

Contribution from the Rudjer Bosković Institute, 41000 Zagreb, Croatia, Yugoslavia, and Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011

## Preparation of a Series of (Imidazole)pentaquachromium(III) Complexes and Kinetics of Their Reduction by 1-Hydroxy-1-methylethyl Radicals

A. Bakac,<sup>\*1a</sup> V. Butkovic,<sup>1b</sup> J. H. Espenson,<sup>\*1a</sup> R. Marcec,<sup>1b</sup> and M. Orhanovic<sup>\*1b</sup>

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A series of (imidazole)pentaquachromium(III) complexes,  $(\text{H}_2\text{O})_5\text{Cr}(\text{Im-X,Y})^{3+}$  were prepared and characterized in acidic aqueous solution. These complexes are reduced by  ${}^{\bullet}\text{C}(\text{CH}_3)_2\text{OH}$  radicals with rate constants that vary with substituents on the imidazole ring. At 25 °C the values of the rate constants,  $k/10^5 \text{ L mol}^{-1} \text{ s}^{-1}$  (X, Y), are 1.1 (1-CH<sub>3</sub>, H), 2.1 (2-CH<sub>3</sub>, H), 3.8 (4-CH<sub>3</sub>, H), 6.6 (H, H), 7.2 (4-CH<sub>3</sub>, 5-CONH<sub>2</sub>), and 16 (4-Cl, 5-Cl). A mechanism is proposed whereby the initial electron transfer takes place at coordinated imidazole, followed by a rapid intramolecular electron transfer to yield  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  and X,Y-ImH<sup>+</sup>.

### Introduction

A very interesting question arises in the area of electron transfer to metal complexes of N-heterocycles coordinated to metal ions, Cr(III)-imidazole complexes in particular. In previous work we have examined the mechanism by which free pyridinium<sup>2</sup> and imidazolium<sup>3</sup> ions are reduced by the 1-hydroxy-1-methylethyl radical,  ${}^{\bullet}\text{C}(\text{CH}_3)_2\text{OH}$ . Generally speaking these rates are sensitive to ring substituents as represented by the species X-pyH<sup>+</sup> and X,Y-ImH<sup>+</sup>.

We then extended these studies to radical reduction of complexes between the substituted pyridines and the trivalent metals Co, Ru, and Cr.<sup>4-6</sup> Among these, there are clear differences in reactivity that were seen in the substituent effects on the values of *k*, particularly as revealed by successful linear free energy correlations with the Hammett  $\sigma\rho$  equation.

The corresponding issues attending the mechanism of reduction of  $\text{M}^{\text{III}}(\text{Im-X,Y})^{3+}$  complexes are the subject of continuing interest here. This field continues to attract attention because imidazoles, like pyridines, are ligands of interest in the context of biological electron transfer. In general, a Hammett-type correlation is not available<sup>7</sup> for imidazoles, and so the kinetic effects of ring substituents must be evaluated in a different way. Data are already available<sup>3</sup> for the complexes  $(\text{NH}_3)_5\text{Co}(\text{Im-X,Y})^{3+}$ . They suggest that the cobalt center, not the imidazole, is the immediate site of electron transfer. We turn here to reactions between the complexes  $(\text{H}_2\text{O})_5\text{Cr}(\text{Im-X,Y})^{3+}$  and  ${}^{\bullet}\text{C}(\text{CH}_3)_2\text{OH}$ . The question is the mechanism of reduction, including the question of whether chromium or imidazole is first reduced.

As before, we have approached the experimental measurements by the method of "stored free radicals",<sup>2,8</sup> since the reversible homolysis of  $(\text{H}_2\text{O})_5\text{Cr}(\text{CH}_3)_2\text{OH}^{2+}$  provides a convenient method for the generation of the radical in a controlled, time-released manner.

