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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[1] Espenson, J. H. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 1.

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

[3] Sisley, M. J.; Jordan, R. B. *Inorg. Chem.* **1987**, *26*, 273.

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

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Table I. Product Yield Studies at 25 °C in 0.05 M $HClO_4$/0.2–0.3 M $NaClO_4$

reactant concn, M		reacn	% yield[a] of
[Cr(II)]	$[BrCH_2CH_2SO_3^-]$	time, h	$CrCH_2CH_2SO_3^+$
0.20	0.098	17	25.4
0.19[b]	0.084	23	20.2
0.35	0.088	21	46.0
0.49	0.25	18.5	39.7

[a] Based on the organic reactant and determined from total Cr as $CrCH_2CH_2SO_3^+$ after ion-exchange separation. [b] Reaction in the presence of the zinc metal reducing agent used to produce Cr(II) from Cr(III).

dipositive products can be difficult to separate. In order to find a more readily available organochromium complex, the reaction of chromium(II) and $BrCH_2CH_2SO_3^-$ has been studied. Because of its low charge, the product of interest, $(H_2O)_5CrCH_2CH_2SO_3^+$, should be easily separated from $(H_2O)_5CrBr^{2+}$ and any air oxidation products of chromium(II).

A further point of interest with this system is that there have been few complexes prepared in which the organic function has a potential site for coordination. The examples that are available are with CH_2CN,[5] CH_2CO_2H,[6] and $CH_2C(O)NH_2$.[7] A problem with these systems is that a significant amount of product has chromium(III) on the substituent, such as $(H_2O)_5CrNCCH_3^{3+}$. This reduces the yield and therefore the general utility of this as a preparative method. This may not be a problem with ethanesulfonate because the sulfonate substituent is not on the same methylene group as the Br in the starting material. These advantages and possibilities and the properties of the organochromium product are the subject of this study.

Results

Preparation and Characterization. Preliminary experiments confirmed that the reaction of Cr(II) and $NaO_3SCH_2CH_2Br$ in aqueous perchloric acid produces a golden-yellow species which elutes easily from Dowex 50W-X8 with 0.05M $HClO_4$/0.1 M $NaClO_4$. This product has properties typical of an organochromium(III) complex as described below.

Studies on the yield of the organochromium(III) product are summarized in Table I. The results in Table I indicate that better yields are obtained with higher concentrations of chromium and with chromium(II) in stoichiometric excess. This occurs because the reaction does not go to completion in the reaction times used. Much longer times were not taken, partly as a matter of convenience and partly because of the aquation of the product discussed below. For the first experiment in Table I, the yield of bromide ion was determined as AgBr to be 26.4% of the organic reactant. This agrees with the amount of organochromium(III) product and is consistent with the expectation that the bromide is abstracted from $BrCH_2CH_2SO_3^-$.

The electronic spectrum of the golden-yellow product has absorbance maxima at 526, 396, and 267 nm with molar absorptivity coefficients of 19.2, 257, and 3.3×10^3 M^{-1} cm^{-1}, respectively. The general features of this spectrum are quite typical of organochromium(III) species. The electronic spectrum between 330 and 470 nm shows no significant variation with perchloric acid concentration over the range 0.025–2.24 M investigated.

Reaction of $(H_2O)_5CrCH_2CH_2SO_3^+$ and Hg(II). A characteristic of $(H_2O)_5CrR^{n+}$ species is their rapid reaction with Hg(II) to produce HgR. The reaction results in a bleaching of the characteristic yellow to red color to yield an almost colorless or pale blue solution depending on the total chromium concentration. The golden-yellow product described above reacts in exactly this manner with aqueous $Hg(ClO_4)_2$, and this provides further confirmation of the spectrophotometric evidence that this species is $(H_2O)_5CrCH_2CH_2SO_3^+$.

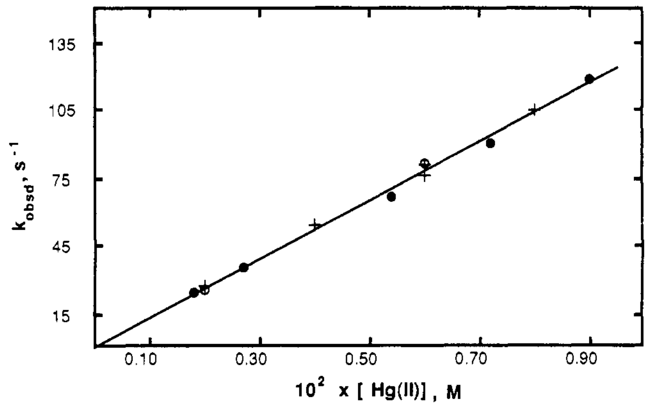

Figure 1. Variation of k_{obsd} with $[Hg^{2+}]$ in reaction with $(H_2O)_5CrCH_2CH_2SO_3^+$ at $[H^+]$ values of 0.01 (●), 0.050 (+), and 0.10 M (o), in 1.0 M $NaClO_4/HClO_4$ at 25 °C.

