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Electrochemical Studies of Niobium Chlorides in "Superdry" Acetonitrile: Electron-Transfer-Induced Ligand-Exchange Reactions

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The electrochemical properties of niobium halides Et_4NNbCl_6, $(Et_4N)_2NbCl_6$, $NbCl_5$, and $NbCl_4(NCMe)_2$ were investigated in carefully dried acetonitrile (10^{-5} M H_2O) by using cyclic voltammetry and constant-potential electrolysis. A special vacuum electrochemical cell equipped with a sample-loading device and an Al_2O_3 column was used in order to prevent hydrolysis of niobium chlorides with the small amount of water present in "dry" acetonitrile. Two one-electron reduction waves were observed for all Nb(V) species that correspond to consecutive Nb(V) → Nb(IV) and Nb(IV) → Nb(III) reductions. $E_{1/2}$ values for the Nb(V)/Nb(IV) reduction process are critically dependent upon the number of Cl^- ligands. As the Cl^- number is increased from 4 to 5 and 6, it becomes more difficult, by 0.5 V, to reduce Nb(V) to Nb(IV). In comparison to that of $NbCl_6^-$ and $NbCl_4(NCMe)_2$, the electrochemical behavior of $NbCl_5NCMe$ is more complicated. After the initial one-electron reduction, the product $NbCl_5NCMe^-$ reacts with the starting material to produce $NbCl_6^-$ and $NbCl_4(NCMe)_2$. Further reduction of electrochemically generated $NbCl_6^-$ produces $NbCl_6^{2-}$, which reacts with $NbCl_4(NCMe)_2$ to give $NbCl_5NCMe^-$. It was found that the reduction product of $NbCl_5NCMe$ depends upon the selection of the potential used for the electrolysis; thus, $NbCl_5NCMe^-$ or a mixture of $NbCl_6^-$ and $NbCl_4(NCMe)_2$ can be obtained. Depending upon the applied potential, the similar reoxidation of $NbCl_5NCMe^-$ produces either $NbCl_5NCMe$ or a mixture of $NbCl_6^-$ and $NbCl_4(NCMe)_2$. The chemical steps that follow the initial electron-transfer process are chloride ligand exchange reactions. It is believed that the reduction of $NbCl_5NCMe$ directly to Nb(III), depending upon the temperature and the applied potential, may proceed simultaneously by three different electrochemical-chemical reaction pathways.

Introduction

There has been renewed interest in the chemistry of niobium, particularly in its metal-cluster chemistry,[1,2] organometallic reactions, and the possible catalytic application thereof.[3] The early work on niobium chemistry was dominated by the study of its complexes in a 5+ oxidation state. In addition to its metal-cluster compounds, very few mononuclear complexes of niobium in its lower oxidation states have been known until recently. Recent work has shown that stable Nb(III) complexes that have unique and unsuspected chemical properties can be isolated. They show very unusual reactivity toward small molecules such as CO_2,[4] PhN=NPh,[1] RC≡CR,[5] CNR,[6] and NCMe.[7]

Niobium halides have been used very frequently as starting materials for the preparation of a variety of other niobium compounds. They have very interesting, although not yet fully explored, redox chemistry. When chemically reduced, niobium pentahalide forms, depending on the reaction conditions, either simple monomeric species or various types of metal-cluster compounds. Metal-metal-bonded dimers,[8] trimers,[9] tetramers,[10] and hexamers[11] have been prepared. For example, the reduction of NbX_5 (X = Cl, Br) with Cd yields the hexameric clusters $Nb_6X_{12}^{2+}$,[11] while the reduction with Al in an $AlCl_3$ melt in the presence of C_6Me_6 gives the trimeric cation $Nb_3(C_6Me_6)_3Cl_6^+$.[9] $NbCl_5$ could also be reduced with Na/Hg in toluene in the presence of PMe_3, but the reduction product is the metal-metal-bonded dimer $Nb_2Cl_6(PMe_3)_4$.[12] On the other hand, the reduction of $NbCl_5$ with Al in MeCN produces monomeric $NbCl_4(MeCN)_2$.[13] However, if the reduction is performed with Zn instead of Al, an unusual dimer, $(MeCN)Cl_4NbNC(Me)=C(Me)NNbCl_4(NCMe)^{2-}$, is formed, where two Nb atoms are connected with a dimer of acetonitrile.[7] Apparently, Nb(V) is first reduced to a Nb(III) species that is oxidized by acetonitrile, giving dimers in which the formal oxidation state of Nb is 5+.

Although niobium pentahalide shows such a rich and interesting redox chemistry, surprisingly there are only a few papers published in the literature that deal with the electrochemical reduction of niobium halides in nonaqueous solvents.[14,15] The reason for this is in part due to the very high sensitivity of halides to hydrolysis with the small amount of water present in "dry" solvents. In this report we present a systematic investigation of the electrochemistry of niobium halides $NbCl_5MeCN$, $NbCl_6^-$, $NbCl_6^{2-}$, and $NbCl_4(MeCN)_2$ in rigorously dry acetonitrile. A detailed reduction mechanism for the reduction of $NbCl_5$ to Nb(IV) and Nb(III) species is also presented, describing the sequence of chemical reactions that follow the initial electrochemical steps.

Experimental Section

Instrumentation. A three-electrode PAR Model 173 potentiostat/galvanostat equipped with PAR 179 digital coulometer, PAR Model 178 electrometer probe, and PAR 175 universal programmer was used for the cyclic voltammetry and controlled-potential electrolysis experiments. Current-potential curves were recorded on a Model 2000 X-Y Houston Omnigraphic recorder. Electronic spectra of MeCN solutions were recorded in the range 200-600 nm with a Varian Model 2300 spectrophotometer interfaced with an Apple II+ computer. Solutions of niobium chlorides were made directly in a 0.1-mm quartz cell attached to a vacuum line.[16]

Cell Description. Since some of the investigated compounds are extremely sensitive to the small amount of water (10^{-3} M) present in "dry" acetonitrile, a specially constructed vacuum electrochemical cell was used. The cell was equipped with a loading device for the introduction of air-sensitive samples and an Al_2O_3 column that served for the further removal of water impurity down to a level below 10^{-5} M. The cell is a modification of the original designs of Geiger[17] and Kiesele.[18]

A schematic representation of the cell and the Al_2O_3 column are given in Figure 1. The cell consisted of two halves connected with a Viton

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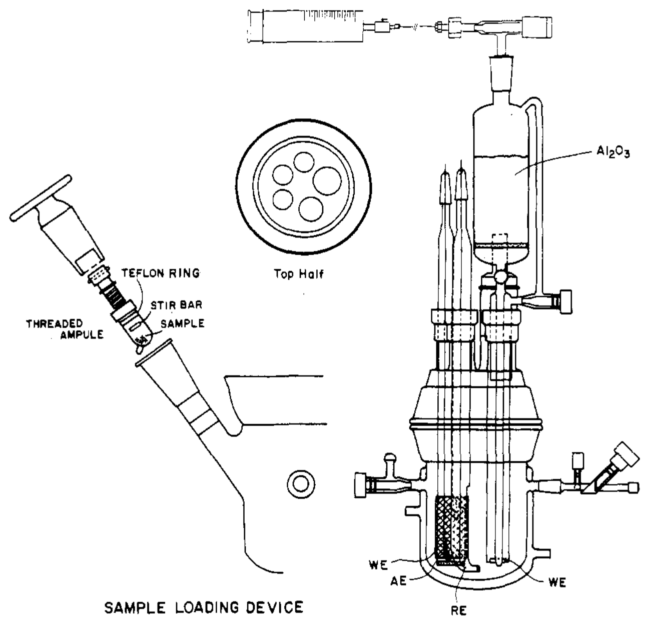

Figure 1. Electrochemical cell with upper and lower halves, electrodes, access ports, sample delivery module components, solvent introduction port, and alumina column.