### Experimental Section

**Materials.** Six different (imidazole)pentaquachromium(III) complexes in acidic aqueous solution,  $(\text{H}_2\text{O})_5\text{Cr}(\text{Im-X,Y})^{3+}$ , where X and Y are substituents on the imidazole ring, were prepared by the reduction of the respective imidazole adducts of diperoxychromium(VI) species with acidic ferrous perchlorate solution, followed by the separation on a cation-exchange resin. The method is essentially the same as the one previously used to prepare analogous pyridine<sup>9</sup> and pyridine *N*-oxide<sup>10</sup>

**Table I.** Visible Absorption Maxima of the  $(\text{H}_2\text{O})_5\text{Cr}(\text{Im-X,Y})^{3+}$  Ions<sup>a</sup>

X	Y	$\lambda_1/\text{nm}$ ( $\epsilon/\text{L mol}^{-1} \text{ cm}^{-1}$ )	$\lambda_2/\text{nm}$ ( $\epsilon/\text{L mol}^{-1} \text{ cm}^{-1}$ )
4-Cl	5-Cl	562 (15.9)	398 (20.7)
2-CH <sub>3</sub>	H	560 (16.7)	400 (23.2)
H	H	558 (14.5)	398 (19.4)
4(5)-CH <sub>3</sub>	H	550 (15.5)	398 (21.4)
1-CH <sub>3</sub>	H	550 (15.0)	398 (19.5)
4(5)-CH <sub>3</sub>	5(4)-CONH <sub>2</sub>	545 (29.3)	400 (33.6)

<sup>a</sup>In 3 M HClO<sub>4</sub>.

complexes. The composition of the (imidazole)chromium(III) complexes was determined and checked by chromium analysis<sup>11</sup> and by qualitative and quantitative determination of the imidazole by UV spectrometry after aqution of the complex at about 100 °C. The stock solutions (3-4)  $\times 10^{-3}$  M (imidazole)chromium(III) in 3 M HClO<sub>4</sub> contained also (6-8)  $\times 10^{-4}$  M  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ . The latter was tolerated because it has no kinetic effect at these levels, and its complete separation from (imidazole)chromium(III) on Dowex 50W resin results in an impractical dilution of the latter.

Commercial imidazole and its 1-CH<sub>3</sub>, 2-CH<sub>3</sub>, 4(5)-CH<sub>3</sub>, and 4,5-Cl<sub>2</sub> derivatives (all Aldrich), as well as its disubstituted 4(5)-CH<sub>3</sub>-5(4)-CONH<sub>2</sub> derivative (available from a previous stock)<sup>12</sup> were carefully purified before use by sublimation (imidazole and 4(5)-CH<sub>3</sub>), distillation (1-CH<sub>3</sub>), and recrystallization from 50% ethanol-water.

The source of 1-hydroxy-1-methylethyl radicals was the organochromium complex  $(\text{H}_2\text{O})_5\text{Cr}(\text{CH}_3)_2\text{OH}^{2+}$ . It was prepared in a spectrophotometric cell immediately before use, as described previously.<sup>2-6</sup> Solutions of  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  were prepared by zinc amalgam reduction of  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  solutions, which were made from triply recrystallized  $[\text{Cr}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$ . 2-Propanol was redistilled at least weekly and kept in a dark bottle. Lithium perchlorate was recrystallized four times from water. Anaerobic conditions were maintained in all the kinetic and stoichiometric experiments by use of purified argon, which was first passed over a heated copper catalyst and then through a Cr<sup>2+</sup> scrubbing tower. All starting chemicals were analytical grade. Triply distilled water was used throughout.

**Techniques.** A Cary 219 instrument was used for spectral characterization of the prepared (imidazole)chromium(III) complexes, for the analytical determinations and for the kinetic investigations. The reaction kinetics of 1-hydroxy-1-methylethyl radicals with a particular (imidazole)chromium(III) complex was followed indirectly by monitoring a decrease of absorbance at 311 nm, the wavelength of maximum absorption of  $(\text{H}_2\text{O})_5\text{Cr}(\text{CH}_3)_2\text{OH}^{2+}$  ( $\epsilon = 2599 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). The reagents competing for the  ${}^{\bullet}\text{C}(\text{CH}_3)_2\text{OH}$  radical (formed by homolysis of  $(\text{H}_2\text{O})_5\text{Cr}(\text{CH}_3)_2\text{OH}^{2+}$ ), (imidazole)chromium(III) and  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ , were used in at least 10-fold excess over the organochromium concentration to ensure pseudo-first-order conditions. Straight lines obtained by plotting  $\ln(A_t - A_\infty)$  versus time were used to evaluate the rate constants.

