

Figure 3. Suggested geometric arrangement for the redox reaction between $\text{MoOCl}_3(\text{OPPh}_3)$ and NO_2 , allowing for overlap of the d_{xy} orbital of the former with the a_1' ($\text{N}-\text{O} \sigma^*$, $\text{O}-\text{O} \sigma$) orbital of the latter.

NOCl was also obtained by reacting NO_2^- with MoOCl_4 .

Discussion

The oxidation of Mo(V) by N(IV) in CH_2Cl_2 solution has been shown to occur in one observable step, the kinetic data for which are consistent with concomitant pathways involving terms in $[\text{NO}_2]$ and $[\text{NO}_2]^2$. Although the term in $[\text{NO}_2]$ is interpreted simply as a reaction between Mo(V) and NO_2 , it is not essential to consider the term in $[\text{NO}_2]^2$ as involving N_2O_4 . One alternative here is the disproportionation (7),



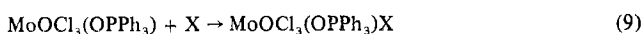
followed by the reaction of NO_3^- with $\text{MoOCl}_3(\text{OPPh}_3)_2$ in an analogous manner to that described previously.¹

The dependence of k_{obsd} upon the initial $\text{MoOCl}_3(\text{OPPh}_3)_2$ and added Ph_3PO concentrations suggests that the dissociation (5) of Ph_3PO from the parent molybdenum complex is essential for reaction. Plots of $1/k_{\text{obsd}}$ vs. $[\text{Ph}_3\text{PO}]$ and $[\text{MoOCl}_3(\text{OPPh}_3)_2]$ (Figure 2) are linear and, since the expression

$$k_{\text{obsd}} = \frac{(k_2[\text{NO}_2] + K_1 k_3[\text{NO}_2]^2)K_5}{K_5 + [\text{Ph}_3\text{PO}]} \quad (8)$$

adequately describes the data, it appears that only the five-coordinate $\text{MoOCl}_3(\text{OPPh}_3)$ species is reactive. Solving (8) for K_5 gives a value of $5.1 \times 10^{-4} \text{ M}$, which is far higher than previous estimates⁵ for this dissociation of $\text{MoOCl}_3(\text{OPPh}_3)_2$ in CH_2Cl_2 solution. Consequently, a special interaction between nitrogen(IV) oxides and either $\text{MoOCl}_3(\text{OPPh}_3)$ or Ph_3PO is suggested and, in view of the interactions between donor solvents and nitrogen(IV) oxides characterized earlier,⁶ the $\text{Ph}_3\text{PO}-\text{NO}_2/\text{N}_2\text{O}_4$ interactions seem the more probable.

Because of the interpretive difficulties of the reaction pathway involving $[\text{NO}_2]^2$ terms, we can only discuss the process which is first order in $[\text{NO}_2]$. It is not possible to present a definite mechanism for this process; however, considerations of the kinetic data obtained and the likely requirements^{7,8} for this redox reaction lead to a suggested mechanism. As shown in Figure 3, an NO_2 molecule could achieve a weak coordination to $\text{MoOCl}_3(\text{OPPh}_3)$ trans to the oxo group which would facilitate electron transfer from the molybdenum $4d_{xy}$ orbital into the a_1' ($\text{N}-\text{O} \sigma^*$, $\text{O}-\text{O} \sigma$) half-filled orbital⁹ of the NO_2 . "O²⁻" transfer could then occur to afford the *cis*-dioxomolybdenum(VI) and NO^+ moieties in a manner analogous to that demonstrated here between MoOCl_4 and NO_2^- . The observations that the NO_2 oxidation proceeds at a much slower rate than the NO_3^- and NO_2^- oxidations and with $\text{S}_{\text{N}}2$ rather than $\text{S}_{\text{N}}1$ behavior are suggested to arise primarily because of the very poor coordinating ability of NO_2 . Thus, for process 5 followed by (9) (where



$\text{X} = \text{NO}_3^-, \text{NO}_2^-, \text{Cl}^-, \text{Br}^-, \text{or } \text{NO}_2$), for $\text{NO}_3^-, \text{NO}_2^-, \text{Cl}^-, \text{or}$