O-ring about 3 in. in diameter. The top half of the cell provided the mountings for the electrodes and the alumina column. The bottom half consisted of a deep-well chamber (approximately 120 mL) surrounded by a jacket chamber for the temperature control. The bottom half was also fitted with a vacuum-line mounting, sample-loading-device mounting, and a N$_2$/solvent introduction port. The sample-loading device[17] consisted of a T-bar handle attached to a threaded Teflon plug to which a threaded glass ampule containing a sample, a Teflon ring, and a Teflon-coated magnet was attached. The role of the Teflon ring was to prevent the escape of the small stirrer during the dissolving of the sample. The alumina column (Figure 1) consisted of a closed glass cylinder approximately 1 in. in diameter equipped with a medium glass frit at the bottom. An inlet tube that reached from the bottom of the deep-well chamber to the top of the glass cylinder was attached to the outside of the cylinder. A second tube was attached to the glass cylinder, just below the frit to approximately half the length of the first tube, to act as an outlet. Each of the tubes contained a Teflon-needle valve. The top of the cylinder was closed off by a Teflon-needle valve leading to a 100-mL syringe by means of a stainless steel needle.

Voltammetry experiments employed a conventional three-electrode configuration: a glassy-carbon working electrode (Pine Instruments Co.), a Pt-wire auxiliary electrode, and an Ag-wire quasi-reference electrode. For coulometric measurements a Pt-gauze electrode fitted over the auxiliary electrode chamber was used as a working electrode. The Pt-wire auxiliary electrode was isolated from the bulk solution by a fine-porosity fritted compartment. The Ag-wire reference electrode was contained in a glass tube with a 90° bend at the lower end and a medium-porosity frit at the end. The tip of the reference electrode compartment was positioned near the working electrode in order to minimize the solution-resistance effect.

Cell Operation. All glass parts of the cell were cleaned, rinsed with acetone, and kept at 140 °C. The Pt-wire auxiliary electrode was cleaned in concentrated nitric acid, while the Pt-gauze working electrode was first cleaned in molten sodium bisulfate, followed by treatment with nitric acid. The glassy-carbon electrode was polished before use with 225-mesh alumina powder. The Ag-wire reference electrode was sanded with fine emery cloth. The cell was assembled after all glass components were cooled in the entry port of the drybox under vacuum. The bottom half of the cell was placed into the cell holder, and the N$_2$/solvent introduction port was attached. The electrolyte (Bu$_4$NPF$_6$), a few milligrams of internal standard (9,10-diphenylanthracene), and an oval Teflon-coated stirring bar were placed in the cell. The sample-loading device previously filled in a drybox with the known amount of the sample was inserted into its appropriate receptacle. The reference, auxiliary, and working electrodes and their receptacles were mounted in the top half of the cell. The halves of the cell were then joined by an O-ring seal and clamped together. The alumina column was installed in the cell top, and hot, previously activated (550 °C) neutral alumina was carefully poured into it. The cell and the alumina column were then evacuated for several hours (10^{-4} mmHg), during which time the alumina was heated to 170 °C. Approximately 100 mL of dry acetonitrile was added by way of the entry port, which was equipped with a rubber septum and a stainless steel needle attached to a glass bottle containing purified acetonitrile.

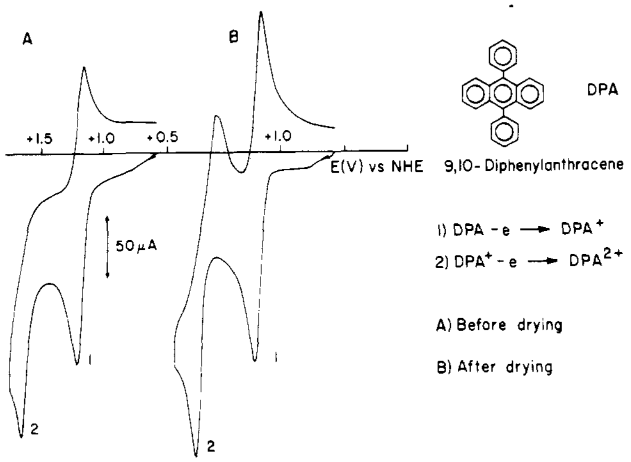

Figure 2. Cyclic voltammograms of 9,10-diphenylanthracene in 0.1 M Bu$_4$NPF$_6$/MeCN (A) before and (B) after contact with activated alumina.

Oxygen was removed at ambient temperature on a vacuum line by expansion of the dissolved gases into an evacuated 1-L flask.[19] Removal of the oxygen was monitored with cyclic voltammetry by observing the disappearance of the wave at −0.98 V vs NHE, which corresponded to the reduction of O_2 to O_2^-.

Moisture was removed from the solvent by passing the oxygen-free acetonitrile/electrolyte solution, cooled to 0 °C, over the activated-alumina column. This was accomplished by drawing the solution into the top of the alumina column and passing it through the alumina and out the bottom by a syringe attached to the column top. The temperature was controlled by pumping 3-propanol coolant through the water jacket of the cell.

The removal of the water was monitored with cyclic voltammetry by observing the stability of the electrogenerated DPA$^{•+}$ and DPA^{2+}. DPA can be oxidized by two one-electron steps to DPA$^{•+}$ and DPA^{2+}. In the presence of traces of water, DPA^{2+} is not stable, and the cyclic voltammogram does not display a cathodic current due to the reduction of DPA^{2+} to DPA$^{•+}$ (trace A, Figure 2). After water is removed from the system by passing the solution several times over the Al$_2$O$_3$ column, the DPA^{2+} becomes stable and the voltammogram displays the coupled cathodic current on the reverse scan (trace B, Figure 2). In addition, DPA also served as an internal standard since a quasi-reference electrode was used. In order to express half-wave potentials in terms of NHE, all peak potentials were measured by assigning the half-wave potential of DPA$^+$/DPA a value of +1.21 V vs NHE. This value was obtained by using ferrocene, which is known to have $E_{1/2} = 0.400$ V vs NHE.[20] Problems associated with under- or overcompensated solution resistance were avoided by adjusting the IR compensation so that DPA$^+$/DPA cyclic voltammograms showed a peak separation of 60 mV.

Materials. Acetonitrile for the electrochemical studies was "distilled in glass" grade (Burdick and Jackson) and contained 0.005% water. It was purified by refluxing over calcium hydride for several hours, distilled under nitrogen, and stored in a closed glass bottle under nitrogen. The electrolytes for the electrochemical measurements, Et$_4$NCl and Bu$_4$NPF$_6$, were obtained from Southwestern Analytical Chemicals. Bu$_4$NPF$_6$ was recrystallized three times from an acetone/ether solution and dried at 130 °C. Et$_4$NCl was recrystallized six times from an ethanol/ether solution. The internal standard, 9,10-diphenylanthracene (DPA), was obtained from Aldrich Chemicals. Neutral alumina (80–225 mesh) was obtained from Fisher Chemical Co. NbCl$_5$ was purchased from Alfa Products. The purity was confirmed by niobium and chloride analysis. Et$_4$NNbCl$_6$, (Et$_4$N)$_2$NbCl$_6$, and NbCl$_4$(MeCN)$_2$ were prepared by published procedures.[13,21] Because all of the investigated compounds were extremely sensitive to air and moisture, the synthesis and subsequent handling of the compounds was done on the high-vacuum manifold and in a nitrogen atmosphere drybox.