The stoichiometry of the reaction between the (imidazole)chromium(III) complexes and the radicals was checked by evaluation of the chromium(II) present in the reaction mixture after completion of the reaction by allowing chromium(II) to react with added  $(\text{NH}_3)_5\text{CoCl}^{2+}$ ; the resulting cobalt(II) produced was determined spectrophotometrically.<sup>13</sup>

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**Table II.** Kinetic Data for the Reduction of  $(\text{H}_2\text{O})_5\text{Cr}(\text{Im-XY})^{3+}$  Complexes by 1-Hydroxy-1-methylethyl Radicals at 25 °C,  $[\text{H}^+] = 0.5 \text{ M}$ , and  $\mu = 1.0 \text{ M}$  ( $\text{HClO}_4 + \text{LiClO}_4$ ) in 1 M Aqueous 2-Propanol<sup>a</sup>

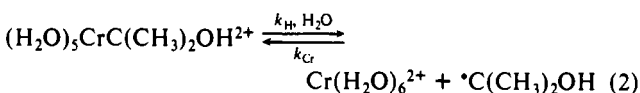
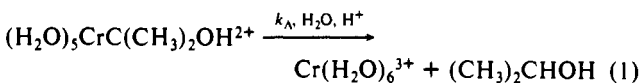
X	Y	slope/ $10^2 \text{ s}^{b,c}$	$k_R/10^5 \text{ L mol}^{-1} \text{ s}^{-1}$
1-CH <sub>3</sub>	H	36.0 ± 0.9	1.1
2-CH <sub>3</sub>	H	19.1 ± 0.7	2.1
4(5)-CH <sub>3</sub>	H	10.6 ± 0.3	3.8
H	H	6.1 ± 0.3	6.6
4(5)-CH <sub>3</sub>	5(4)-CONH <sub>2</sub>	5.6 ± 0.15	7.2
4-Cl	5-Cl	2.55 ± 0.08	16.0

<sup>a</sup>  $(\text{H}_2\text{O})_5\text{Cr}(\text{Im-X,Y})^{3+}_0 = (2.3\text{--}11.2) \times 10^{-4} \text{ M}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6^{2+}]_0 = (1.0\text{--}4.6) \times 10^{-4} \text{ M}$ ,  $[(\text{H}_2\text{O})_5\text{CrC}(\text{CH}_3)_2\text{OH}^{2+}]_0 = (1\text{--}2) \times 10^{-5} \text{ M}$ .  
<sup>b</sup> Uncertainties quoted are standard deviations. <sup>c</sup> The slope of plots of  $(k_{\text{obsd}} - k_A)^{-1}$  vs  $[\text{Cr}(\text{H}_2\text{O})_6^{2+}]/[(\text{H}_2\text{O})_5\text{Cr}(\text{Im-X,Y})^{3+}]$ .

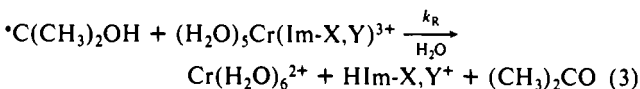
## Results

**Characterization of the (Imidazole)chromium(III) Ions.**  $(\text{H}_2\text{O})_5\text{Cr}(\text{Im-X,Y})^{3+}$  ions are eluted from a Dowex 50W-X8 ion-exchange column somewhat less readily than  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  ions. This behavior is compatible with a 3+ charge and with the size of the ions. The chromium to ligand ratio in these complexes is 1:1. Features of the visible spectra are shown in Table I. The long-wavelength d-d transitions for the six (imidazole)chromium(III) ions lie in the range 545–562 nm. This is consistent with the complexes having a bond between chromium(III) and the pyridinyl nitrogen of the imidazole ligands. Namely, monosubstituted chromium ions with pyridine ligands were previously found to have their first absorption maxima in the same range (3-Cl-py at 561 nm and 4-NH<sub>2</sub>COpy at 555 nm).<sup>9,14</sup> Two other nitrogen-bonded  $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}$  ions have absorption maxima at 570 nm ( $\text{NCS}^-$ )<sup>15</sup> and at 545 nm ( $\text{NH}_3$ ).<sup>16</sup>

