Electron Transfer through Organic Structural Units. VIII. Reductions of Pentaamminecobalt(III) Complexes in Poly(vinylsulfonic acid) Solution[1]

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Abstract: The Cr(II) reductions of positively charged organic pentaamminecobalt(III) derivatives are, as expected, markedly accelerated by addition of poly(vinylsulfonate). With [Co(III)] near 10^{-5} *M*, [Cr(II)] near 10^{-4} *M*, and [$HClO_4$] = 0.01 *M*, maximum specific rates are observed near 0.001 *N* polysulfonate for dipositive oxidants and in the range 0.003–0.004 *N* polysulfonate for unipositive oxidants. No such accelerations are noted with monomeric alkanesulfonates. Specific rates of reduction of 23 complexes in 0.0030 *N* polysulfonate are compared to those at unit ionic strength in the absence of polyelectrolyte. Acceleration factors are 1000–4500 for tripositive oxidants, 470–790 for dipositive, and 86–390 for unipositive. The magnitude of acceleration does not depend on reaction mechanism, but rather on the layout of electrostatic charge within the oxidant. For Co(III) complexes having a positive nitrogen, acceleration is greatest when that nitrogen is closest to cobalt; for complexes having a negative sulfonate group, acceleration is greatest when the sulfonate is farthest from cobalt. Among the oxidants studied, 52 instances were noted in which the relative rates of reduction of two complexes are reversed if they are compared in 0.003 *N* polysulfonate instead of at unit ionic strength in the absence of polymer. Of these "inversions," 14 involve comparison of complexes of equal charge.

Reactions between like-charged ions in solution are strikingly accelerated by polyions of opposite charge. For example, the benzidine rearrangement, which occurs through the reaction of two unipositive ions, is over 100 times as rapid in 0.05 *N* poly(styrenesulfonic acid) as in 0.05 *N* benzenesulfonic acid.[2] More dramatically, 5×10^{-5} *N* poly(vinylsulfonic acid), under appropriate conditions, accelerates the Hg^{2+}-catalyzed aquation of $Co(NH_3)_5Cl^{2+}$ (a reaction involving two dipositive cations) by more than 10^5.[3a] The magnitudes of these rate increases show an important dependence on the nature and concentration of the polyelectrolyte, the charges on the reacting species, and the concentrations of nonparticipating salts,[3a] but it is not clear how sensitive such effects are to variation in the detailed structure of the reactants[4] or to changes in reaction mechanism.

Pentaamminecobalt(III) derivatives of organic ligands with a wide variety of structures have been prepared in recent years. The reductions of these, with Cr^{2+}, proceed at specific rates falling within a very large range and involve several mechanistic variations.[5] In the present study, the rates of a number of such reductions in dilute poly(vinylsulfonic acid) are compared to the corresponding rates in the absence of polyelectrolyte. Accelerations due to the polyanion in this series do not appear to be related to reaction mechanism but show significant variation with the structure of the oxidant.

Experimental Section

Materials. Pentaamminecobalt(III) complexes were prepared in water from aquopentaamminecobalt(III) perchlorate as described[5a,b] or were available from previous studies.[6] Cr(II) solutions were prepared by reduction of a 0.855 *M* $Cr(ClO_4)_3$ solution in 1 *M* $HClO_4$ using zinc amalgam.[6b] Polyelectrolyte solutions were made with sodium poly(vinylsulfonate) ($M_w \sim 60{,}000$), obtained as a research sample from Hercules Inc. through the courtesy of Dr. David Breslow; this polyelectrolyte has been used and described by Ise.[3c]

Kinetic Experiments. Reactions were carried out under pseudo-first-order conditions with the ratio Cr(II)/Co(III) between 6 and 10, and were monitored by following the decrease in absorbance at the high-wavelength visible absorption maximum of the Co(III) complex. Absorbancy changes were read on the Cary Model 14 recording spectrophotometer using the 0–0.2 slidewire. Initial Co(III) concentrations were 2×10^{-5} *M* for tripositive cations and about 4×10^{-5} *M* for dipositive and unipositive cations. All reductions were carried out in 0.01 *M* $HClO_4$. In most cases, solutions were 0.003 *N* in polyelectrolyte. Temperatures were 25.0 ± 0.2°. Reactions were carried out in a 10.0-cm cylindrical cell through which solutions were added through rubber serum caps.[7] Reactions were allowed to proceed for at least five half-life periods, and good pseudo-first-order plots were generally obtained. Rate constants taken from several points in a single run agreed to better than 6%, and those from different runs checked to better than 10%. With the carboxylato complexes, a gradual downward drift of absorbance at the conclusion of the redox reaction (due possibly to polyelectrolyte-catalyzed hydrolysis of the Cr(III) product) was sometimes observed, introducing slight uncertainty in the "infinity" reading. A more serious difficulty, frequently encountered during the early stages of this work, was the coacervation of the polyelectrolyte in the presence of metal salts, resulting in a sudden increase in the apparent optical density

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[1] Work sponsored by the Petroleum Research Fund, administered by the American Chemical Society, under Grant No. 2868-A3; this support is gratefully acknowledged.