The kinetics of the reaction of $Hg(ClO_4)_2$ and $(H_2O)_5CrCH_2CH_2SO_3^+$ have been studied by stopped-flow methods. The results, which are displayed in Figure 1, show that the reaction is first order in $[Hg^{2+}]$ and independent of $[H^+]$ with a rate constant of $(1.3 \pm 0.02) \times 10^4$ M^{-1} s^{-1} (25 °C, 1.0 M $NaClO_4/HClO_4$).

The products of the reaction with Hg(II) proved to be more unusual. A solution initially containing 1.0×10^{-2} M $Hg(ClO_4)_2$ and 4.73×10^{-3} M $(H_2O)_5CrCH_2CH_2SO_3^+$ was subjected to ion-exchange chromatography on Dowex 50W-X8 at 4 °C. A green band formed at the top of the column with no initial indication of other species. But slow elution with increasing concentrations of $NaClO_4$ in 0.05 M $HClO_4$ caused this band to partially resolve into upper green and lower violet portions. The bands were moved, but not fully resolved, by elution with 0.95 M $NaClO_4$/0.05 M $HClO_4$. The initial violet eluate has absorbance maxima (nm) (absorptivity coefficients, M^{-1} cm^{-1}) at 574 (14.6) and 407 (16.8), while for the later green fractions, the values are 586 (16.7) and 411 (18.4). When the latter fraction is allowed to sit overnight at ambient temperature the values change slightly to 581 (15.0) and 410 (17.0). Qualitative tests indicate that there is mercury in these colored fractions. The spectrum of the violet product is consistent with that of $Cr(OH_2)_6^{3+}$, and the change with time for the green product is consistent with its eventual aquation to $Cr(OH_2)_6^{3+}$.

The amount of mercury held back in the colored fractions was determined by utilizing the color change associated with the reaction of $(H_2O)_5CrCH_2CH_2SO_3^+$ with mercury(II) species. The basis of the analytical method is given in a later section. Equimolar amounts of $(H_2O)_5CrCH_2CH_2SO_3^+$ and $Hg(ClO_4)_2$ were allowed to react for 3 min at room temperature. Then the reaction solution was adsorbed on a column of Dowex 50W-X8 at 4 °C, and a volume of eluant equal to that of the reaction solution plus two column volumes was collected and analyzed for $HgCH_2CH_2SO_3^+$ by reaction with $(H_2O)_5CrCH_2CH_2SO_3^+$. The color change at 396 nm shows that 46.6% of the total mercury passed through the column under these conditions. The column was washed with 1.95 M $NaClO_4$/0.05 M $HClO_4$ until the colored species moved about halfway down the column. The column was allowed to stand at room temperature for 60 h and then eluted with two column volumes of the same eluant. This eluant was analyzed for mercury as before and found to contain 44.5% of the initial mercury. The unaccounted for 9% of mercury may be in the intermediate washings or may still be retained on the column.

These experiments show that at least 44.5% of the mercury is retained with the chromium products on the column in the form of a species of 3+ charge. This retention can be explained if one of the reaction products is $(H_2O)_5CrO_3SCH_2CH_2Hg^{3+}$, which aquates during the 60 h on the column to $Cr(OH_2)_6^{3+}$ and $HgCH_2CH_2SO_3^+$.

Acidolysis of $(H_2O)_5CrCH_2CH_2SO_3^+$. This reaction is rather slow at 25 °C, but the absorbance decrease at 396 nm has been used to monitor the kinetics over 1–1.5 half-times under various

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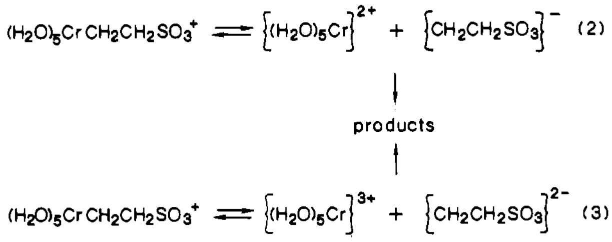
(5) Kupferschmidt, W. C.; Jordan, R. B. *J. Am. Chem. Soc.* **1984**, *106*, 991.
(6) Kita, P.; Jordan, R. B. *Inorg. Chem.* **1985**, *24*, 2701.
(7) Kita, P.; Jordan, R. B. *Inorg. Chem.* **1986**, *25*, 4791.