**Reduction of Cr(III)–Imidazole Complexes by  $\cdot\text{C}(\text{CH}_3)_2\text{OH}$ .** The reaction scheme is analogous to that given for the reduction of pentaammine(imidazole)cobalt(III) complexes.<sup>3</sup> The complex  $(\text{H}_2\text{O})_5\text{CrC}(\text{CH}_3)_2\text{OH}^{2+}$  reacts in two parallel processes, acidolysis and homolysis (eqs 1 and 2). The latter yields the radical, which



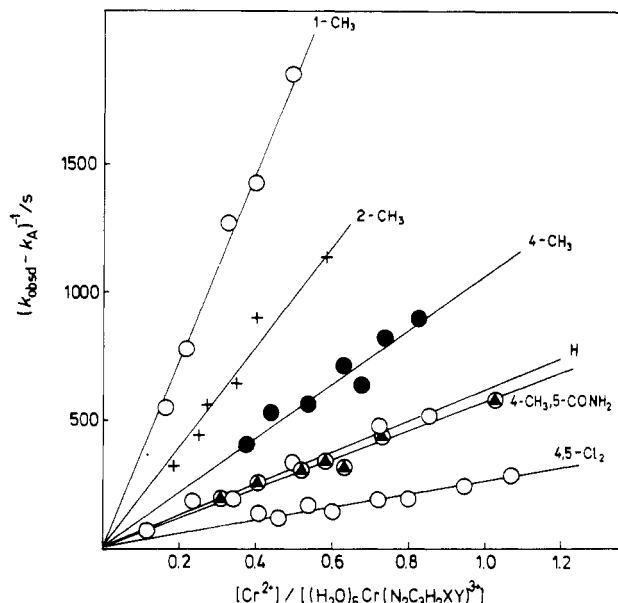
in the next step either reduces  $(\text{H}_2\text{O})_5\text{Cr}(\text{Im-X,Y})^{3+}$  (eq 3) or re-forms the chromium–carbon bond in the reverse of eq 2. The steady-state approximation for the radical yields the rate law of eq 4. Values of the rate constants  $k_A$  ( $3.31 \times 10^{-3} + 4.91 \times$



$$\frac{-d[(\text{H}_2\text{O})_5\text{CrC}(\text{CH}_3)_2\text{OH}^{2+}]}{dt} = \left( k_A + \frac{k_{\text{H}}k_R[(\text{H}_2\text{O})_5\text{Cr}(\text{Im-X,Y})^{3+}]}{k_R[(\text{H}_2\text{O})_5\text{Cr}(\text{Im-X,Y})^{3+}] + k_{\text{Cr}}[\text{Cr}(\text{H}_2\text{O})_6^{2+}]} \right) \times [(\text{H}_2\text{O})_5\text{CrC}(\text{CH}_3)_2\text{OH}^{2+}] \quad (4)$$

$$\frac{1}{k_{\text{obsd}} - k_A} = \frac{1}{k_{\text{H}}} + \frac{k_{\text{Cr}}}{k_R k_{\text{H}}} \frac{[\text{Cr}(\text{H}_2\text{O})_6^{2+}]}{[(\text{H}_2\text{O})_5\text{Cr}(\text{Im-X,Y})^{3+}]} \quad (5)$$

$10^{-3} [\text{H}^+] \text{ s}^{-1}$ ,  $k_{\text{H}}$  ( $0.127 \text{ s}^{-1}$ ), and  $k_{\text{Cr}}$  ( $5.1 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ ) are known from earlier work.<sup>17–19</sup> Rearrangement of eq 4 yields eq



**Figure 1.** Linear variation of the inverse of the rate constant enhancement over the background acidolysis rate constant,  $(k_{\text{obsd}} - k_A)^{-1}$ , with the concentration ratio as given in eq 5.