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Table I. Electrochemical Data for Niobium Chlorides in Acetonitrile[a]

	Nb(V) + e⁻ → Nb(IV)						Nb(IV) + e⁻ → Nb(III)		
complex	E_{pc}[b]	E_{pa}[b]	ΔE_p[c]	i_{pc}/i_{pa}	$E_{1/2}$[b]	n	E_{pc}[b]	E_{pa}[b]	i_{pa}/i_{pc}
$NbCl_6^-$	0.11	0.17[d]	60	1.0	0.14	0.97	−1.26	−1.15	
$NbCl_5NCMe$	0.53	0.59	60	1.78[c]	0.56	0.48	−0.83	−0.74	0.67[e]

	Nb(IV) − e⁻ → Nb(V)						Nb(IV) + e⁻ → Nb(III)			
complex	E_{pc}[b]	E_{pa}[b]	ΔE_p[c]	i_{pc}/i_{pa}	$E_{1/2}$[b]	n	E_{pc}[b]	E_{pa}[b]	i_{pa}/i_{pc}	n
$NbCl_6^{2-}$	0.11	0.17	60	1.0	0.14		−1.26			
$NbCl_4(NCMe)_2$	1.00	1.06	60	2.0[f]	1.03	0.99	−0.38	−0.27	1.62	1.01

[a] Concentration of electroactive species in the range 1–5 mM; 0.1 M Bu_4NPF_6 used as supporting electrolyte; glassy-carbon electrode used as working electrode; scan rate = 50 mV/s; T = 20 °C. [b] V vs NHE. [c] mV. [d] Scan rate = 200 mV/s. [e] T = 0 °C. [f] Scan rate = 500 mV/s.

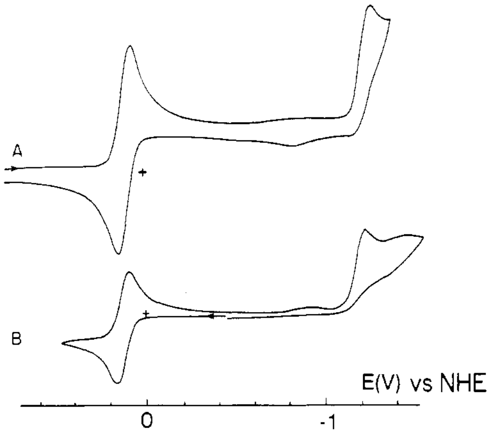

Figure 3. Cyclic voltammograms of (A) 1.4×10^{-3} M Et_4NNbCl_6 and (B) 0.8×10^{-3} M $(Et_4N)_2NbCl_6$, both in 0.1 M Bu_4NPF_6/MeCN solution. Sweep rate = 50 mV/s.

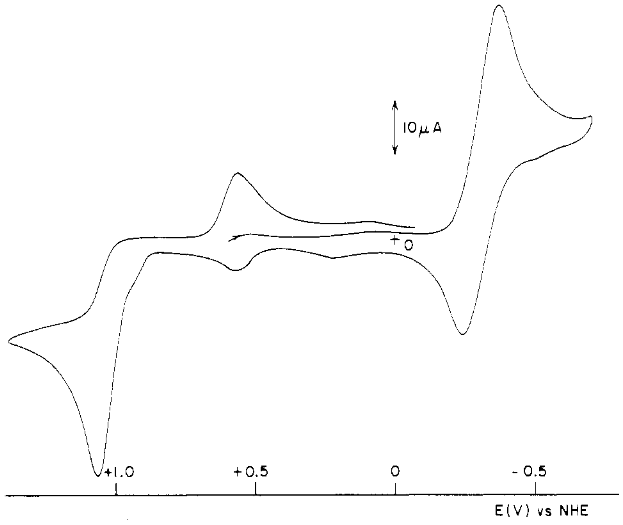

Figure 4. Cyclic voltammogram of $NbCl_4(NCMe)_2$ in 0.1 M Bu_4NPF_6 at a glassy-carbon electrode. Sweep rate = 50 mV/s.

Results and Discussion

The electrochemical properties of Et_4NNbCl_6, $(Et_4N)_2NbCl_6$, $NbCl_5$, and *cis*-$NbCl_4(NCMe)_2$ in acetonitrile/Bu_4NPF_6 solution in the temperature range of −20 to +25 °C were investigated by using a glassy-carbon electrode. When dissolved in acetonitrile, all the aforementioned compounds produce monomeric octahedral species; thus, $NbCl_6^-$, $NbCl_6^{2-}$, $NbCl_5NCMe$, and *cis*-$NbCl_4(NCMe)_2$ are obtained.[22-27] The identity of each of these species in solution was also confirmed by UV/vis spectroscopy. Since some of the species are extremely sensitive to hydrolysis with the small amount of water present in dry acetonitrile, a special vacuum electrochemical cell equipped with an Al_2O_3 column was used for the further removal of water to a level below 10^{-5} M as described in the Experimental Section.

$NbCl_6^-$. The electrochemical properties of $NbCl_6^-$ species in acetonitrile at a glassy-carbon (GC) electrode are relatively simple and well-defined. The cyclic voltammogram of Et_4NNbCl_6 obtained in acetonitrile with Bu_4NPF_6 as the supporting electrolyte is shown in Figure 3A. The voltammogram shows two well-defined reduction waves of approximately the same heights at E_{pc} = 0.11 and −1.26 V vs NHE. As indicated by data contained in Table I, the first electrode process was electrochemically reversible. The peak potential separation, ΔE_p, did not change with the scan rate and the peak current ratio, i_{pc}/i_{pa}, for scan rates between 20 and 100 mV/s was 1.00. A plot of i_{pc} vs the square root of scan rate, $v^{1/2}$, was linear, indicating that the electrode process was diffusion controlled. From this plot the diffusion coefficient, D, was calculated to be 0.8×10^{-5} cm²/s at 20 °C with the Randless–Sevcik equation.[28] Constant-potential coulometry performed at 0 °C at a potential slightly more negative to the first reduction wave (+0.10 V) gave an n value (mol of e/mol of $NbCl_6^-$) of 0.97. This corresponds to the one-electron reduction of $NbCl_6^-$ to $NbCl_6^{2-}$.

The cyclic voltammogram obtained in the solution after electrolysis at 0 °C showed a voltammogram similar to the one obtained before electrolysis except that the first wave involved an oxidation process. The peak current for this oxidation wave was approximately of the same magnitude as was the peak current for the reduction wave before electrolysis, indicating that the concentration of the hexachloroniobate species did not change during the electrolysis.

The magnitude of the second reduction wave at E_{pc} = −1.15 V was approximately the same as that of the first reduction wave. However, contrary to the first wave, no oxidation wave was observed upon the potential reversal for the slow scan rates. At fast scan rates (200 mV/s), a small anodic wave was observed at E_{pc} = −1.15, indicating that the second wave involves a one-electron reduction process followed by a fast chemical reaction (EC mechanism) rather than an irreversible electron-transfer process.

$$NbCl_6^{2-} + e^- \rightarrow NbCl_6^{3-} \rightarrow ?$$

The electrochemically generated $NbCl_6^{3-}$ species are not stable on the time scale of the cyclic voltammetry experiment and give an unidentified product.

$NbCl_6^{2-}$. The cyclic voltammogram of $(Et_4N)_2NbCl_6$ obtained in acetonitrile with Bu_4NPF_6 as the supporting electrolyte on a GC electrode is similar to the voltammogram of the $NbCl_6^-$ species except that the first wave is an oxidation process corresponding to the one-electron oxidation of $NbCl_6^{2-}$ to $NbCl_6^-$ (Figure 3B).