Br^- the rate-determining step¹⁻³ is the dissociation of (5), whereas for NO_2 it is probably the association of (9). This latter process for NO_2 is also considered to be significantly slower than the ligand reorganization about the molybdenum(V) center which leads to the redox process and some further observations are perhaps useful in this respect. Approximation to the highest reasonable symmetry of the reactant centers ($\text{Mo}^{\text{VO}}, \sim C_{4v}$; coordinated $\text{NO}_3^-, \text{NO}_2^-, \text{and } \text{NO}_2, \sim C_{2v}, C_s, \text{ and } C_s$, respectively), plus the criterion that there should be significant overlap between the highest filled orbital of the reductant and the lowest orbital or partially filled MO of the oxidant, leads to the formal conditions that NO_3^- and NO_2^- should achieve coordination via one oxygen atom at one of the four sites cis to the oxo group of the Mo^{VO} center,^{1,2} whereas for NO_2 , one of the oxygen atoms should simply approach the molybdenum(V) between two of these cis sites (Figure 3).

Conclusion

The oxidation of $\text{MoOCl}_3(\text{OPPh}_3)_2$ by $\text{NO}_3^-, \text{NO}_2^-, \text{or } \text{NO}_2$ each produces a *cis*-dioxomolybdenum(VI) center and $\text{NO}_2, \text{NO}, \text{or } \text{NO}^+$, respectively, by a one-electron-transfer process which also involves the transfer of one oxygen atom from the oxidant to the reductant. The differences in kinetic behavior observed, for NO_2 on the one hand as compared to NO_3^- and NO_2^- on the other, are considered to arise, primarily, because of the poor ligating characteristics of NO_2 .

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Registry No. $\text{MoOCl}_3(\text{OPPh}_3)_2$, 19247-59-7; NO_2 , 10102-44-0.

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Electrode Reaction Pathways for the Reduction of Chromium(III)-Ammine Complexes at Mercury Electrodes

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In recently reported studies¹ criteria were described for distinguishing between inner- and outer-sphere reaction pathways for the electroreduction of eight pentaquo complexes of chromium(III). Similar experiments have now been conducted with a large set of ammine complexes of Cr(III) to explore more fully the general applicability of the proposed diagnostic criteria. The results reveal significant differences in the kinetic behavior of the aquo and ammine complexes which make it somewhat less straightforward to infer mechanisms for the latter set of complexes on the basis of the previously proposed criteria.¹ The purposes of this note are to report the most relevant electrode kinetic data obtained for the chromium(III)-ammine complexes, to compare them with corresponding data for the analogous aquo complexes, and to

Table I. Kinetic Data for the Reduction of Chromium(III)-Ammine Complexes at Mercury Electrodes

Complex	Ref for prepn of complex	Potential range where kinetic data were obtained, $-E$, mV vs. SCE	α_{app}^a	$-\log(k_{app}, \text{cm s}^{-1})^b$ at -900 mV	$\Delta \log(k_{app}, \text{cm s}^{-1})^c$ from I ⁻ adsorption	$\Delta \log(k_{app}, \text{cm s}^{-1})^d$ at -900 mV from change in ionic strength
Tripositive Ions						
$\text{Cr}(\text{NH}_3)_6^{3+}$	<i>i</i>	930-1045	0.74	3.34	1.0	-0.65
$\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+}$	<i>j</i>	880-990	0.72	2.69	0.91	-0.64
<i>cis</i> - $\text{Cr}(\text{NH}_3)_4(\text{OH}_2)_2^{3+}$	<i>k</i>	830-970	0.68	2.32	0.71	-0.55
$\text{Cr}(\text{OH}_2)_6^{3+}$		850-1000	0.60	2.63	0.23	-0.50
Dipositive Ions						
$\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$	<i>l</i>	805-975	0.54	2.28	0.52	-0.33
$\text{Cr}(\text{NH}_3)_5\text{NO}_3^{2+}$	<i>j</i>	800-990	0.49	2.27	0.54	-0.40
$\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$	<i>m</i>	930-1060	0.65	3.47	0.53	
$\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$ ^e	<i>n</i>	910-1060	0.63	3.23	0.66	-0.35
$\text{Cr}(\text{NH}_3)_4\text{F}^{2+}$	<i>l</i>	1120-1260	0.73	5.92 ^f	<i>g</i>	
$\text{Cr}(\text{OH}_2)_5\text{F}^{2+h}$	<i>o</i>	700-1200	0.58	4.9	~0.2	
Monopositive Ions						
<i>trans</i> - $\text{Cr}(\text{en})_2\text{Cl}_2^+$	<i>p</i>	720-870	0.63	1.2	0.88	-0.27
<i>trans</i> - $\text{Cr}(\text{en})_2(\text{NCS})_2^+$ ^e	<i>q</i>	770-850	0.67	1.79	-0.20	-0.12
$\text{Cr}(\text{OH}_2)_5\text{OSO}_3^+$ ^h	<i>r</i>	600-1150	0.56	3.5	~0.06	