conditions. The rate is independent of $[H^+]$ in the range 0.01–0.1 M with an average rate constant of $2.5 \times 10^{-6}\ s^{-1}$ at 25 °C under an argon atmosphere in 1 M $NaClO_4/HClO_4$. In the presence of 1.06×10^{-2} M Cr^{2+}, the rate constant is marginally larger with a value of $2.9 \times 10^{-6}\ s^{-1}$. In the presence of 1.65×10^{-2} M Fe^{3+}, the rate constant is significantly but not dramatically larger at $3.6 \times 10^{-6}\ s^{-1}$. The increase in rate caused by oxidizing agents has been attributed[1] to a homolytic reaction pathway (eq 2) in which the oxidizing agent reacts with the Cr^{2+} formed and thereby accelerates the reaction. The heterolytic pathway (eq 3) is dominant for this complex since oxidizing agents have a small effect on the rate.



$$(H_2O)_5CrCH_2CH_2SO_3^+ \rightleftharpoons \{(H_2O)_5Cr\}^{2+} + \{CH_2CH_2SO_3\}^- \tag{2}$$

$$\downarrow$$

products

$$\uparrow$$

$$(H_2O)_5CrCH_2CH_2SO_3^+ \rightleftharpoons \{(H_2O)_5Cr\}^{3+} + \{CH_2CH_2SO_3\}^{2-} \tag{3}$$

The rate and products[8] were studied at ~50 °C. When a solution of $(H_2O)_5CrCH_2CH_2SO_3^+$ was allowed to react for 20 h and then subjected to ion-exchange chromatography, the only product observed was $Cr(OH_2)_6^{3+}$. The rate constant at 49.5 °C is $4.9 \times 10^{-5}\ s^{-1}$. The activation parameters can be estimated as $\Delta H^* \approx 22.6$ kcal mol^{-1} and $\Delta S^* \approx -8.4$ cal mol^{-1} deg^{-1}. These values are quite typical for the heterolysis pathway in other $(H_2O)_5CrR^{2+}$ systems.[1]

Analysis for Mercury(II) by $(H_2O)_5CrCH_2CH_2SO_3^+$. The fairly high molar absorptivity coefficient and rapid reactivity of $(H_2O)_5CrCH_2CH_2SO_3^+$ with mercury(II) species makes this chromium complex a potentially useful reagent for the spectrophotometric analysis of mercury(II). It should be noted that both Hg^{2+} and monoalkylmercury(II) species (RHg^+) will react according to eq 4 and 5, respectively and that the overall stoichiometry with Hg^{2+} is 1:2. The alkyl species react about 100 times more slowly than Hg^{2+}. The latter reaction was investigated briefly with methylmercury. When $[CrCH_2CH_2SO_3^+] = 1.4 \times 10^{-3}$ M, $[H_3CHg^+] = 7.9 \times 10^{-4}$ M, and $[H^+] = 0.05$ M, all of the H_3CHg^+ was consumed in 40 min. Under the same conditions, Hg^{2+} is consumed well within 20 s or essentially on mixing.

$$(H_2O)_5CrCH_2CH_2SO_3^+ + Hg^{2+} \rightarrow HgCH_2CH_2SO_3 + Cr(OH_2)_6^{3+}$$

$$(H_2O)_5CrCH_2CH_2SO_3^+ + HgCH_2CH_2SO_3 \rightarrow Hg(CH_2CH_2SO_3)_2^{2-} + Cr(OH_2)_6^{3+} \tag{4}$$

$$(H_2O)_5CrCH_2CH_2SO_3^+ + RHg^+ \rightarrow RHgCH_2CH_2SO_3^- + Cr(OH_2)_6^{3+} \tag{5}$$

The sensitivity of this analysis can be judged from the HgR^+ concentration, which will produce a 0.1 absorbance change in a 2 cm path length cell. At 396 nm, this concentration is 1.95×10^{-3} M, while at 267 nm it is 1.6×10^{-5} M. It should be noted that the reactivity difference between Hg^{2+} and HgR^+ might be exploited to develop an analysis that would differentiate between these two forms of mercury(II).