$NbCl_4(CH_3CN)_2$. Figure 4 shows the cyclic voltammogram of $NbCl_4(MeCN)_2$ obtained in 0.1 M Bu_4NPF_6/MeCN. The po-

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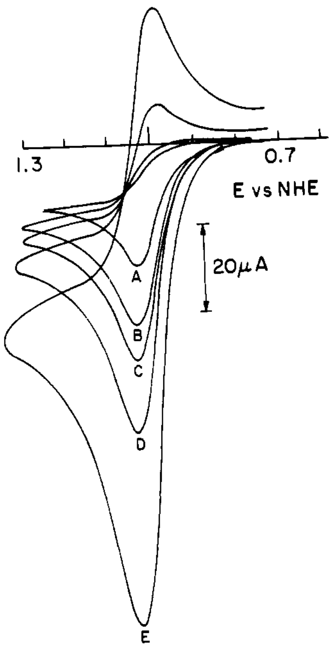

Figure 5. Effect of scan rate on the reversibility of the anodic electrode process $NbCl_4(NCMe)_2 - e^- \rightarrow NbCl_4(NCMe)_2^+$. Scan rates are (A) 20 mV/s, (B) 50 mV/s, (C) 100 mV/s, (D) 200 mV/s ($i_{pc}/i_{pa} = 2.5$), and (E) 500 mV/s ($i_{pc}/i_{pa} = 2.0$); $T = 20$ °C. Values of i_{pc}/i_{pa} were used to estimate the rate of the chemical reaction following the electron-transfer step.

tential was initiated at 0.8 V vs NHE and first scanned in a negative direction. The voltammogram shows a reduction wave at $E_{pc} = -0.38$ V and an oxidation wave at $E_{pa} = +1.06$ V. As indicated by the data in Table I, the reduction process at $E_{pc} = +0.38$ V is quasi-reversible, since the peak potential separation, ΔE_p, was larger than 60 mV and increased at faster sweep rates.[29] The ratio of the cathodic peak current to the anodic peak current, i_{pc}/i_{pa}, was greater than 1, indicating that the reduction product was not stable on a time scale of the cyclic voltammetry experiment.

Assuming that the diffusion coefficients for $NbCl_4(NCMe)_2$ and $NbCl_6^-$ are similar, a comparison of their peak currents, i_{pc}, for the first reduction process indicates that the reduction process at $E_{pc} = -0.38$ V could be assigned to a one-electron-transfer process. Controlled-potential electrolysis conducted at −1.1 V gave an *n* value of 0.99. Therefore, the reduction process at $E_{pc} = -0.38$ V could be assigned to a one-electron reduction of Nb(IV) to Nb(III). However, Nb(III) species $NbCl_4(NCMe)_2^-$ formed upon reduction of $NbCl_4(NCMe)_2$ was unstable on the time scale of the coulometry experiment.

$$NbCl_4(NCMe)_2 + e^- \rightarrow NbCl_4(NCMe)_2^- \rightarrow ?$$

Similarly, on the basis of constant-potential electrolysis ($n = 1.01$) the anodic wave at $E_{pa} = 1.02$ V was assigned to the one-electron oxidation of $NbCl_4(NCMe)_2$ to $NbCl_4(NCMe)_2^+$. The product of the oxidation was unstable on the time scale of the CV experiment, and no cathodic current was observed on the reverse negative scan at scan rates below 50 mV/s. At faster scan rates, however, cathodic currents were observable, and the ratio i_{pa}/i_{pc} increased with increasing sweep rate. The peak potential separation, ΔE_p, was 60 mV, indicating that the electron-transfer process was electrochemically reversible. The effect of the sweep rate on i_{pc} is shown in Figure 5.

It can be seen from Figure 5 that the peak current ratio, i_{pa}/i_{pc}, reaches a value of about 2 at 500 mV/s. The values obtained for the peak current ratio at different scan rates were used to estimate the rate constant, *k*, for the chemical reaction following the oxidation step.[30] Since the best estimates of *k* are obtained for the peak current ratios between 2.5 and 1.25, only the fast scan rates of 200 and 500 mV/s were used. The value of *k* was estimated to be 1.1 s^{-1} at 25 °C.

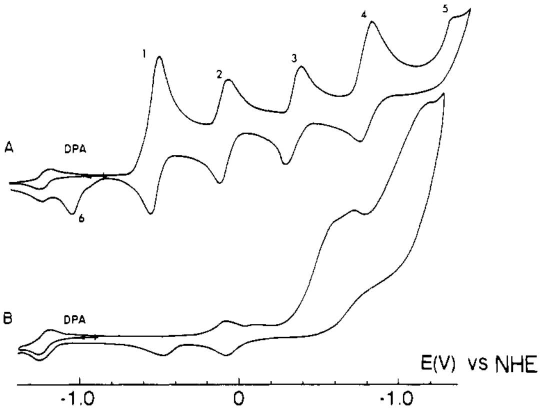

Figure 6. Cyclic voltammograms of 1.0×10^{-3} M solutions of $NbCl_5$ in 0.1 M Bu_4NPF_6/MeCN. The solutions were (A) 5×10^{-3} M in H_2O and (B) 10^{-5} M in H_2O.

The cyclic voltammogram in Figure 4, in addition to the two large oxidation and reduction waves, also exhibits a small wave at $E_{pc} = 0.53$ V, a position identical with the one of the authentic samples of $NbCl_5NCMe$. This wave is not observed if the potential is initiated at 0.8 V and scanned in a negative direction. However, it is observable if the potential is first swept in a positive direction and reversed at a potential slightly more positive than the oxidation peak. This cathodic wave at 0.53 V increased in size upon repetitive sweeping between 1.2 and 0.4 V. This indicates that $NbCl_5NCMe$ is formed from $NbCl_4(NCMe)_2^+$ by a chemical reaction that follows the electron-transfer step.

$$NbCl_4(NCMe)_2 - e^- \rightarrow NbCl_4(NCMe)_2^+ \xrightarrow{Cl^-} NbCl_5NCMe + ?$$

This was also confirmed by the partial oxidation of the $NbCl_4(NCMe)_2$ solution at a potential of 1.2 V. A voltammogram obtained after oxidation reveals the presence of $NbCl_5NCMe$. We do not know with certainty what the source of the Cl^- ions is in the chemical step. It might involve the reaction of $NbCl_4(NCMe)_2^+$ with an impurity in acetonitrile or with the unoxidized starting material $NbCl_4(NCMe)_2$.

The cyclic voltammogram of $NbCl_4(NCMe)_2$ in 0.1 M Et_4NCl/MeCN is identical with that of $NbCl_6^{2-}$ (Figure 3B), indicating that, with an excess of Cl^-, $NbCl_4(NCMe)_2$ forms $NbCl_6^{2-}$.

$NbCl_5CH_3CN$. In comparison to that of $NbCl_6^-$, the electrochemical behavior of $NbCl_5NCMe$ in acetonitrile is rather complex and depends upon the purity of the solvent, temperature, and the length of time that the original $NbCl_5$ was dissolved in MeCN. When normally dry MeCN is used, containing 5×10^{-3} M H_2O, a cyclic voltammogram shown in Figure 6B is obtained. This voltammogram is very similar to that of $NbOCl_3(NCMe)_2$. It appears that $NbCl_5$ reacts with the small amount of water in dry acetonitrile and produces $NbOCl_3(NCMe)_2$. The investigated solution was 10^{-3} M in $NbCl_5$, and therefore, an adequate amount of water was present in dry acetonitrile. In order to prevent the hydrolysis reaction of $NbCl_5$ in dry acetonitrile, we have used a special vacuum electrochemical cell equipped with an Al_2O_3 column in which the concentration of water in acetonitrile was lowered to below 10^{-5} M. In this "superdry" acetonitrile, the voltammogram of $NbCl_5$ shown in Figure 6A is obtained. The cyclic voltammogram displays five reduction waves and a new oxidation wave (6), which was observed on the reverse scan.

One would be tempted to assign these reduction waves to the stepwise reduction of $NbCl_5NCMe$ to Nb(IV), Nb(III), Nb(II), Nb(I), etc. However, this is not the case. When one compares

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(29) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

(30) Nicholson, R. S.; Shain, J. *Anal. Chem.* **1964**, *36*, 706.

