E(0)(Ox/Red) can be read from the graph and can then be used to calculate the excited-state redox potential $E(^3Pt^{4-}/Pt^{5-})$ from the following relationship:

$$E(^3Pt^{4-}/Pt^{5-}) = E(0)(Ox/Red) - (W_p - W_r) \qquad (11)$$

Assuming that the product $\nu_{et}K_d$ and the reorganizational barrier $\Delta G^{\ddagger}$ (=λ/4) remain reasonably constant throughout the series of quenchers, then the required estimate of $k_q'(0)$ may be obtained by the following equation:

$$\ln k_q'(0) = \ln k_{11}k_{22} + \frac{W_{11} + W_{22} - 2W_r}{2RT} \qquad (12)$$

which is derived from the Marcus "cross-reaction" equation,[27] $k_q' = (k_{11}k_{22}K_e)^{1/2}$. Here $K_e = k_e/k_{-e} = 1$ ($\Delta G = 0$), and k_{11} and k_{22} are the self-exchange rate constants for the quencher and excited-state couples, and W_{11} and W_{22} are the electrostatic work terms for bringing together the reactants for the two self-exchange reactions. The electron transfer self-exchange rate for $^3Pt_2(pop)_4^{4-}/Pt_2(pop)_4^{5-}$ has been estimated to have a maximum value of $2 \times 10^3\ M^{-1}\ s^{-1}$.[3] The self-exchange rates of the nickel complexes were estimated using the self-exchange rate constant measured for Ni(cyclam)$^{2+}$, a value of $2 \times 10^{-3}\ M^{-1}\ s^{-1}$.[28] Using an estimate of $k_q'(0) = 1.07 \times 10^{12}\ s^{-1}$, a range of 1.42 to 1.52 V was determined for E(0)(Ox/Red) based on the bracketing asymptotes shown in Figure 4. Correcting these values for the work terms W_p and W_r gave an estimated range for the value of the excited-state redox potential $E(^3Pt^{4-}/Pt^{5-})$ of 1.29 ± 0.05 (vs NHE). This is in excellent agreement with and provides support for the previous literature value of 1.34 V vs NHE estimated by Nagle.

Conclusions

Quenching of $^3Pt_2(pop)_4^{4-}$ by Ni(II) complexes occurs by reductive electron transfer, leading to net redox products by a low-efficiency cage escape route that is enhanced in the presence of oxygen. The variation of the quenching rate constant with the free energy change of the electron transfer is accounted for by Rehm−Weller and Marcus−Hush electron transfer theory and leads to a reorganizational energy for the process of ~60 kJ mol^{-1} and a potential for the $E(^3Pt_2(pop)_4^{4-}/Pt_2(pop)_4^{5-})$ redox couple of 1.29 ± 0.05 V vs NHE. The transmission coefficient for the forward electron transfer is on the order of 10^{-4}, in the weakly nonadiabatic region and the back electron transfer occurs to give the ground states of the two complexes.

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