^a Tafel plots ($\log k_{app}$ vs. E) were essentially linear throughout the specified potential range. ^b Supporting electrolyte: 1 M NaClO₄-0.01 M HClO₄. ^c Supporting electrolyte was changed from 1 M NaClO₄-0.01 M HClO₄ to 0.67 M NaClO₄-0.33 M NaI-0.01 M HClO₄ except for $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$ and $\text{Cr}(\text{en})_2(\text{NCS})_2^+$ where the change was 0.32 M Na₂SO₄-0.04 M NaHSO₄ to 0.33 M NaI-0.04 M NaHSO₄. ^d Supporting electrolyte was changed from 0.02 M La(ClO₄)₃-0.01 M HClO₄ to 0.1 M La(ClO₄)₃-0.01 M HClO₄. ^e Supporting electrolyte was 0.32 M Na₂SO₄-0.04 M NaHSO₄ because of the low solubility of this complex in concentrated perchlorate electrolytes. ^f Value obtained by linear extrapolation of the Tafel plot from -1100 mV. ^g Kinetic data could not be obtained at potentials positive enough to produce significant iodide adsorption. ^h Data from ref 1. ⁱ M. Mori, *Nippon Kagaku Zasshi*, 74, 253 (1953). ^j M. Mori, *Inorg. Synth.*, 5, 131 (1957). ^k P. Pfeiffer, *Ber. Dtsch. Chem. Ges.*, 40, 3126 (1907). ^l E. Kyuno, M. Kamada, and N. Tanaka, *Bull. Chem. Soc. Jpn.*, 40, 1848 (1967). ^m M. Linhard, H. Siebert, and M. Weigel, *Z. Anorg. Chem.*, 278, 287 (1955). ⁿ M. Linhard and W. Berthold, *Z. Anorg. Chem.*, 279, 173 (1955). ^o T. W. Swaddle and E. L. King, *Inorg. Chem.*, 4, 532 (1965). ^p P. Pfeiffer, P. Koch, G. Londo, and A. Treishman, *Ber. Dtsch. Chem. Ges.*, 37, 4255 (1904). ^q C. L. Rollinson and J. C. Bailar, *Inorg. Synth.*, 2, 200 (1946). ^r N. Fogel, J. Tai, and J. Yarborough, *J. Am. Chem. Soc.*, 84, 1145 (1962).

comment on possible origins of the observed differences.

Experimental Section

Materials. The chromium(III) complexes were prepared and purified according to the published procedures referred to in Table I. Supporting electrolytes were prepared from reagent grade salts except for perchlorates which were prepared by reacting perchloric acid with sodium carbonate or lanthanum oxide. Solutions were prepared with triply distilled water and oxygen was removed from all solutions by purging with prepurified nitrogen which had been passed successively through a chromium(II) solution and copper turnings at 450 °C.