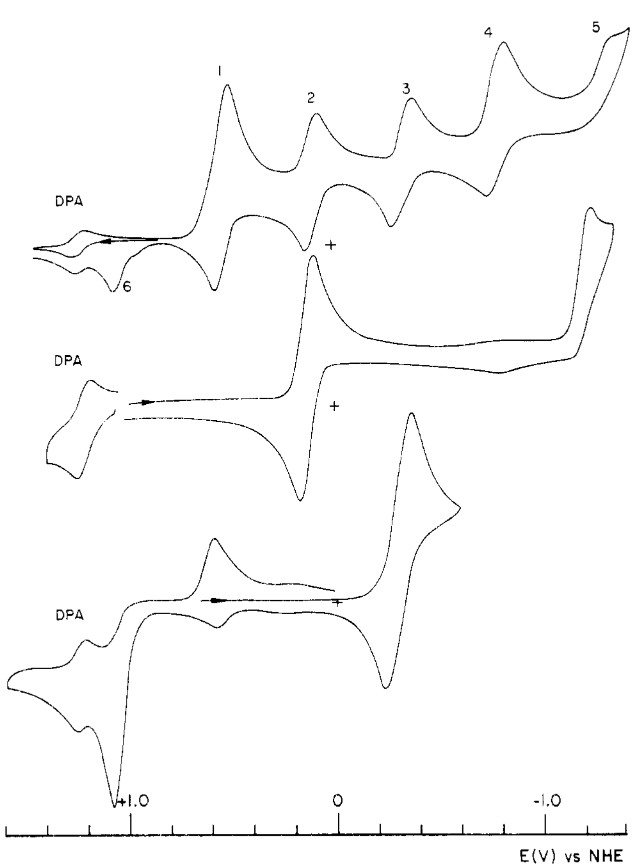

Figure 7. Comparison of cyclic voltammograms of (top) $NbCl_5NCMe$, (middle) $NbCl_6^-$, and (bottom) $NbCl_4(NCMe)_2$. Sweep rate = 50 mV/s; $T = 0$ °C.

cyclic voltammograms of $NbCl_6^-$ and $NbCl_4(NCMe)_2$ to that of $NbCl_5NCMe$ (Figure 7), waves 2 and 5 can be assigned to the reduction of $NbCl_6^-$ and waves 3 and 6 to the reduction and oxidation of $NbCl_4(NCMe)_2$, respectively. Waves 1 and 4 we have assigned to the reduction of $NbCl_5NCMe$ to $NbCl_5NCMe^-$ and to $NbCl_5NCMe^{2-}$. All six assignments are shown as follows:

wave 1: $NbCl_5NCMe + e^- \rightarrow NbCl_5NCMe^-$

wave 2: $NbCl_6^- + e^- \rightarrow NbCl_6^{2-}$

wave 3: $NbCl_4(NCMe)_2 + e^- \rightarrow NbCl_4(NCMe)_2^-$

wave 4: $NbCl_5NCMe^- + e^- \rightarrow NbCl_5NCMe^{2-}$

wave 5: $NbCl_6^{2-} + e^- \rightarrow NbCl_6^{3-}$

wave 6: $NbCl_4(NCMe)_2 - e^- \rightarrow NbCl_4(NCMe)_2^+$

$NbCl_6^-$ and $NbCl_4(NCMe)_2$ could be formed from $NbCl_5NCMe$ either by a chemical reaction that precedes the electrochemical step (CE mechanism) or by a chemical reaction that follows the electrochemical step (EC mechanism).

It was previously postulated by Nyholm[31] and Gutman,[32] on the basis of conductivity studies, that $NbCl_5$ self-ionizes in acetonitrile according to the reaction

$$2NbCl_5 \rightleftarrows NbCl_4^+ + NbCl_6^-$$

The possibility also exists that $NbCl_6^-$ is formed by the reaction of $NbCl_5NCMe$ with free Cl^-, generated either by the hydrolysis of $NbCl_5NCMe$ with traces of water present in acetonitrile or by the reduction of $NbCl_5NCMe$ with acetonitrile or impurities in acetonitrile. To establish whether or not the hydrolysis reaction was responsible for the formation of $NbCl_6^-$, we have subsequently added a small amount of water into a superdry solution of $NbCl_5$ in MeCN until the $H_2O/NbCl_5$ ratio was 1 and recorded a cyclic voltammogram after each addition of water. Cyclic voltammograms clearly showed that as the amount of water was increased, the waves resulting from $NbCl_5NCMe$ and $NbCl_6^-$ decreased until they finally disappeared. Simultaneously, two new waves at $E_{pc} = -0.7$ and -1.2 V appeared. When the equimolar amount of water was added, a voltammogram identical with the one shown in Figure 6B was obtained. A similar voltammogram was also obtained for the original sample of $NbOCl_3$. This proves that $NbCl_6^-$ is not formed by partial hydrolysis of $NbCl_5NCMe$.

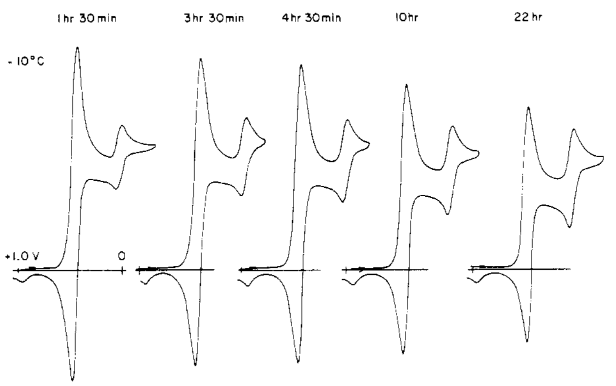

Figure 8. Cyclic voltammograms of $NbCl_5$ in Bu_4NPF_6/MeCN at -10 °C obtained at various time intervals.

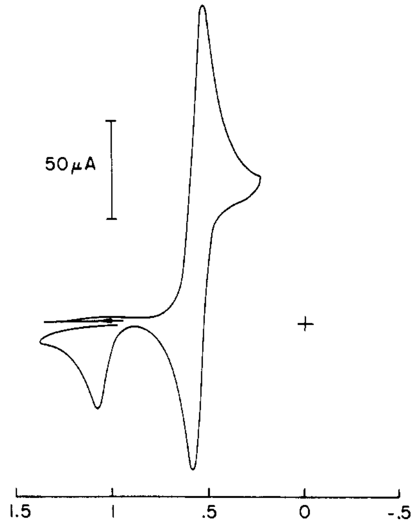

Figure 9. Cyclic voltammogram of $NbCl_5$ in 0.1 M Bu_4NPF_6/MeCN. Sweep rate = 50 mV/s; $T = +5$ °C. Switching potentials used were +1.35 and +0.25 V.

In order to obtain more information about the self-ionization reaction of $NbCl_5NCMe$ in acetonitrile, we recorded voltammograms of $NbCl_5$ in acetonitrile as a function of time and temperature. Figure 8 shows the voltammograms obtained at -10 °C at various time intervals. Trace A was obtained $1^1/_2$ h after dissolving $NbCl_5$ in acetonitrile. A small cathodic wave due to $NbCl_6^-$ at $E_{pc} = 0.11$ V and a very small anodic wave at $E_{pa} = 1.06$ V due to $NbCl_4(NCMe)_2$ can be observed. The cathodic wave increased in size with time while simultaneously the wave due to $NbCl_5NCMe$ at $E_{pc} = 0.53$ V decreased. However, this increase in the $NbCl_6^-$ wave and decrease in the $NbCl_5NCMe$ wave were less than 5% after $3^1/_2$ h. At room temperature the increase in the $NbCl_6^-$ wave was more pronounced, and after 3 h the wave due to $NbCl_6^-$ was of approximately the same magnitude as the $NbCl_5NCMe$ wave. Contrary to the cathodic wave, the anodic wave at $E_{pa} = 1.06$ V did not increase during 22 h. This ruled out the possibility of formation of $NbCl_4(NCMe)_2 + Cl^-$ by chemical reduction of $NbCl_5NCMe$ with acetonitrile or impurity in acetonitrile. Upon cooling of the $NbCl_5NCMe$ solution from +20 to -20 °C, the $NbCl_6^-$ cathodic wave did not decrease and the $NbCl_5NCMe$ wave did not increase to its original

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[31] Kepert, D. L.; Nyholm, R. S. *J. Chem. Soc.* **1965**, 2871.