Discussion and Conclusions

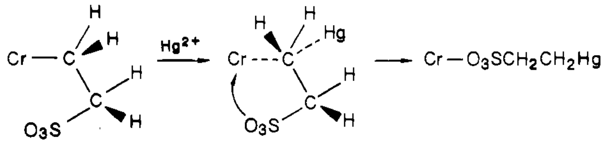
In previous studies[5-7] of the reaction of Cr^{2+} and ICH_2Y, where Y is a potential coordinating group (CO_2H, $C(O)NH_2$, CN) a mixture of products has been obtained as shown in Scheme I. However in the present case, no $CrO_3SCH_2CH_3^{2+}$ has been found. This may be because the unpaired electron in the radical intermediate $\{{}^\bullet CH_2CH_2SO_3^-\}$ is highly localized on the carbon center, whereas the electron can be delocalized onto the Y substituent in the other examples.

Scheme I

$$Cr^{2+} + YCH_2X \rightarrow CrX^{2+} + \{YCH_2{}^\bullet\}$$

$$Cr^{2+} + \{YCH_2{}^\bullet\} \xrightarrow{H^+} CrCH_2Y^{2+} + CrYCH_3^{3+}$$

Since there are two methylene groups between the Cr and SO_3^-, it seems suprising that the reaction of the alkylchromium(III) complex with Hg^{2+} yields almost 50% $CrO_3SCH_2CH_2Hg^{3+}$. The negative charge on the SO_3 group may favor its location near the Cr as the Cr–C bond is broken as shown by the following diagrams.



In other systems[6,7,9] in which $CrYCH_2Hg$ type products have been observed it is easier to envision how the Y group on the α-carbon can move into the coordination sphere of Cr as the Cr–C bond is broken.

The general reactivity of $(H_2O)_5CrCH_2CH_2SO_3^+$ might be expected to be similar to $(H_2O)_5CrCH_2CH_2CH_3^{2+}$ because the $CH_2SO_3^-$ group is inductively neutral[10] and steric differences are one methylene group removed from the reaction site. Indeed, the rate constants for reaction with Hg(II) are similar at 3.5×10^4 and 1.3×10^4 M^{-1} s^{-1} for $CH_2CH_2CH_3$ and $CH_2CH_2SO_3^-$, respectively. However the $CH_2CH_2SO_3^-$ complex is much less reactive toward acidolysis than the $CH_2CH_2CH_3$ species.[11] The latter has an acid-independent rate constant of $3 \times 10^{-4}\ s^{-1}$ compared to $2.5 \times 10^{-6}\ s^{-1}$ for the former. The $[H^+]$-dependent acidolysis also is slower for $(H_2O)_5CrCH_2CH_2SO_3^+$ since the value is $<1 \times 10^{-6}$ M^{-1} s^{-1} compared to 6.5×10^{-5} with $(H_2O)_5CrCH_2CH_2CH_3^{2+}$. The lower charge on the sulfonato complex might have been expected to make it more susceptible to electrophilic attack rather than less so. For the acid-independent pathway, these observations could be rationalized by Espenson's suggestion[1,12] that a coordinated water is involved. The lower charge would have compensating effects of making the coordinated H_2O less electrophilic while making the alkyl group more nucleophilic.

Experimental Section

The preparation and handling of standard reagents, the analytical methods, and the instrumentation have been described previously.[5,6,9] $Na(BrCH_2CH_2SO_3)$ was used as supplied (Eastman Organic).

In a typical analysis for $HgCH_2CH_2SO_3$, 4.50 mL of sample solution in 0.05 M $HClO_4$ was mixed with 1.30 mL of 6.69×10^{-3} M $CrCH_2CH_2SO_3^+$ in a 2 cm path length cell. The absorbance was monitored at 396 nm until no further change was observed (30–40 min). The absorbance for complete dealkylation was determined by adding 1 drop of 0.75 M $Hg(ClO_4)_2$ to the sample solution in the cell.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Registry No. $NaO_3SCH_2CH_2Br$, 4263-52-9; $(H_2O)_5CrCH_2CH_2SO_3^+$, 114185-94-3; $Hg(ClO_4)_2$, 7616-83-3; $(H_2O)_5CrO_3SCH_2CH_2Hg^{3+}$, 114185-95-4; CH_3Hg^+, 22967-92-6; $(H_2O)_5CrCH_2CH_2CH_3^{2+}$, 52653-40-4; Cr(II), 22541-79-3; Hg(II), 14302-87-5.

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[8] A reviewer has suggested that β-elimination could give ethylene and sulfite. No gaseous products were observed, and tests for sulfate after exposure to air were negative.

[9] Sisley, M. J.; Jordan, R. B. *Inorg. Chem.* **1986**, *25*, 3547.

[10] Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119.

[11] This reactivity difference is convenient for the mercury(II) analysis because it allows stock solutions of $(H_2O)_5CrCH_2CH_2SO_3^+$ to be kept in a refrigerator for extended periods.

[12] Kirker, G. W.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *102*, 1244.