Apparatus and Procedure. The rates of reduction of the complexes were calculated from pulse polarograms² obtained by means of a standard Princeton Applied Electronics Model 174 Polarograph and recorded on a Houston-Omnigraph X-Y recorder. The two-compartment H-cell, dropping-mercury electrode, and operating procedures were all conventional. The mechanically controlled drop time was 1 s and the mercury flow rate was 1.5 mg s⁻¹. The effective current-sampling time of the unmodified PAR 174 instrument is ca. 48 ms. In cases where evidence for polarographic maxima³ appeared (usually only at the lowest concentrations of supporting electrolyte) the reactant concentration was decreased until no evidence of maxima was apparent in individual current-time curves. The analysis of the normal pulse polarograms to obtain the rate constants involved a least-squares fitting of the current-potential data to the equations given in ref 2 by means of a minicomputer. The programs were tested by applying them to pulse polarograms for the reduction of hexa-aquochromium(III) for which extensive rate-potential data are available.⁴

Reactant concentrations were typically 0.5-1 mM but were sometimes decreased to 0.2 mM to avoid maxima. Experiments were conducted at 22 ± 1 °C. Potentials were measured vs. a sodium chloride-saturated calomel electrode but are reported with respect to a conventional SCE.

Results and Discussion

Two primary criteria have been utilized to distinguish between the inner- and outer-sphere electroreductions of cationic aquo complexes of chromium(III):¹ the response of

the reaction rate to adsorption of iodide anions on the electrode surface and the magnitude of the potential dependence of the reaction rate (i.e., the value of the apparent transfer coefficient, α_{app}). Inner-sphere reductions were signaled by values of α_{app} smaller than 0.5 and decreased reaction rates in the presence of adsorbed iodide while reductions following outer-sphere pathways exhibited the converse behavior. Table I summarizes the relevant experimental data obtained for the various ammine complexes of chromium(III) and, for comparison, the corresponding data for selected aquo complexes.

All of the tripositive complexes in Table I lack likely bridging ligands. Not surprisingly, they also exhibit values of α_{app} well above 0.5 and increases in reduction rates in the presence of adsorbed iodide—both signals of outer-sphere reaction pathways. However, both the value of α_{app} and the magnitude of the kinetic responses to adsorbed iodide are much larger than those for the hexa-aquochromium(III) complex which has the same charge and is reduced by an outer-sphere pathway¹ (Table I). The differences in the responses to iodide adsorption cannot be accommodated on the basis of conventional double-layer models⁵ because all ions bearing the same charge are predicted to respond equally to iodide adsorption so long as they follow outer-sphere reaction pathways.

With the exception of $\text{Cr}(\text{NH}_3)_5\text{F}^{2+}$, the dipositive and monopositive complexes in Table I all contain anionic ligands which enabled the corresponding penta-aquo complexes to follow inner-sphere reduction pathways. Nevertheless, these ammine complexes register values of α_{app} well above 0.5 (except for the nitrate complex) which would be taken as a signal of an outer-sphere reaction in the penta-aquo series. Moreover, iodide adsorption enhances the reaction rate (at -900 mV) of every complex except *trans*- $\text{Cr}(\text{en})_2(\text{NCS})_2^+$ under conditions where small rate depressions were found for the penta-aquo complexes containing the same heteroligands. Despite the fact that most of these dipositive and monopositive ammine complexes display qualitative behavior which would

classify them as outer-sphere reactants on the basis of the two criteria previously proposed,¹ it seems highly unlikely that inner-sphere pathways are not accessible to these complexes. The apparent contradiction may be understood if the outer-sphere reduction of the ammine complexes is assumed to proceed at positions within the double layer that lie closer to the electrode surface than those utilized by the aquo complexes. That reaction sites which lie within the compact portion of the double layer may be reasonably invoked to account for otherwise anomalous electrode kinetic behavior is a notion that has been supported in several previous studies.⁶⁻⁸ Weaver⁹ has suggested that the kinetic behavior of chromium(III)-ammine complexes might also be interpretable on this basis and has assembled evidence to support the assumption of differing reaction sites for the differing complexes. The objective of what follows is to show that the data in Table I are compatible with such an interpretation.

Effects of Differing Reaction Sites on α_{app} . Fawcett⁶ has given a clear analysis of the way in which variations in the distance separating the electrode surface and the reaction site may affect the kinetics of electrode reactions. It can be shown from Fawcett's treatment that two outer-sphere reactants bearing the same charge, Z , but having reaction sites which lie at positions x_r and x_r' from the electrode surface will exhibit values of α_{app} that differ by an amount given by eq 1 where

$$\Delta\alpha_{app} = (\alpha_1 - Z) \left(\frac{x_r' - x_r}{x_2} \right) \left[1 - \left(\frac{\partial\phi_2}{\partial E} \right) \right] \quad (1)$$

α_1 is the intrinsic transfer coefficient,¹⁰ assumed to be the same for each reactant, x_2 is the position of the outer Helmholtz plane (oHp), ϕ_2 is the potential there, and E is the electrode potential. (Fawcett's treatment⁶ also includes the possibility of spatial variations in the value of the dielectric constant within the double layer. We have neglected this added complication in deriving eq 1.)