5, according to which the inverse of the difference of rate constants is a linear function of the concentration ratio  $[\text{Cr}(\text{H}_2\text{O})_6^{2+}]/[(\text{H}_2\text{O})_5\text{Cr}(\text{Im-X,Y})^{3+}]$ .

From the slopes of the plots according to eq 5 (Figure 1), we obtained the values of  $k_R$  listed in Table II.

**Stoichiometry of the reaction between  $(\text{H}_2\text{O})_5\text{Cr}(4,5\text{-Cl}_2\text{Im})^{3+}$  and  $\cdot\text{C}(\text{CH}_3)_2\text{OH}$**  was checked by a careful analysis of the concentration of  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  produced. This experiment was conducted at higher initial concentrations than those used in the kinetics experiments to increase the precision of the  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  analysis. The relative concentrations were also different to diminish the extent of nonproductive acidolysis pathway relative to the  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ -producing steps. The experiment was run at 25 °C with  $[\text{H}^+] = 0.50 \text{ M}$  and  $\mu = 1.0 \text{ M}$ . The initial concentrations were  $[(\text{H}_2\text{O})_5\text{CrC}(\text{CH}_3)_2\text{OH}^{2+}]_0 = 8.4 \times 10^{-5} \text{ M}$ ,  $[(\text{H}_2\text{O})_5\text{Cr}(4,5\text{-Cl}_2\text{Im})^{3+}]_0 = 5.1 \times 10^{-4} \text{ M}$ , and  $[\text{Cr}(\text{H}_2\text{O})_6^{2+}]_0 = 3.0 \times 10^{-5} \text{ M}$ . The experimental value found for the increase in  $[\text{Cr}(\text{H}_2\text{O})_6^{2+}]$  was  $1.2 \times 10^{-4} \text{ M}$ . This compares well with the calculated value of  $1.3 \times 10^{-4} \text{ M}$ . The calculation was based on a numerical integration of the family of simultaneous differential rate equations from eqs 1–3, which was carried out with the program KINSIM.<sup>20</sup>

## Discussion

The reaction of  $(\text{H}_2\text{O})_5\text{Cr}(\text{Im-X,Y})^{3+}$  with  $\cdot\text{C}(\text{CH}_3)_2\text{OH}$  results in the net reduction of the metal center according to eq 3. This is analogous to the case of a series of  $(\text{NH}_3)_5\text{Co}(\text{Im-X,Y})^{3+}$  complexes.<sup>3</sup> However, the site of initial attack by the radical appears to be different in the two series of metal–imidazole complexes, as explained below.

The rather narrow range of rate constants observed for  $(\text{NH}_3)_5\text{Co}(\text{Im-X,Y})^{3+}$ ,  $k_R = (1.4\text{--}18.5) \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ , and the correlation between the rate constants and positions of the lowest energy d-d bands were taken<sup>3</sup> as evidence that the radical reduces the cobalt center directly. The case of  $(\text{NH}_3)_5\text{Co}(2\text{-CH}_3\text{-Im})^{3+}$  provides an especially strong argument in favor of direct electron transfer. The rate constant for this complex is comparable to those for all the other  $(\text{NH}_3)_5\text{Co}(\text{Im-X,Y})^{3+}$  complexes, whereas the free ion,  $2\text{-CH}_3\text{ImH}^+$ , reacts much more

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**Table III.** Summary of the Rate Constants ( $k/10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ ) for the Reactions of  ${}^{\circ}\text{C}(\text{CH}_3)_2\text{OH}$  with Imidazolium Ions  $\text{X}, \text{Y}-\text{ImH}^+$  and Metal-Imidazole Complexes  $\text{M}(\text{Im}-\text{X}, \text{Y})^{3+}$ <sup>a</sup>

