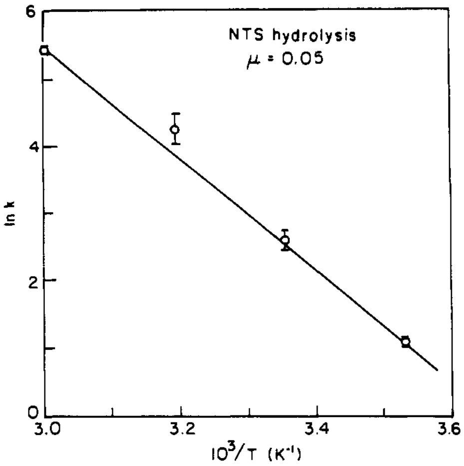

Figure 1. Arrhenius plot for the hydrolysis rate constant for NTS.

dependence was correct.[1] Using buffers to maintain the solutions at pH 5.0, runs were made in which the NTS concentration was varied from 1×10^{-3} to 10×10^{-3} M. A weighted least-squares fit to the data gives a value of 1.12 ± 0.10 for the slope, indicating that the rate has first-order dependence on NTS concentration.

The hydrolysis rate dependence of H^+ concentration was studied at both 298 and 313 K. The runs were done with 2.5×10^{-3} M NTS, and the solution pH ranged from 4.1 to 6.7. A least-squares fit to the points gives a slope of 0.99 ± 0.05. The measurements at 313 K gave similar results. The first-order dependence on hydrogen ion concentration indicates that the observed reaction is acid-catalyzed.

The temperature dependence of the hydrolysis reaction was studied by making measurements at 283, 298, 313, and 333 K. The alkaline NTS solution and the buffer solution were brought to the desired temperature before mixing. The mixed solutions were kept in controlled-temperature water baths. Since the H^+ concentration was maintained at a nearly constant level by the buffer solution, the rate equation can be expressed as

$$\ln ([\mathrm{NTS}]_0/[\mathrm{NTS}]_t) = k[\mathrm{H}^+]_t$$

At an ionic strength of $\mu = 0.05$, the following values of the rate constant were obtained:

T, K	k, L mol^{-1} s^{-1}
283	3.03 ± 0.17
298	12.7 ± 2.0
313	70 ± 18
333	227 ± 12

An Arrhenius plot of these values is shown in Figure 1. If the rate constant is expressed as $k = A \exp(-E_a/RT)$, then a weighted least-squares fit to the data gives $A = (1.5 \pm 0.7) \times 10^{13}$ L mol^{-1}, s^{-1} and $E_a = 16.5 \pm 0.3$ kcal/mol.

The effect of ionic strength on the rate of the hydrolysis reaction was studied over the range of $\mu = 0.028$–0.52 M. All measurements were done with an NTS concentration of 2.5×10^{-3} M at 298 K and pH 4.8–5.2.

Brønsted's equation for the influence of ionic strength on a reaction rate constant can be written as[5]

$$\log k = \log k_0 + 2Az_1z_2\frac{\mu^{1/2}}{1 + \mu^{1/2}}$$

where k_0 is the limiting rate constant as the ionic strength approaches zero, A is the Debye–Hückel coefficient (0.5065), z_1 and z_2 are the charges on the reacting ions, and μ is the ionic strength. With this equation, the influence of the ionic strength on the rate of reaction can be used to determine the charge states of the reacting species. A plot of log k vs. $\mu^{1/2}/(1 + \mu^{1/2})$ is shown in Figure 2. The best fit to the points is a line with a slope of −2.88 ± 0.25 and an intercept of 1.651 ± 0.063. The slope indicates that the charge on NTS is −3 and it is reacting with H^+. The intercept gives a value of $k_0 = 44.8$ L mol^{-1} s^{-1} at 298 K.