[32] Gutman, V. *Coordination Chemistry in Non-Aqueous Solutions*; Springer: Wien, 1968.

Table II. Effect of Temperature on Peak Current Ratio for the Process $NbCl_5NCMe + e^- \rightarrow NbCl_5NCMe^-$

temp, °C	i_{pc}/i_{pa}	temp, °C	i_{pc}/i_{pa}
10	1.78	−10	1.18
5	1.69	−20	1.00
0	1.49		

value, indicating that the self-ionization reaction is not reversible. Our electrochemical investigation of $NbCl_4(NCMe)_2$ showed that $NbCl_4(NCMe)_2^+$ is not stable in acetonitrile solution even on the time scale of the CV experiment and forms an unidentified product. Therefore we propose that $NbCl_6^-$ species are formed by the self-ionization of $NbCl_5NCMe$ as follows:

$$2NbCl_5NCMe \rightarrow NbCl_6^- + NbCl_4(NCMe)_2^+$$

$$NbCl_4(NCMe)_2^+ \xrightarrow{k} \text{product?}$$

Due to the instability of $NbCl_4(NCMe)_2^+$ the overall self-ionization is chemically irreversible. This dissociation reaction is relatively slow and could be quenched at a lower temperature.

We have further established that both $NbCl_6^-$ and $NbCl_4(NCMe)_2$ are formed by a chemical reaction that follows the electrochemical step (CE mechanism). Figure 9 shows a cyclic voltammogram of $NbCl_5$ solution in acetonitrile in the potential range between +1.35 and +0.25 V, where both $NbCl_5NCMe$ and $NbCl_4(NCMe)_2$ are electroactive. The potential was initiated at +0.75 V and scanned first in a positive direction. No anodic peak due to the oxidation of $NbCl_4(NCMe)_2$ was observed, confirming that $NbCl_4(NCMe)_2$ was not initially present in the solution. However, this anodic peak was observed when the potential was scanned in the negative direction and reversed at +0.25 V, which is slightly more negative than the first reduction peak.

For the reduction peak at $E_{pc} = 0.53$ V the current ratio, i_{pc}/i_{pa}, was larger than 1.0. At lower temperatures this ratio decreased and eventually reached a value of 1.0 at −20 °C (see Table II). The reduction wave at $E_{pc} = +0.53$ V was assigned to a one-electron reduction process:

$$NbCl_5NCMe + e^- \rightarrow NbCl_5NCMe^-$$

The evidence for this includes the cyclic voltammetric $i_p/(v^{1/2}C)$ value, obtained at −20 °C, which is very near that for the reduction of $NbCl_6^-$, a coulometrically known one-electron process. The electrochemially generated $NbCl_5NCMe^-$ is not stable and undergoes further chemistry and produces $NbCl_4(NCMe)_2$. Low-temperature cyclic voltammetry has shown that as the temperature is decreased, peaks 2, 3, 5, and 6 become smaller in comparison to peaks 1 and 4. This is illustrated in Figure 10, which contains the voltammograms of $NbCl_5NCMe$ at 0 and −20 °C.

Mechanism of Chemical Reactions That Follow the Electrochemical Reduction of $NbCl_5NCMe$. Cyclic voltammetry showed that, after the initial one-electron reduction of $NbCl_5NCMe$, the product, $NbCl_5NCMe^-$, is not stable and reacts with the starting material to produce $NbCl_6^-$ and $NbCl_4(NCMe)_2$. This was confirmed by constant-potential coulometry (Figure 11). In order to minimize the formation of $NbCl_6^-$ by self-ionization, electrolysis was performed at −10 °C. Trace B shows a cyclic voltammogram of $NbCl_5NCMe$ after reduction of 0.45 V. Peaks 1 and 4, which are due to the reduction of $NbCl_5NCMe$, have disappeared while peaks 2, 3, 5, and 6 have increased in size. They are all of approximately the same height, and their peak current, i_p, is about half as large as the peak current for the first wave before electrolysis. Only 0.5 mol of e/mol of $NbCl_5NCMe$ was used. The following mechanism is proposed for the first reduction process:

$$\text{E} \quad NbCl_5NCMe + e^- \rightarrow NbCl_5NCMe^-$$

$$\text{C} \quad NbCl_5NCMe^- + NbCl_5NCMe \xrightarrow{k} NbCl_6^- + NbCl_4(NCMe)_2$$

After the initial charge-transfer step, a secondary chemical process was consuming the starting material $NbCl_5NCMe$. The proposed reaction scheme is an example of case IIb as treated by Bard and Geske when the rate constant of the following reaction, k, is large:[33]

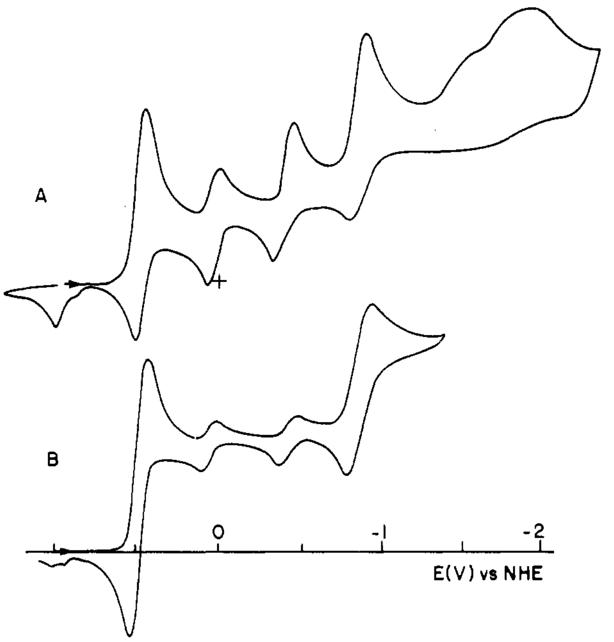


Figure 10. Cyclic voltammograms of $NbCl_5$ in 0.1 M Bu_4NPF_6/MeCN at (A) 0 °C and (B) −20 °C. Sweep rate = 50 mV/s.

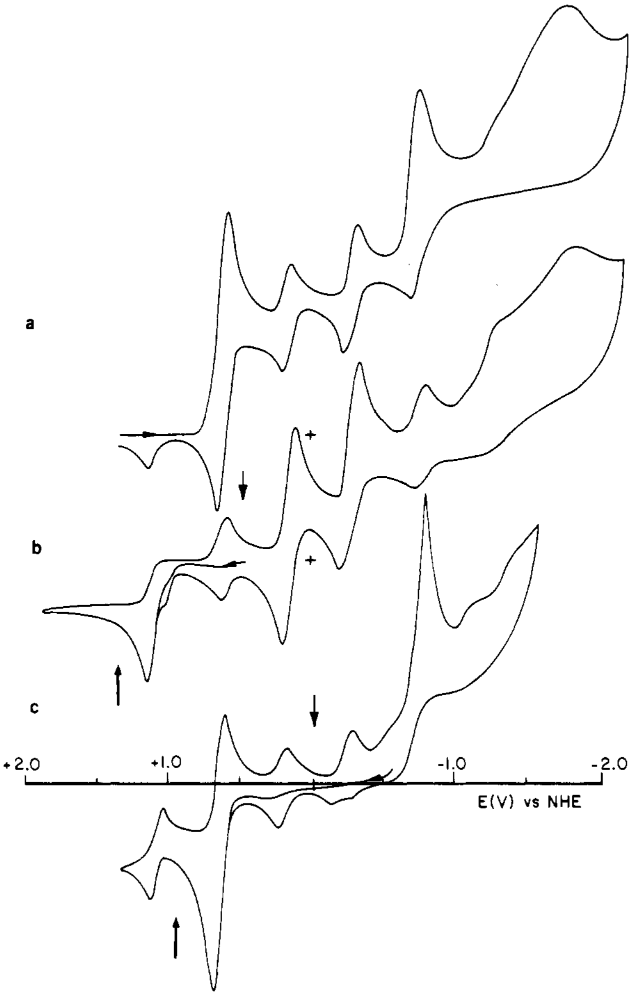


Figure 11. Cyclic voltammograms of 2.0×10^{-3} M $NbCl_5$ in 0.1 M Bu_4NPF_6/MeCN at 0 °C (a) before electrolysis, (b) after electrolysis at +0.45 V, and (c) after electrolysis at 0.0 V.