For some typical values of the parameters in eq 1, namely, $\alpha_1 = 0.5$, $Z = +3$, and $\partial\phi_2/\partial E \approx 0.05$

$$\Delta\alpha_{app} = -2.4 \left(\frac{x_r' - x_r}{x_2} \right) \quad (2)$$

Thus, the uniformly larger values of α_{app} for the tripositive chromium(III)-ammine complexes in Table I can be understood if they undergo reduction at sites 5-10% closer to the electrode surface than that utilized by the hexaaquo complex of chromium(III).

Among the dipositive and monopositive ammine complexes in Table I only $\text{Cr}(\text{NH}_3)_5\text{F}^{2+}$ seems likely to react exclusively by an outer-sphere pathway and the value of α_{app} for this complex is also much larger than that for $\text{Cr}(\text{OH}_2)_5\text{F}^{2+}$, as predicted by eq 1 if the reaction site for the pentaammine complex lies closer to the electrode surface. The remaining dipositive complexes have α_{app} values smaller or only slightly greater than that for $\text{Cr}(\text{OH}_2)_5\text{F}^{2+}$ which may be evidence of simultaneous contributions from both inner- and outer-sphere pathways inasmuch as α_{app} values smaller than 0.5 have been shown to be indicators of the inner-sphere reduction of anion-bridged, cationic complexes.¹

Responses to Changes in Ionic Strength. The analysis which leads to eq 1 can also be applied to estimate how changes in the ionic strength of the supporting electrolyte will affect the reaction rate at constant electrode potential. The result is given in eq 3 where $(\Delta \ln k)_E$ is the change in the rate constant at

$$(\Delta \ln k)_E = (\alpha_1 - Z)(x_r/x_2)\Delta\phi_2 \quad (3)$$

potential E caused by the change, $\Delta\phi_2$, in the potential at the oHp resulting from a change in ionic strength and the other symbols have been defined.

The responses of the complexes in Table I to the change in ionic strength (0.02 M $\text{La}(\text{ClO}_4)_3$ to 0.10 M $\text{La}(\text{ClO}_4)_3$) are rather small and quite similar for each charge type. The $\text{Cr}(\text{OH}_2)_6^{3+}$ complex shows a slightly smaller change in rate than do the other tripositive complexes while the opposite order is expected on the basis of eq 3 if x_r is indeed larger for the hexaaquo complex than for the ammine complexes as was indicated by their relative values of α_{app} . The problem is that eq 3 is based on the assumption that changes in ionic strength cause changes only in ϕ_2 and not in the formal potential for each complex. In fact, the ammine complexes are likely to form ion pairs with perchlorate anions more extensively than do the aquo complexes¹¹ in which case the net overpotential driving the electrode reaction would decrease as the ionic strength is increased at constant potential. This effect acts in the opposite direction to that resulting from the corresponding changes in ϕ_2 so that the differences in the responses of the complexes in Table I to changes in ionic strength are too small to be diagnostically useful.

Responses to Iodide Adsorption. The outer-sphere reactants from the pentaquo series respond to iodide adsorption with rate enhancements that are in reasonably good agreement with those calculated from diffuse-layer theory if the only effect of the adsorbed iodide is assumed to be an increase in the negative charge on the electrode surface, with a corresponding change in ϕ_2 .¹ However, for outer-sphere reactants with reaction planes lying between the outer and inner Helmholtz planes, the rate changes calculated to result from changes in the amount of anion adsorption at the inner Helmholtz plane (iHp) depend upon the model used for the inner layer. If a simple, conventional model¹² is employed in which adsorbed anions are assumed to be on the iHp which is located at a distance x_i from the electrode surface, the change in potential at a reaction site located between the inner and outer Helmholtz planes produced by a change in the quantity of adsorbed anions (at constant potential and ionic strength) will be given by eq 4 where $f = F/RT$, ϕ_i is the potential at the