X	Y	X, Y- ImH <sup>+</sup>	M(Im-X, Y) <sup>3+</sup>	
			M = Co(NH <sub>3</sub> ) <sub>5</sub> <sup>3+</sup>	M = Cr(H <sub>2</sub> O) <sub>5</sub> <sup>3+</sup>
4(5)-CH <sub>3</sub>	5(4)-CN	4.8		
4-Cl	5-Cl	3.3	18.5	1.6
4(5)-CH <sub>3</sub>	5(4)-CONH <sub>2</sub>	2.05		0.72
1-CH <sub>3</sub>	H	1.05	2.2	0.11
4(5)-CH <sub>3</sub>	5(4)-H	0.45	1.8	0.38
H	H	0.17	1.4	0.66
1-CH <sub>2</sub> COOH	H	0.075		
2-CH <sub>3</sub>	H	0.013	3.0	0.21

<sup>a</sup> At 25.0 °C and  $\mu = 1.0 \text{ M}$  ( $\text{HClO}_4 + \text{LiClO}_4$ ).

slowly than the other imidazolium ions listed in Table III. Thus, the attack by  ${}^{\circ}\text{C}(\text{CH}_3)_2\text{OH}$  clearly does not take place at imidazole, which leaves the cobalt center as the only viable alternative.

The reactivity of  $(\text{H}_2\text{O})_5\text{Cr}(\text{Im}-\text{X}, \text{Y})^{3+}$  toward  ${}^{\circ}\text{C}(\text{CH}_3)_2\text{OH}$  is comparable to that of the  $(\text{NH}_3)_5\text{Co}^{\text{III}}$  series. This in itself rules out attack at the Cr center owing to the much lower reducibility of Cr(III) ( $E^{\circ}_{\text{Cr}^{3+}/\text{Cr}^{2+}} = -0.41 \text{ V}$ ) compared to Co(III) ( $E^{\circ}_{\text{Co}(\text{NH}_3)_5/\text{Co}^{2+}} = 0.1 \text{ V}$ ). In fact, the reduction of  $\text{Co}(\text{NH}_3)_5^{3+}$  by  ${}^{\circ}\text{C}(\text{CH}_3)_2\text{OH}$  has a rate constant  $4.1 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ ,<sup>8</sup> comparable to that for  $(\text{NH}_3)_5\text{Co}(\text{Im}-\text{X}, \text{Y})^{3+}$ . Thus, the substitution of one  $\text{NH}_3$  by  $\text{Im}-\text{X}, \text{Y}$  had only a minor effect on the reducibility of the complex. In the Cr(III) case, on the other hand, the effect is dramatic.  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  reacts with  ${}^{\circ}\text{C}(\text{CH}_3)_2\text{OH}$  with  $k = 560 \text{ L mol}^{-1} \text{ s}^{-1}$ ,<sup>21</sup> whereas  $(\text{H}_2\text{O})_5\text{Cr}(\text{Im}-\text{X}, \text{Y})^{3+}$  complexes have  $k = 10^5\text{--}10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ , comparable to those for free imidazolium ions. It is highly unlikely that substitution of one  $\text{H}_2\text{O}$  in  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  by  $\text{Im}-\text{X}, \text{Y}$  would have such a dramatic effect on the reduction potential, given that in the cobalt series the response was negligible. Indeed, if there is a change in  $E^{\circ}$ , one would predict  $(\text{H}_2\text{O})_5\text{Cr}(\text{Im}-\text{X}, \text{Y})^{3+}$  to be even *less reducible* than  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  owing to the fact that imidazoles are good  $\sigma$ - and  $\pi$ -electron donors but poor  $\pi$ -electron acceptors.<sup>22</sup> It thus seems clear that the attack

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of  ${}^{\circ}\text{C}(\text{CH}_3)_2\text{OH}$  has to take place on imidazoles of  $(\text{H}_2\text{O})_5\text{Cr}(\text{Im}-\text{X}, \text{Y})^{3+}$ .