$$O + ne^- \rightarrow R$$

$$R + O \xrightarrow{k} P$$

Scheme I

E $NbCl_5NCMe + e \longrightarrow NbCl_5NCMe^-$

C $NbCl_5NCMe^- + NbCl_5NCMe \longrightarrow NbCl_6^- + NbCl_4(NCMe)_2$

E $NbCl_6^- + e \longrightarrow NbCl_6^{2-}$

C $NbCl_6^{2-} + NbCl_4(NCMe)_2 \longrightarrow NbCl_5NCMe^-$

This type of mechanism can give rise to a value of n_{app} (apparent number of faradays per mole) that approaches n if k is very small and to a value of $n_{app} = n/2$ when k is very large. For intermediate values of k, n_{app} lies between n and $n/2$. In that case the electrolyzed solution will contain both R and P.

Trace C is a cyclic voltammogram obtained after further reduction at 0.0 V, at which potential $NbCl_6^-$ is reduced. Instead of obtaining an anodic peak due to the presence of $NbCl_6^{2-}$, an anodic peak at $E_{pa} = 0.59$ V is obtained that is characteristic of $NbCl_5NCMe^-$ species. At the same time peaks 2 and 3 disappeared although the applied potential was not negative enough to reduce $NbCl_4(NCMe)_2$ (peak 3). This implies that $NbCl_4(NCMe)_2$ undergoes a chemical reaction with electrochemically generated $NbCl_6^{2-}$. Again approximately 0.5 mol of e/mol of $NbCl_6^-$ was consumed.

The second reduction indicated by the arrow in Figure 11c has been assigned to the following reaction sequence:

$$NbCl_6^- \xrightarrow{+e^-} NbCl_6^{2-} \xrightarrow{+NbCl_4(NCMe)_2} 2NbCl_5NCMe^-$$

The small peaks in Figure 11c at $E_{pc} = -0.38$ V and $E_{pa} = 1.0$ V correspond to the $NbCl_4(NCMe)_2$ species, while a peak at $E_{pc} = 0.17$ V corresponds to $NbCl_6^-$ species. They are probably produced by the similar EC mechanism during the CV scan.

$$NbCl_5NCMe^- - e^- \rightarrow NbCl_5NCMe \xrightarrow{+NbCl_5NCMe^-} NbCl_4(NCMe)_2 + NbCl_6^-$$

The electrolysis experiments show that the reduction product of $NbCl_5NCMe$ depends on the selection of the potential used for the electrolysis. If $NbCl_5NCMe$ is reduced at a potential more negative than the $E_{1/2}$ for the reduction of $NbCl_5NCMe$ but below $E_{1/2}$ for the reduction of $NbCl_6^-$ (in the +0.5 to +0.3 V range), the reduction product is a 1:1 mixture of $NbCl_4(NCMe)_2$ and $NbCl_6^-$. If instead, the potential chosen for the reduction is more negative than $E_{1/2}$ for the reduction of $NbCl_6^-$ (in the +0.2 to −0.15 V range), then the reduction will proceed by an ECEC mechanism (Scheme I) and the reduction product is $NbCl_5NCMe^-$.

Similar to the reduction process, bulk reoxidation of electrochemically generated $NbCl_5NCMe^-$ at 0.8 V gave an n_{app} value of 0.46. The cyclic voltammogram of the solution obtained after oxidation was identical with the one shown in Figure 11b; i.e., the voltammogram displayed waves characteristic of $NbCl_4(NCMe)_2$ and $NbCl_6^-$, not of $NbCl_5NCMe$ as would be expected. The reaction scheme probably involves the following EC mechanism:

$$NbCl_5NCMe^- \xrightarrow{-e^-} NbCl_5NCMe \xrightarrow{+NbCl_5NCMe^-} NbCl_4(NCMe)_2 + NbCl_6^-$$

Further oxidation at a more positive potential ($E = 1.3$ V) involved an additional 0.5 mol of e/mol of Nb for the oxidation of $NbCl_4(NCMe)_2$ to $NbCl_4(NCMe)_2^+$. The cyclic voltammogram obtained after electrolysis closely resembled that of $NbCl_5NCMe$; thus, electrochemically generated $NbCl_4(NCMe)_2^+$ reacts with $NbCl_6^-$ and produces $NbCl_5NCMe$.

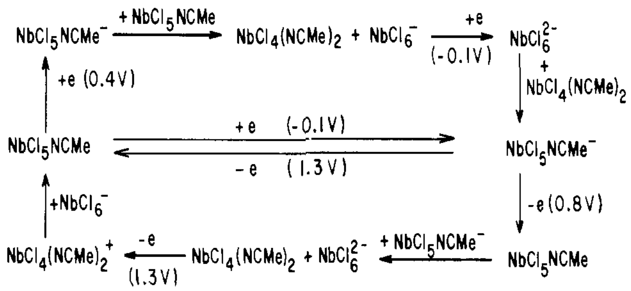
$$NbCl_4(NCMe)_2 \xrightarrow{-e^-} NbCl_4(NCMe)_2^+ \xrightarrow{+NbCl_6^-} 2NbCl_5NCMe$$

The overall redox sequence of $NbCl_5NCMe$ is shown in Scheme II. The chemical steps are simple chloride ligand transfer reactions that are induced by the electron-transfer step. As the oxidation state of niobium is reduced from 5+ to 4+, the chloride ligand acceptor strength of the niobium atom is reduced. This explains the chemical steps that followed the initial electron-transfer process, although the halides $NbCl_6^{2-}$, $NbCl_5NCMe^-$, and $NbCl_4(NCMe)_2$ are stable in acetonitrile solution when present by themselves. By proper choice of the reduction and oxidation potentials, the overall redox reaction

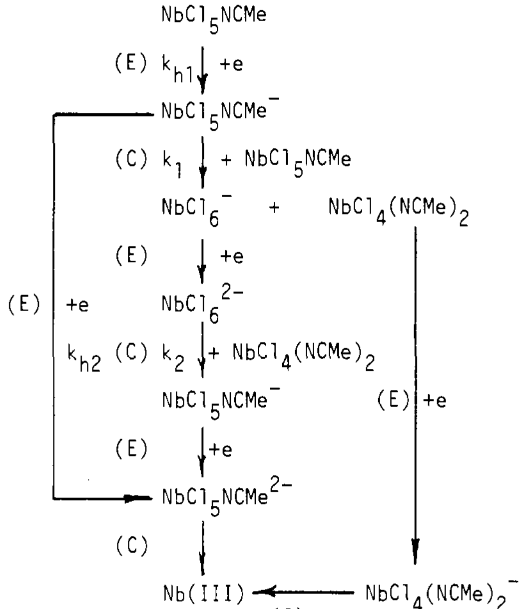
$$NbCl_5NCMe \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} NbCl_5NCMe^-$$

can be made chemically reversible although the reaction mechanism involves the formation of intermediate species as depicted in Scheme II.