$$(\Delta \ln k)_E = f(\alpha_1 - Z) \left[\frac{x_r}{x_2} + \frac{x_2 - x_r}{x_2 - x_i} \left(\frac{\partial\phi_i}{\partial\phi_2} \right)_E \right] \Delta\phi_2 \quad (4)$$

iHp, and the variation of the dielectric constant with position within the inner layer is neglected. The differential coefficient in eq 4 can be evaluated from diffuse-layer theory⁵ to yield eq 5, where $A = 5.86 \mu\text{C cm}^{-2}$ for uni-univalent electrolytes

$$\left(\frac{\partial\phi_i}{\partial\phi_2} \right)_E = \left[1 + \frac{Af}{K_{i,2}} \cosh \left(\frac{f\phi_2}{2} \right) \right] \quad (5)$$

at 25 °C and unit ionic strength and $K_{i,2}$ is the integral capacitance of the region between the inner and outer Helmholtz planes. Combining eq 4 and 5 gives eq 6. Since the second

$$(\Delta \ln k)_E = f(\alpha_1 - Z) \left[1 + \left(\frac{x_2 - x_r}{x_2 - x_i} \right) \frac{Af}{K_{i,2}} \cosh \left(\frac{f\phi_2}{2} \right) \right] \quad (6)$$

term inside the brackets in eq 6 is always positive when $x_r < x_2$, it follows that anion adsorption is expected to produce larger rate responses for reactants with reaction sites located closer to the electrode than the oHp. This prediction is in qualitative accord with the responses listed in Table I. Substitution of representative numerical values for the parameters in eq 6 ($K_{i,2} = 60 \mu\text{F cm}^{-2}$,¹³ $\phi_2 = -40 \text{ mV}$ ⁴) yields eq 7, which predicts that the ratio of the kinetic responses to

$$(\Delta \ln k)_E = f(\alpha_1 - Z) \left[1 + 4.3 \left(\frac{x_2 - x_r}{x_2 - x_i} \right) \right] \Delta\phi_2 \quad (7)$$

iodide adsorption of reactants which react at x_r to those which react at x_2 is

$$\frac{(\Delta \ln k)_E^{x_r}}{(\Delta \ln k)_E^{x_2}} = 1 + 4.3 \left(\frac{x_2 - x_r}{x_2 - x_1} \right) \quad (8)$$

However, the use of eq 8 to account for the large difference shown in Table I for the kinetic response to iodide adsorption of, for example, the hexaquo and hexaammine complexes would require that the ratio $(x_2 - x_r)/(x_2 - x_1)$ have the very large value of ca. 0.8. (If this ratio were unity, the reaction site would lie on the iHp.) For this reason we believe the iodide response data also reflect the presence of specific interactions between the adsorbed iodide anions and the cationic complexes within the inner portion of the double layer. Specific effects of this type have been frequently proposed to account for the kinetic behavior of more complex electrode reactions (especially anion reductions) for which the site of reaction is thought to lie within the compact layer.¹⁴⁻¹⁹ We found no evidence of such effects in previous studies of the reduction of the cationic aquo complexes of chromium(III) and europium(III)^{4,20} but that is to be expected if aquo complexes in general have reaction sites within the outer, diffuse portion of the double layer where the charges on the discrete, adsorbed anions can be screened by the high ionic concentrations within the diffuse layer.