On the basis of the low reactivity of  $2\text{-CH}_3\text{-ImH}^+$ , the complex  $(\text{H}_2\text{O})_5\text{Cr}(2\text{-CH}_3\text{-Im})^{3+}$  was expected to be the least reactive of the chromium complexes. As it turns out, the measured rate constant of  $2.1 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$  is among the lowest in Table III, but it is not exceptionally low. Even more importantly, the range of values of  $k_R$  for the chromium complexes is quite narrow relative to those for imidazolium ions. This signals that substituents have a significant, but variable, effect on  $\pi$ -donation from imidazoles, which alters the reactivity of coordinated imidazoles relative to imidazolium ions.

Unlike in the cobalt series, there is no correlation between the positions of the d-d bands in  $(\text{H}_2\text{O})_5\text{Cr}(\text{Im}-\text{X}, \text{Y})^{3+}$  and rate constants for reaction 3. This is again consistent with the attack at imidazole, such that minor changes in the reducibility of the metal center do not result in the corresponding changes in reactivity.

Previously<sup>2,4-6</sup> we have studied reactions of  ${}^{\circ}\text{C}(\text{CH}_3)_2\text{OH}$  with pyridinium ions and pyridine complexes of  $(\text{H}_2\text{O})_5\text{Cr}^{3+}$  and  $(\text{NH}_3)_5\text{Co}^{3+}$ . The reactivities of the three series were analyzed quantitatively by use of a Hammett correlation. This analysis showed that the cobalt complexes react by direct reduction of the metal, whereas Cr complexes react by initial reduction of the pyridines. Subsequent rapid intramolecular electron transfer yields  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  as a final product. Although a Hammett correlation is not applicable to imidazoles and their complexes,<sup>7</sup> the results of this work strongly indicate the same mechanistic pattern. The basis for such an abrupt change in mechanism by changing the metal from cobalt to chromium must lie in the very different reducibilities of the two parent molecules,  $\text{Co}(\text{NH}_3)_5^{3+}$  and  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ , a point mentioned earlier. The low reducibility of Cr(III) channels the reduction toward the coordinated pyridines and imidazoles.

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Contribution from the Department of Chemistry,  
Kent State University, Kent, Ohio 44242

## Electron Transfer. 101. Reaction of Carboxylato-Bound Chromium(V) with Dimeric Molybdenum(V)<sup>1</sup>

M. C. Ghosh and E. S. Gould\*

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The bridged dimer of molybdenum(V),  $\text{Mo}_2\text{O}_4^{2+}(\text{aq})$ , is rapidly oxidized to Mo(VI) by carboxylato-bound chromium(V). With excess  $(\text{Mo}^{\text{V}})_2$ , a chelated Cr(III) product is obtained, and a pink Cr(IV) intermediate is observed. At high acidities with Cr(V) in excess, the latter is the primary product but undergoes slow reaction with the ligand. No binuclear  $\text{Cr}^{\text{III}}\text{-Mo}^{\text{VI}}$  derivative is found among the reaction products. The intermediacy of Cr(IV) indicates that the oxidation of  $(\text{Mo}^{\text{V}})_2$  proceeds in 1e steps, passing through a reactive transient, taken here to be a mixed-valence complex,  $\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}$ . With  $(\text{Mo}^{\text{V}})_2$  in excess at pH 1, the reaction generates a biphasic kinetic pattern corresponding to consecutive bimolecular transformations. The proposed mechanism includes rate-determining reductions of Cr(V) and Cr(IV) by  $(\text{Mo}^{\text{V}})_2$ , as well as rapid reductions by  $\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}$ . When the reaction is carried out in buffers of the acid form of the ligating group 2-ethyl-2-hydroxybutanoic acid, autocatalytic profiles are observed. The catalytic sequence features a reversal of selectivity, with  $(\text{Mo}^{\text{V}})_2$  reacting more rapidly with Cr(IV) than with Cr(V), but  $\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}$  reacting more rapidly with Cr(V).

In a formal sense, chromium(V) and molybdenum(V) are congeners. However, aside from their propensity to form oxo-substituted complexes, little similarity links the aqueous chemistries

of these d<sup>1</sup> states. Chromium(V) undergoes disproportionation unless incorporated into chelates of hydroxy carboxylic acids<sup>2</sup> or

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