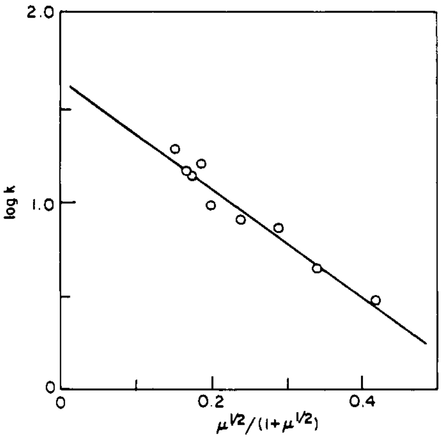

Figure 2. Dependence of the hydrolysis rate constant on ionic strength.

The decomposition of NTS under alkaline conditions was also checked. Solutions of NTS in the range of pH 8–10 exhibit little or no deterioration over a period of many days. This indicates that the uncatalyzed hydrolysis reaction is insignificant compared to the acid-catalyzed hydrolysis.

Acknowledgment. We appreciate the support and encouragement of Michael Perlsweig, Joseph Strakey and John Williams. This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Research, Advanced Environment Control Division of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, PA.

Registry No. $N(SO_3)_3^{3-}$, 72198-01-7.

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Circular Dichroism of the Reduction Products of $Ru(bpy)_3^{2+}$

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Received June 25, 1986

The nature of the metal-to-ligand charge-transfer (MLCT) state of $Ru(bpy)_3^{2+}$ has been of considerable interest for some time. Of particular interest is the degree of ligand localization of the promoted electron. There is an abundance of data, including resonance Raman,[1] absorption,[2] circular dichroism,[3] and excitation photoselection[4] spectra, that strongly argue for ligand localization. Other data suggest a delocalized description when the complex is in a rigid medium.[5,6] However, this result is open to question.[2d,4] Electrochemical reduction also appears to yield species with the added electron(s) localized on a single ligand(s).[7] Thus, an

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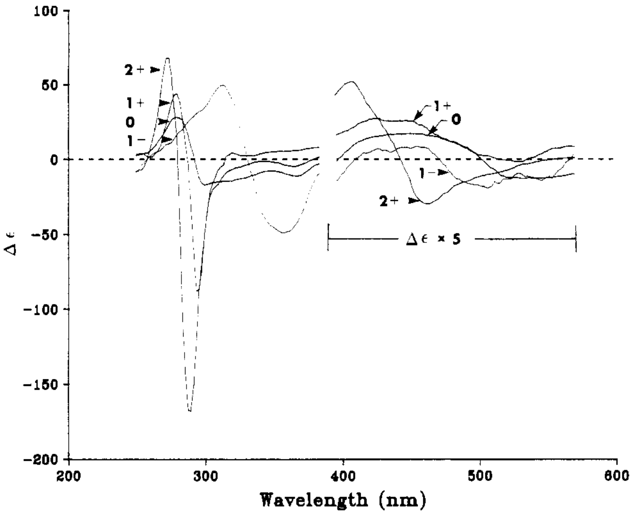

Figure 1. Circular dichroism spectra of $Ru(bpy)_3^{2+}$ and its first three reduction products in CH_3CN at 20 °C. The CD of the $\pi\pi^*$ absorption of bpy at 300 nm decreases with increasing reduction. The CD of the $\pi\pi^*$ absorption of bpy^- at 350 nm is small for $Ru(bpy)_3^+$ and increases with the extent of reduction.

analogy has been made between the MLCT state of $Ru(bpy)_3^{2+}$ and the ground state of $Ru(bpy)_3^+$, since both purportedly have a single-ligand-localized electron. We report here the circular dichroism (CD) spectra of $Ru(bpy)_3^+$, $Ru(bpy)_3^0$, and $Ru(bpy)_3^-$ produced by successive reduction of $Ru(bpy)_3^{2+}$. We show how, consistent with previous results, each of these species is best described as having the added electron localized on an individual ligand.

