interior at the high temperature and this overlaps the narrow aromatic resonance. The short T_1 observed for the aromatic site is also due to its reorientation. It is likely that this motion still exists at room temperature and below since the T_1 remains less than 1 s. Also, there appears to be some distortion or flattening of the aromatic resonance line shape (Figure 1b) before the onset of motional narrowing. Investigation of these details is in progress.

We believe that these results provide the first direct spectroscopic evidence of the molecular sieve effect. They demonstrate that deuterium NMR is a useful tool to study the dynamics of molecules within zeolitic materials to shed new light on size and shape phenomena observed in heterogeneous catalysis and other applications of such materials.

Acknowledgment. We are grateful to Dr. Lloyd Abrams for helpful discussions and R. O. Balback for technical assistance.

Registry No. Perdeuterated *p*-xylene, 41051-88-1.

Electrocatalytic Oxidation of Chloride to Chlorine Based on Polypyridine Complexes of Ruthenium

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In recent work, stoichiometric and catalytic oxidations of a series of inorganic and organic substrates by higher oxidation state complexes of ruthenium have been reported.[1,2] The accessibility of the higher oxidation states is based on a series of closely spaced, coupled proton–electron oxidations of complexes like *cis*-$(bpy)_2Ru^{II}(OH_2)_2^{2+}$ as shown in Scheme I.[2b]

Scheme I (pH 4.0, vs. SSCE)

$$(bpy)_2Ru^{II}(OH_2)_2^{2+} \underset{\substack{+e^-, +H^+\\ E_{1/2} = 0.53\ V}}{\overset{-e^-, -H^+}{\rightleftharpoons}} (bpy)_2Ru^{III}(OH_2)(OH)^{2+}$$

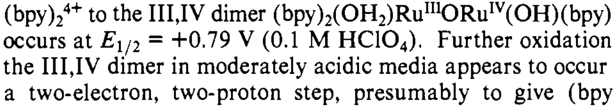
$$\underset{\substack{+e^-, +H^+\\ E_{1/2} = 0.76\ V}}{\overset{-e^-, -H^+}{\rightleftharpoons}} (bpy)_2Ru^{IV}O(OH_2)^{2+} \underset{\substack{+e^-, +H\\ E_{1/2} = 0.94\ V}}{\overset{-e^-, -H^+}{\rightleftharpoons}}$$

$$(bpy)_2Ru^{V}O(OH)^{2+} \underset{\substack{+e^-, +H^+\\ E_{1/2} = 1.07\ V}}{\overset{-e^-, -H^+}{\rightleftharpoons}} (bpy)_2Ru^{VI}O_2^{2+}$$

A commercially important electrolytic process is the oxidation of chloride to chlorine at carbon-, or more recently, at RuO_2-impregnated TiO_2 electrodes.[3] Possible similarities between complexes like $(bpy)_2Ru^{VI}O_2^{2+}$ and catalytically active RuO_2 surface sites, as well as the successful use of an oxidized form of the dimeric complex, $(bpy)_2Ru^{III}(OH_2)ORu^{III}(OH_2)(bpy)_2^{4+}$,[2a,4] as a catalyst for the oxidation of H_2O to O_2,[2a] which is also catalyzed by RuO_2, suggested that soluble ruthenium–oxo complexes might also be capable of acting as catalysts for the oxidation of chloride ion to chlorine. We report here that higher oxidation states of the monomeric and dimeric complexes mentioned above are capable of catalyzing the oxidation of chloride to chlorine at carbon electrodes both with selectivity—preferential oxidation of chloride to chlorine rather than of water to oxygen—and with high thermodynamic efficiency—the catalytic reactions occur with relatively high current densities near the thermodynamic potential for the Cl^-/Cl_2 couple (+1.13 V vs. SSCE, pH 0-3).[5]