Scheme II



Scheme III



Nb(IV) to Nb(III) Reduction Process. Further reduction of $NbCl_5NCMe^-$, $NbCl_6^{2-}$, and $NbCl_4(NCMe)_2^-$ generates Nb(III) species, but they are not stable on a time scale of electrolysis and undergo further chemistry. Using CV, we were not able to establish with certainty whether or not the electrogenerated Nb(III) species react with MeCN and produce a dimer $(MeCN)_2Cl_4NbNC(Me){=}C(Me)NNbCl_4(NCMe)_2^{2-}$ since its diffusion coefficient and therefore i_p were small in comparison to those of the starting material.

While the electrochemical reductions of $NbCl_6^-$ and $NbCl_4(NCMe)_2$ involve simple EE and E mechanisms, respectively, the reduction of $NbCl_5NCMe$ to Nb(III) species, depending on the temperature and applied potential, may proceed simultaneously by three different electrochemical–chemical (EC) reaction series. As is visible from the cyclic voltammogram of $NbCl_5NCMe$ (Figure 6B) and as shown in Scheme III, the first step involves the reduction of $NbCl_5NCMe$ to $NbCl_5NCMe^-$. Since the heterogenous rate constant k_{h2} for the second reduction process $NbCl_5NCMe^- + e^- \rightarrow NbCl_5NCMe^{2-}$ is rather small, and it can

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(33) Geske, D. H.; Bard, A. J. *J. Phys. Chem.* **1959**, *63*, 1057.

be made even smaller if the reduction is performed on the rising portion of the $NbCl_5NCMe^-$ peak, some of the $NbCl_5NCMe^-$ may survive long enough to participate in the homogeneous chemical reaction

$$NbCl_5NCMe^- + NbCl_5NCMe \xrightarrow{k} NbCl_6^- + NbCl_4(NCMe)_2$$

In that case the conversion of $NbCl_5NCMe$ to Nb(III) species proceeds simultaneously by three different electrochemical–chemical reaction pathways. As shown in Scheme III, the first reaction series involves an EEC mechanism, the second is an ECEC process, and the third involves an ECECEC mechanism. At a lower temperature and at a more negative potential, the EEC mechanism is predominant, while at a higher temperature (k_1 and k_2 are larger) and a less negative potential (k_{h2} is smaller), the ECECEC and ECEC mechanisms become significant.

Therefore, the choice of the pathway that produces Nb(III) species is determined by the temperature and by the applied potential. As was pointed out earlier by Walton,[34] the occurrence of several reaction pathways within the same system is very uncommon for inorganic species.

Conclusions

Niobium chlorides $NbCl_6^-$, $NbCl_6^{2-}$, $NbCl_4(NCMe)_2$, and particularly $NbCl_5NCMe$ are sensitive to hydrolysis with the small amount of water present in a "dry" electrolyte solution, even in a vacuum electrochemical cell, in which they produce oxo species. In a rigorously dry solution, purified directly in a vacuum electrochemical cell, this hydrolysis can be avoided, and stable millimolar solutions of niobium halides can be obtained, enabling the use of constant-potential electrolysis for the electrochemical generation of low-oxidation-state species in solution.

In acetonitrile solution $NbCl_6^-$ and $NbCl_5NCMe$ can be reduced by two one-electron reductions to Nb(IV) and Nb(III) species. The first reduction, Nb(V) → Nb(IV), is chemically reversible, and a stable solution of $NbCl_6^{2-}$ and $NbCl_5NCMe^-$ can be generated by constant-potential electrolysis. While $NbCl_6^{2-}$ can also be obtained by the reaction of $NbCl_4(NCMe)_2$ with excess Cl^-, $NbCl_5NCMe^-$ has not been previously prepared. At a higher temperature the one-electron reduction of $NbCl_5NCMe$ to $NbCl_5NCMe^-$ is followed by a coupled chemical reaction (EC mechanism), but the product of the electrochemical reduction is critically dependent upon the potential used for the reduction. Either $NbCl_5NCMe^-$ or a mixture of $NbCl_6^-$ and $NbCl_4(NCMe)_2$ can be generated. Similarly, the product obtained by bulk reoxidation of electrochemically generated $NbCl_5NCMe^-$ depends on the potential used for oxidation. The chemical steps in the EC mechanism involve the transfer of Cl^- from $NbCl_5NCMe^-$ to $NbCl_5NCMe$. Further reduction of Nb(IV) species $NbCl_6^{2-}$, $NbCl_5NCMe^-$, or $NbCl_4(NCMe)_2$ generates Nb(III) species, but they are not stable even on the time scale of the CV experiment. The reduction of $NbCl_5NCMe$ directly to Nb(III), depending on the temperature and the applied potential, may proceed simultaneously by three different electrochemical–chemical reaction pathways.

Inspection of Table I shows that the Nb(V) state is stabilized by electron-rich Cl^- ligands relative to MeCN. The $NbCl_4(NCMe)_2^+$ species is a thermodynamically more potent oxidizing agent, by 0.5 V, compared to $NbCl_5NCMe$, and by 0.9 V, compared to $NbCl_6^-$. Replacement of coordinated MeCN by Cl^- makes the reduction Nb(V) → Nb(IV) more difficult by approximately 0.5 V. A similar trend is observed for the Nb(IV)/Nb(III) couple. As was reported earlier, the electrochemical data are in good agreement with the model of ligand additivity and with the Fenske–Hall MO calculation.[15]

It is somewhat surprising to observe that $NbCl_5NCMe$ and particularly $NbCl_4(NCMe)_2^+$ are good oxidizing agents since the most common and stable oxidation state of niobium is 5+. It appears that strong π-donors such as O^{2-}, F^-, and Cl^- stabilize the 5+ state by transferring the electron density to Nb^{5+}. Therefore, a choice of suitable ligands should afford the formation of thermodynamically stable low-oxidation-state complexes of niobium.

This work also demonstrates the feasibility of CV to characterize various niobium species in solution. This is of particular importance since Nb(V) complexes exhibit featureless electronic spectra, and many of the niobium low-oxidation-state species are paramagnetic, thus hindering characterization by NMR.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Support from NSF Grant No. PRM-8111214 for the purchase of the Varian 2300 UV/vis/nir spectrophotometer is also gratefully acknowledged.

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[34] Brant, P.; Salmon, D. J.; Walton, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 4424.

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Preparation and Reactions of $(H_2O)_5CrCH_2CH_2SO_3^+$

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The preparation and reactions of the organochromium(III) complex $(H_2O)_5CrCH_2CH_2SO_3^+$ have been studied. This species can be prepared and easily separated from other products by the reaction of aqueous Cr(II) and $BrCH_2CH_2SO_3^-$. The kinetics of the acidolysis and Hg^{2+} reactions of $(H_2O)_5CrCH_2CH_2SO_3^+$ have been studied. The acidolysis is about 100 times slower than that of $(H_2O)_5CrCH_2CH_2CH_3^{2+}$, but the reactions with Hg^{2+} have quite similar rates for the two complexes. In the former case at least 45% of the product is $(H_2O)_5CrO_3SCH_2CH_2Hg^{3+}$. It is shown that $(H_2O)_5CrCH_2CH_2SO_3^+$ can be used as a spectrophotometric analytical probe for mercury(II) and its monoalkyl complexes.

Introduction

It is known[1] that Cr(II) reacts with organic halides (RX) to produce organochromium complexes of varying stability as shown in eq 1.

$$Cr(OH_2)_6^{2+} + RX \rightarrow (H_2O)_5CrR^{2+} + (H_2O)_5CrX^{2+} \quad (1)$$

The organochromium(III) complexes are potentially useful preparative reagents for chromium(III) complexes because they are so much more substitution labile than is normal for chromium(III).[2-4] A preparative limitation of eq 1 is that the two

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[2] Bakac, A.; Espenson, J. H.; Miller, L. P. *Inorg. Chem.* **1982**, *21*, 1557.

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[4] Sisley, M. J.; Jordan, R. B. *Inorg. Chem.* **1987**, *26*, 2833.

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