Experimental Section

The reduced species were prepared by electrochemical reduction of Δ-$Ru(bpy)_3^{2+}$, which was prepared by the method of Dwyer and Gyarfas.[8] Electrochemical reductions were performed in a nitrogen-atmosphere glovebox by using a carbon-cloth electrode in acetonitrile solutions with tetrabutylammonium perchlorate (0.1 M) as the supporting electrolyte. The production of each species was done at −1.82, −1.97, and −2.24 V against a Ag/Ag^+ electrode. CD spectra were measured on a Jasco J-500C spectropolarimeter using a sealed, strain-free 1-mm cell.

Results

Figure 1 shows the CD spectra of $Ru(bpy)_3^{2+}$ and of the subsequent reduction products in acetonitrile. The spectrum of $Ru(bpy)_3^{2+}$ is in agreement with the previously reported spectrum.[9] Upon reduction, the CD of the $\pi\pi^*$ ligand absorption at 300 nm is seen to monotonically decrease, while a concurrent increase in the CD of the $\pi\pi^*$ ligand absorption at 350 nm is observed. The CD of the charge-transfer bands near 420 nm also decreases monotonically with reduction.

Discussion

Recently we reported the CD of the excited-state absorption of $Ru(bpy)_3^{2+}$.[3] The small CD ($\Delta\epsilon \approx -3$) of the 370-nm $\pi\pi^*$ absorption is indicative of a single-ligand-localized state. Exciton coupling theory predicts a larger CD for a transition that spans all three ligands.[10] For $Ru(bpy)_3^+$ a $\Delta\epsilon$ of −6 is observed in this region of the $\pi\pi^*$ absorption. Again this small CD suggests a single-ligand-localized transition. This $\Delta\epsilon$ is of the same magnitude as that for the $\pi\pi^*$ transition of $Co(phen)(en)_2$.[11] The magnitude of the CD of this band increases with increasing reduction, consistent with increased coupling. If the added electrons in the partially reduced species were completely delocalized, much larger CD's would be expected for this band. In $Ru(bpy)_3^{+/0}$ this band appears in the region from 350 to 380 nm, while the absorption band itself is reported to range from 320 to 400 nm.[7a] This suggests that in these species the CD's of these $\pi\pi^*$ bands are partially obscured by CD signals from other transitions. Ligand-to-metal charge transfer might be expected in this region and would exhibit a moderate CD ($\Delta\epsilon \approx$ 10–20).

The $\pi\pi^*$ band centered near 300 nm decreases monotonically with increasing reduction. This is consistent with the transitions being exciton-coupled. Since the rotational strength of the transitions arise from the helical arrangement of coupled chromophores around the central metal atom, the CD in these transitions should decrease as the number of coupled chromophores decreases. As an example, the $\Delta\epsilon$ for the ligand $\pi\pi^*$ transition decreases from 100 to 25 to 10 in the series $Co(bpy)_3^{3+}$, $Co(bpy)_2(NO_2)_2^{3+}$, and $Co(phen)(en)_2^{3+}$.[11,12] Thus, the CD of the $\pi\pi^*$ transition in the reduction products of $Ru(bpy)_3^{2+}$ strongly indicates that reduction results in the sequential formation of $Ru^{II}(bpy)_2(bpy^-)$, $Ru^{II}(bpy)(bpy^-)_2$, and $Ru^{II}(bpy^-)_3$.

The sample was not observed to rapidly racemize at any stage during the reduction. If reduction were taking place at the metal, occupation of the e orbital would be expected to increase the lability of the complex and perhaps allow for thermal racemization.

Conclusions

The monotonic decrease in the CD of the bpy $\pi\pi^*$ transition near 300 nm is consistent with reduction being essentially localized on the ligands. The magnitude of the CD for the bpy $\pi\pi^*$ transition near 350 nm is consistent with the added electron(s) occupying orbital(s) localized on individual ligand(s).

Acknowledgment. We thank Matthew Gebhard and Drs. Nate Lewis and Ed Solomon for their assistance with the experiments. We also thank Dr. David Kliger for his constant encouragement and support and the National Institutes of Health for financial support under Grant GM35158.

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