[2] C. L. Arcus, T. L. Howard, and D. S. South, *Chem. Ind.* (*London*), 1756 (1964).

[3] (a) H. Morawetz and B. Vogel, *J. Amer. Chem. Soc.*, **91**, 563 (1969), briefly reviews recent work in the area; for additional references, see (b) I. Sakurada, Y. Sakaguchi, T. Ono, and T. Ueda, *Makromol. Chem.*, **91**, 243 (1966); (c) N. Ise and F. Matsui, *J. Amer. Chem. Soc.*, **90**, 4242 (1968).

[4] Morawetz and Vogel[3a] report that Hg^{2+}-catalyzed aquation of $Co(NH_3)_5Cl^{2+}$ is accelerated slightly more markedly than is the aquation of the corresponding bromo complex under similar conditions, but describe no more drastic structural modification in their substrate.

[5] See, for example (a) E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964); (b) E. S. Gould, *ibid.*, **87**, 4730 (1965); (c) H. Taube and E. S. Gould, *Accounts Chem. Res.*, **2**, 321 (1969).

[6] (a) E. S. Gould, *J. Amer. Chem. Soc.*, **88**, 2983 (1966); (b) *ibid.*, **89**, 5792 (1967); (c) Y. Wang and E. S. Gould, *ibid.*, **91**, 4998 (1969).

[7] The usual procedure in which dissolved oxygen is removed by purging the reaction mixture with oxygen-free nitrogen before addition of Cr(II) was modified, since bubbling nitrogen through the polyelectrolyte solution resulted in foaming which made the preparations difficult to handle. Instead, distilled water was boiled, then purged with nitrogen, and the resulting oxygen-free water was used to prepare solutions of reagents and polyelectrolyte which were stored, transferred, and mixed under nitrogen.

Table I. Kinetic Data for Chromous Reductions of Carboxylatopentaamminecobalt(III) Complexes in the Absence of Polyelectrolyte

Organic ligand	Added acid (*M*)	μ	*k*[a]
Formato[b]	$HClO_4$ (0.01)	0.014	2.2
	TosOH[c] (0.01)	0.014	2.0
	$HClO_4$ (0.12)	0.124	3.6
	$HClO_4$ (1.20)	1.20	7.3
Acetato[b]	$HClO_4$ (0.01)	0.05	0.081
	$HClO_4$ (0.01) + TosOH[c] (0.01)	0.06	0.10
p-Sulfobenzoato[b]	$HClO_4$ (1.0)	1.08	0.20
	$HClO_4$ (0.095)	1.16[d]	0.22
m-Sulfobenzoato	$HClO_4$ (1.0)	1.16	0.22
	$HClO_4$ (0.095)	1.16[d]	0.22
o-Sulfobenzoato	$HClO_4$ (1.0)	1.08	0.50
	$HClO_4$ (0.095)	1.08[d]	0.53
o-Methylbenzoato	$HClO_4$ (1.20)	1.26	0.087
Sulfoacetato	$HClO_4$ (1.0)	1.04	2.3
	$HClO_4$ (0.095)	1.04[d]	2.4

[a] Specific rates in M^{-1} sec^{-1} at 25°; $[Co(III)]_0 = 5 \times 10^{-5}$–$5 \times 10^{-4}$ *M;* $[Cr(II)]/[Co(III)]_0 = 10$–$40$. [b] Reported rate constants ($\mu = 1.0$) are 7.2 for the formato complex, 0.35 for the acetato,[5c] and 0.16 for the *p*-sulfobenzoato.[9] [c] *p*-Toluenesulfonic acid. [d] Supporting electrolyte, $LiClO_4$.