The dipositive ammine complexes in Table I all show rate enhancements in the presence of adsorbed iodide which are larger than that of the dipositive, outer-sphere analogue $\text{Cr}(\text{OH})_2\text{F}^{2+}$. This probably results because these complexes react by both inner-sphere and outer-sphere pathways which are more competitive than was true for the pentaquo series because the ammine complexes can approach the electrode surface more closely, even when they react by an outer-sphere pathway. The iodide adsorption test cannot provide a clear distinction between reaction mechanisms, of course, in cases where neither pathway is kinetically predominant. The successful use of this test with the pentaquo complexes¹ depended upon the rates of inner-sphere pathways being so much larger than those of outer-sphere pathways that the iodide enhancement of the latter was more than counterbalanced by its repression of the former. The single complex in Table I which shows a decreased rate upon iodide adsorption, $\text{trans-Cr}(\text{en})_2(\text{NCS})^+$, is also very strongly adsorbed on mercury.²¹ Its response to iodide adsorption seems a clear signal that this complex is reduced predominantly by an inner-sphere mechanism. The relatively large value of α_{app} for this complex could reflect a parallel and less efficient outer-sphere pathway but, more likely, it results from the increase in the adsorption of the complex with more negative potentials²¹—a trend which is opposite from that observed with most isothiocyanato complexes of Cr(III). Values of α_{app} larger than 0.5 are to be expected¹ for inner-sphere reactants which show increased adsorption at more negative potentials.

Conclusions

As suggested by Weaver⁹ the data summarized in Table I can be interpreted as indicating that $\text{Cr}(\text{NH}_3)_6^{3+}$, $\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+}$, and $\text{cis-Cr}(\text{NH}_3)_4(\text{OH}_2)_2^{3+}$ are reduced at mercury by outer-sphere mechanisms in which the reaction site lies closer to the mercury surface than it does during the outer-sphere reduction of $\text{Cr}(\text{OH}_2)_6^{3+}$. With the exception of $\text{Cr}(\text{NH}_3)_5\text{F}^{2+}$, the dipositive and monopositive complexes in Table I appear to be reduced by parallel inner-sphere and outer-sphere pathways at rates that are too similar to permit mechanistic diagnoses as clear-cut as proved possible with analogous pentaquo complexes.¹ The ability of the ammine complexes to approach the electrode surface more closely than the aquo complexes appears to be the origin of the greater reactivity displayed by the former complexes in their outer-sphere reduction at electrodes. The previously proposed criteria for distinguishing between inner- and outer-sphere electrode

reaction pathways¹ are not vitiated by the results presented here but it seems clear that the demands on the quantity and precision of kinetic data will be much greater if rate constants for both inner- and outer-sphere pathways are to be evaluated when they make comparable contributions to overall reaction rates.

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Registry No. $\text{Cr}(\text{NH}_3)_6^{3+}$, 14695-96-6; $\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+}$, 15975-47-0; $\text{cis-Cr}(\text{NH}_3)_4(\text{OH}_2)_2^{3+}$, 42402-01-7; $\text{Cr}(\text{OH}_2)_6^{3+}$, 14873-01-9; $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$, 14482-76-9; $\text{Cr}(\text{NH}_3)_5\text{NO}_3^{2+}$, 21350-86-7; $\text{Cr}(\text{NH}_3)_5\text{N}_3^{2+}$, 22317-10-8; $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$, 16884-60-9; $\text{Cr}(\text{NH}_3)_5\text{F}^{2+}$, 19443-25-5; $\text{Cr}(\text{H}_2\text{O})_5\text{F}^{2+}$, 19559-07-0; $\text{trans-Cr}(\text{en})_2\text{Cl}_2^+$, 14403-88-4; $\text{trans-Cr}(\text{en})_2(\text{NCS})_2^+$, 29845-02-1; $\text{Cr}(\text{OH}_2)_5\text{OSO}_3^+$, 19163-97-4.

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Temperature and Pressure Effects on the Electronic Transitions of Nickel(II) Complexes with C,C-Dimethylethylenediamine and N,N-Dimethylethylenediamine¹

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Complexes of the type $\text{M}(\text{Et}_2\text{en})_2\text{X}_2$, where $\text{M} = \text{Cu}(\text{II})$ or $\text{Ni}(\text{II})$, $\text{Et}_2\text{en} = N,N$ -diethylethylenediamine and $\text{X} =$ an inorganic anion, manifest thermochromic behavior.³⁻⁸ Lever and co-workers⁵⁻⁶ have provided convincing support for a model of tetragonal distortion in these complexes, in which the in-plane bond strength increases as the axial ligation decreases, as the mechanism for thermochromism.⁶ Pressure and thermal studies of the copper and nickel complexes in the electronic and infrared regions (mid- and far-infrared) by Ferraro et al.⁸ have confirmed Lever's mechanism as the