Starting with either $(bpy)_2Ru^{II}(OH_2)_2^{2+}$ or the one-electron oxidized form of the dimer, $(bpy)_2(OH_2)Ru^{III}ORu^{IV}(OH)(bpy)_2^{4+}$, oxidation either chemically (using excess Ce(IV)) or electrochemically ($E_{appl} \geqslant +1.20$ V) in the presence of chloride results in the generation of chlorine gas as identified by mass spectrometry. In a typical electrocatalytic experiment, electrolysis at a "coarse" (12 holes/linear in.) reticulated vitreous carbon electrode potentiostated at +1.20 V in ca. 30 mL of a 0.05 M HCl solution containing 1.35×10^{-5} mol of $[(bpy)_2(OH_2)Ru^{III}ORu^{IV}(OH)(bpy)_2](ClO_4)_5$ gave 1.04×10^{-4} mol of chlorine in 132 min. The background current was <12% of the catalyzed current. Chlorine was swept by an argon purge from the working electrode compartment into a cold, aqueous basic solution, and chloride was determined by standard iodometric titration techniques. Comparing the electrochemical stoichiometry as equivalents of electrons passed with moles of chlorine titrated gave a current efficiency of 44% and a turnover number of 7. H_2 was produced at a platinized Pt electrode in the second cell compartment, and the volume of H_2 produced was consistent with the electrochemical current efficiency within experimental error. Blank experiments show that the major loss mechanism in our relatively unsophisticated cell design is the diffusion of chlorine to the cathode compartment. The electrocatalytic reaction is notable, since no significant production of O_2 was observed by gas chromatography. At a glassy carbon disk electrode (geometric area = 0.035 cm^2),[6] current densities of 1.5 mA/cm^2 were reached (using 10^{-3} M dimer, 0.1 M NaCl, 0.1 M $HClO_4$) although it should be noted that the actual surface area of the electrode is probably considerably larger than the geometric area, since large surface pits are characteristic of glassy carbon surfaces. Current densities for both the monomer and dimer systems decrease notably after extended electrolysis times.

The results of independent electrochemical, spectral, and chemical isolation studies provide insight into the details of the catalyzed oxidations. The decrease in catalytic current with time is attributed to anation by chloride as shown in eq 1 for the Ru(III)–Ru(IV) dimer. Neither of the chloride-containing dimers are effective as catalysts for the oxidation of chloride to chlorine.[6] On the basis of cyclic voltammetry in the absence of chloride, oxidation of the III,III dimer $(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2^{4+}$ to the III,IV dimer $(bpy)_2(OH_2)Ru^{III}ORu^{IV}(OH)(bpy)_2^{4+}$ occurs at $E_{1/2} = +0.79$ V (0.1 M $HClO_4$). Further oxidation of the III,IV dimer in moderately acidic media appears to occur by a two-electron, two-proton step, presumably to give $(bpy)_2(OH)Ru^{IV}ORu^{V}O(bpy)_2^{4+}$, although no information is yet available concerning either structure or an appropriate description of the oxidation state because of the reactivity of the three-electron oxidized dimer. The Ru(IV)–Ru(V) dimer appears to be the reactive component in the catalytic oxidation of Cl^- to Cl_2 via the



$$(bpy)_2\underset{OH_2}{\underset{|}{Ru}}{}^{III}O\underset{OH}{\underset{|}{Ru}}{}^{IV}(bpy)_2^{4+} \xrightarrow[-OH^-]{+Cl^-} (bpy)_2\underset{Cl}{\underset{|}{Ru}}O\underset{OH_2}{\underset{|}{Ru}}(bpy)_2^{4+} \xrightarrow[-H_2O]{+Cl^-} (bpy)_2\underset{Cl}{\underset{|}{Ru}}O\underset{Cl}{\underset{|}{Ru}}(bpy)_2^{3+} \quad (1)$$

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(5) All potentials are reported vs. the saturated sodium chloride calomel electrode, which is +0.234 V vs. the normal hydrogen electrode (see: Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980).

(6) The appearance of $(bpy)_2ClRuORu(OH_2)(bpy)_2^{4+}$ and $(bpy)_2ClRuORuCl(bpy)_2^{3+}$ can be followed either electrochemically or spectroscopically. For $(bpy)_2ClRuORu(OH_2)(bpy)_2^{4+}$ in 0.1 M $HClO_4$ $E_{1/2} = +0.67$ V, λ_{max} 465 nm, and for $(bpy)_2ClRuORu(Cl)(bpy)_2^{3+}$, $E_{1/2} = +0.54$V, λ_{max} 470 nm. Note that we are assuming that the dimer $(bpy)_2ClRuO(OH_2)(bpy)_2^{4+}$ exists dominantly as the aquo ion in 0.1 M $HClO_4$ by analogy with $(bpy)_2(OH_2)RuORu(OH)(bpy)_2^{4+}$.