Table II. Variation, with Polyelectrolyte Concentration, of Specific Rates for Reductions of Carboxylatopentaamminecobalt(III) Complexes with Chromium(II)

Organic ligand	[Polyelectrolyte], equiv/l. × 1000	*k*[a]
2-Aminopyridine-3-carboxylato (II)	0.67	*b*
	1.0	340
	2.0	240
	3.0	194
p-Dimethylaminobenzoato (VI)	0.67	190[c]
	1.0	320
	2.0	195
	3.0	152
Propionato	0.67	113
	1.0	142
	1.5	145
	2.0	108
	3.0	97
o-Methylbenzoato	0.50	38[c]
	0.75	73
	1.0	107
	3.0	66
	6.0	37
p-Sulfobenzoato (VIII)	0.67	34
	1.0	51
	1.5	60
	2.0	76
	3.0	81
	4.0	68
	6.0	47
o-Sulfobenzoato	2.0	35
	3.0	45
	4.0	57
	6.0	52[c]

[a] Specific rates in M^{-1} sec^{-1} at 25°; $[Co(III)]_0 = 5 \times 10^{-5}$ *M;* $[Cr(II)]/[Co(III)]_0 = 7$–10; $[HClO_4] = 0.10$ *M.* [b] Coacervation of polyelectrolyte observed during early stages of reaction. [c] Coacervation observed during later stages of reaction.

of the sample. This occurred when too slight an excess of polyelectrolyte was taken, or when considerable quantities of $Cr(H_2O)_6{}^{3+}$ (from outer-sphere reduction of the Co(III) complex) or its dimer (from oxidation of Cr^{2+} by traces of oxygen in solution) were formed.[8] Coacervation was sometimes observed also when a solution of the Co(III) complex was added to a dilute solution of the polyelectrolyte (rather than addition in the reverse manner), but in such cases, the turbidity disappeared when the sample was agitated and allowed to stand for a few minutes.

Results and Discussion

Kinetic data are presented in Tables I–III. Table I lists reductions carried out in the absence of polyelectrolyte, including those for SO_3H-substituted carboxylato complexes; with the exception of the *p*-sulfobenzoato complex,[9] rate constants for derivatives of this type have not yet been reported. Specific rates for the sulfo complexes are independent of acidity, even when (as in the case of the *o*-sulfobenzoato and the sulfoacetato complexes) the sulfonate group lies near the carboxyl-bound cobalt; for each of these reductions, only one form of the complex is kinetically significant. Note that addition of *p*-toluenesulfonic acid, a "mono" analog of the polyelectrolyte used, affected the observed specific rates only slightly, although its molar concentration was well above the normal concentration of the polyanion taken in experiments involving the latter.

Table II illustrates variations in reaction rates with concentration of polyelectrolyte for six of the Co(III) complexes. Specific rates at first increase with concentration of polyion, reach a maximum, then decrease once more. This pattern parallels that described for the Hg(II)-catalyzed aquation by Morawetz and Vogel;[3a] these authors attribute the rate decreases at higher polymer concentrations to partition of the reacting cations between competing polymer domains, and it is likely that much the same picture applies here. The maximum rates in these studies occur at polyanion concentrations at least an order of magnitude greater than the optimum poly(vinylsulfonate) concentrations reported for the aquation studies, doubtless because the smaller changes in molar absorptivities in the present systems necessitated working at much higher reagent concentrations.

For reductions of dipositive complexes, optimum polyanion concentrations lie near 0.001 *N*, whereas for unipositive complexes rate maxima occur at polymer concentrations near 0.003–0.004 *N*. As to the tripositive complexes, although one of these (complex VI) is found to be reduced most rapidly at in 0.001 *N* polysulfonate, the optimum polyanion concentration falls more usually in the range where coacervation occurs early in the progress of reduction, thus being indeterminate by the present methods. From the small number of cases here examined, it is clear that the optimum polymer concentration shows significant variation not only with the net charge of the oxidant but also with ligand structure within a given charge type. In general, the optimum polyanion concentration appears to be lowest for those reactions most markedly accelerated.

In an attempt to compare rates in a common reaction medium, reductions in 0.003 *N* poly(vinylsulfonate)

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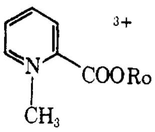
[8] When $Cr(ClO_4)_3$ solution was added to 0.00025–0.006 *N* poly(vinylsulfonate) at 25°, coacervation was observed if [Cr(III)] exceeded one-tenth the normal concentration of the polyelectrolyte. When Cr(III) was added as a dipositive carboxylato complex, this ratio could be raised to about 0.5 before turbidity was apparent. With Cr(II) in oxygen-free solution, the ratio was about 1.5 at the onset of coacervation. These values appeared to be nearly independent of added $HClO_4$ in the concentration range 10^{-4}–10^{-2} *M*. Coacervation from poly(styrenesulfonate) solutions was observed at much lower ratios of salt to polyelectrolyte. For a detailed study of coacervation phenomena in solutions containing poly(vinylsulfonate) and transition metal ions, see F. Millich and M. Calvin, *J. Phys. Chem.*, 66, 1070 (1962).