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$(bpy)_2(OH)Ru^{IV}ORu^{V}O(bpy)_2^{4+}/(bpy)_2(OH_2)Ru^{III}ORu^{IV}(OH)(bpy)_2^{4+}$ couple.

The pH dependences of the dimer couples dictate that $\Delta E^{\circ\prime}$ for the Cl^-/Cl_2 interconversion should be zero at pH $\simeq 3.5$. As expected from the thermodynamic potentials, significant catalytic ($2Cl^- \rightarrow Cl_2$) currents are observed for the dimer/Cl^- system only below pH 3. Above pH 4 Cl_2 (or HOCl) oxidizes the Ru(III,III) or Ru(III,IV) dimers, and in basic solution OCl^- can be used to drive the dimer-catalyzed oxidation of water to oxygen. The results of the pH-dependence studies lead to two significant conclusions: (1) Even at pH 2 where $\Delta E^{\circ\prime} \simeq 0.07$ V, significant catalytic currents are observed, showing that a remarkably low overpotential exists for the catalytic oxidation of chloride. (2) The oxidation of $(bpy)_2(OH_2)Ru^{III}ORu^{IV}(OH)(bpy)_2^{4+}$ by solutions containing chlorine at pH >4 show that the catalytic system can operate in either direction as might have been expected on the basis of microscopic reversibility.

Oxidation of solutions containing $(bpy)_2Ru^{IV}O(OH_2)^{2+}$ at a potential sufficient to give $(bpy)_2Ru^{VI}(O)_2^{2+}$ also results in the electrocatalytic oxidation of chloride to chlorine. The details of the catalyzed reaction are similar to those described for the dimer, but the following points should be noted: (1) Loss of catalytic activity occurs over extended electrolysis times because of chloride anation to give $(bpy)_2Ru(OH_2)Cl^+$ and its higher oxidation state components. (2) The active oxidation catalyst appears to be Ru(VI) via the $(bpy)_2Ru^{VI}(O)_2^{2+}/(bpy)_2Ru^{IV}O(OH_2)^{2+}$ couple. (3) In the absence of chloride, $(bpy)_2Ru^{VI}(O)_2^{2+}$ decomposes slowly to give O_2 (by GC) and an, as yet unidentified, complex of Ru(III).

Catalytic, chemically modified electrodes based on the monomer and dimeric couples have been prepared on carbon paste electrodes by the following procedures: (1) The electrodes were coated with *p*-chlorosulfonated polystyrene ($-CH_2(p-C_6H_4SO_2Cl-)_n$, which was hydrolyzed and deprotonated to form a polyanionic film as described elsewhere.[7] (*2*) The dimeric or monomeric catalysts were ion-exchanged into the film-coated electrodes to achieve apparent surface coverages (Γ_{app})[8] of up to 10^{-10} mol/cm^2 for the dimer and 10^{-9} mol/cm^2 for the monomer. A monomer-incorporated carbon paste electrode ($\Gamma_{app} \simeq 7 \times 10^{-10}$ mol/cm^2)[11] held at a constant potential of 1.20 V in a 0.1 M $HClO_4$ solution containing 5.0 M NaCl gave an initial catalytic current density of 8 mA/cm^2 that slowly decreased to 0.5 mA/cm^2 after 20 min. One useful feature associated with the catalytic properties of the electrodes is that the loss mechanism associated with chlorine anation can be reversed simply by cycling the potential of the coated electrode from +0.2 to +1.20 V in a 0.1 M $HClO_4$ solution free of Cl^-. After several minutes, reaquation of the bound chloro groups occurs, which regenerates the diaquo catalytic sites, and the electrodes regain their full catalytic activity for the generation of Cl_2.

We are currently investigating the mechanistic details of the Cl^- oxidation reactions. Hopefully such details will give insight into both the heterogeneous oxidation of Cl^- to Cl_2 at RuO_2-impregnated electrodes and into the design of stable, chemically modified electrodes for the interconversion of Cl_2 and Cl^-.

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Registry No. *cis*-$(bpy)_2Ru^{II}(OH_2)_2^{2+}$, 72174-09-5; $(bpy)_2Ru^{III}(OH_2)ORu^{III}(OH_2)(bpy)_2^{4}$, 56110-87-3; $(bpy)_2(OH_2)Ru^{III}ORu^{IV}(OH)(bpy)_2^{4+}$, 86045-59-2; $(bpy)_2Ru^{IV}O(OH_2)^{2+}$, 84988-22-7; $(bpy)_2Ru^{VI}(O)_2^{2+}$, 84988-24-9; Cl^-, 16887-00-6; Cl_2, 7782-50-5; C, 7440-44-0.

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(7) Ellis, C. D.; Meyer, T. J., submitted for publication in *Inorg. Chem.*

(8) Apparent surface coverages (Γ_{appl}; moles per square centimeter) were calculated by using the equation $\Gamma_{appl} = Q_c/n\mathcal{F}A$. Q_c is the total charge obtained by planimetric integration of the reductive component of the Ru(III)/Ru(II) or Ru(III,IV)/Ru(III,III) cyclic voltammetric waves, *n* is the number of electrons per molecule reduced, $\mathcal{F}$ is Faraday's constant, and *A* is the electrode area in square centimeters.

On the Nature of the Bicyclo[3.2.1]octa-3,6-dien-2-yl Anion. A ^{13}C NMR Spectroscopic Study[†]

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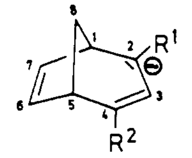
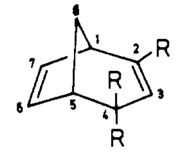
The title anion **1** is the most widely cited example of homoaromaticity in anionic systems. π-Delocalization was suggested to account for the rapid base-catalyzed H/D exchange at C-4 in bicyclo[3.2.1]octa-2,6-diene (**2**)[1] in comparison with bicyclo[3.2.1]oct-2-ene, and further experimental support was provided by the ^1H NMR spectrum of **1**.[2,3]

Two recent theoretical investigations[4,5] did not find a homoaromatic stabilization for **1** and related anions; a third one,[6] however, came to the opposite conclusion. Here we wish to report results that on an experimental basis give a clear insight into the nature of **1**.



1, $R^1 = R^2 = H$
1-*d*, $R^1 = D; R^2 = H$
1-d_2, $R^1 = R^2 = D$



2, R = H
2-d_3, R = D

Table I shows the ^{13}C NMR parameters of **1**,[7] its 2-deuterio derivative **1**-*d*,[8] its 2,4-dideuterio derivative **1**-d_2,[9] and, for comparison, those of **2** and its 2,4,4-trideuterio derivative **2**-d_3.[10] Based on the known chemical shifts of simple allyl anions,[11,12] the assignments in the spectrum of **1** are straightforward.

The most striking feature in the spectrum of **1** is the upfield shift of the C-6,7 resonance in comparison with **2** by 39.0 and 48.5 ppm, respectively. Two interpretations of this effect may be advanced: (i) Anion **1** is in fact the bishomoaromatic species **1d**. Then, the shielding of C-6,7 could be the consequence of the charge transfer from the allyl anion portion. (ii) Anion **1** consists of a rapidly equilibrating mixture of the allyl anion derivative **1a** and its tricyclic and tetracyclic isomers **1b** and **1c**, respectively (Scheme I). In this case, which was once considered but rejected,[2] C-6,7 would adopt in part the character of a cyclopropyl carbon and that of a carbanionic center, which would account for the shielding observed.

[†] Dedicated to Professor John D. Roberts on the occasion of his 65th birthday.

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(7) Prepared from *exo*-4-methoxybicyclo[3.2.1]octa-2,6-diene with Na/K alloy as described.[2,3]

(8) The precursor [4-D]*exo*-4-methoxybicyclo[3.2.1]octa-2,6-diene was obtained from bicyclo[3.2.1]octa-2,6-diene-4-one with $LiAlD_4$, subsequent methylation of the mixture of alcohols, and preparative GC separation of the isomeric methyl ethers according to the procedure for the unlabeled compound: Kirmse, W.; Olbricht, T. *Chem. Ber.* **1975**, *108*, 2616–2628.

(9) From **2**-d_3[10] and *N*-bromosuccinimide the tricyclic bromide was prepared as described for the **2**: Japenga, J.; Klumpp, G. W.; Stapersma, J. *Tetrahedron* **1977**, *33*, 2847–2849. Solvolysis of the tricyclic bromide in methanol containing $AgBF_4$ afforded a mixture of methylethers, from which [2,4-D_2]*exo*-4-methoxybicyclo[3.2.1]octa-2,4-diene, the precursor of **1**-d_2, was isolated by means of preparative GC.

(10) Prepared from **2** with Me_2SO-d_6 and $KOC(CH_3)_3$ as described.[1]

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