[9] R. T. M. Fraser, *J. Amer. Chem. Soc.*, 84, 3436 (1962).

Table III. Specific Rates for Chromous Reductions of Pentaamminecobalt(III) Complexes, $R(NH_3)_5Co^{III}$, in 0.003 *N* Poly(vinylsulfonate)

R	k_{PVS}[a]	k_1[b]	k_{PVS}/k_1
Tripositive complexes			
Pyridine	18	0.0040[c]	4500
N-Methylpyridine-2-carboxylato (I)	380	0.087[d]	4400
3,5-Dimethylpyridine	9.2	0.0022[c]	4200
2-Aminopyridine-3-carboxylato (II)	194	0.047[e]	4100
Dimethylformamide	20	0.0072[f]	2800
Pyridine-3-carboxylato (III)	230	0.10[d]	2300
N,*N*-Dimethylinicotinamide (IV)	61	0.030[f]	2000
N-Methylpyridine-3-carboxylato (V)	250	0.13[d]	1900
p-Aminobenzoato	173	0.13[d]	1300
p-Dimethylaminobenzoato (VI)	152	0.15[e]	1000
Dipositive complexes			
o-Methylbenzoato	66	0.084	790
2,4,6-Trimethylbenzoato	33	0.045[g]	730
Acetato	250	0.35[h]	720
o-Bromobenzoato	56	0.081[d]	690
o-Iodobenzoato	54	0.080[d]	680
Benzoato	97	0.15[h]	650
Propionato	97	0.15[g]	650
o-Methoxybenzoato	118	0.23[d]	510
Benzofuran-2-carboxylato (VII)	198	0.42[g]	470
Unipositive complexes			
p-Sulfobenzoato (VIII)	81	0.21	390
m-Sulfobenzoato	62	0.22	280
Sulfoacetato (IX)	310	2.3	135
o-Sulfobenzoato	45	0.52	86

[a] Specific rates in M^{-1} sec^{-1} at 25°; $[Co(III)]_0 = 2 \times 10^{-5}$–$4 \times 10^{-5}$ *M;* $[Cr(II)]/[Co(III)]_0 = 6$–10; solutions 0.01 *M* in $HClO_4$. [b] Specific rates at unit ionic strength. [c] See ref 6c. [d] See ref 5a. [e] See ref 5b. [f] See ref 6b. [g] See ref 6a. [h] See ref 5c.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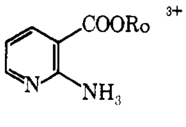
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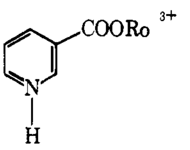
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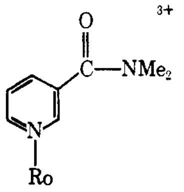
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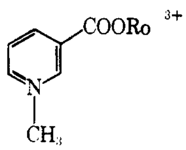
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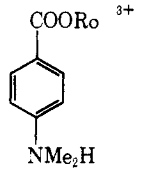
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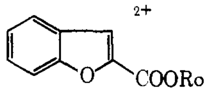
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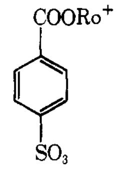
VIII

$O_3S—CH_2—COORo^+$

IX

Ro = "roseo" = $(NH_3)_5Co^{III}$

have been selected. This concentration lies well above the value for maximum acceleration with the dipositive and tripositive oxidants, but is near the lower limit necessary to preclude coacervation during reductions of each of the tripositive complexes. In Table III, the specific rates of reductions of a number of diverse cobalt(III) complexes in 0.003 *N* polyelectrolyte are listed, as are the corresponding rates at unit ionic strength in the absence of polyelectrolyte; the ratios, k_{PVS}/k_1, are the acceleration factors appearing in the final column. For a more appropriate comparison, rates in solutions 0.01 *M* in $HClO_4$ and 0.003 *M* in ethanesulfonic acid should be used in the denominator instead. The use of the latter rates, which are not presently available, would increase the acceleration factors about threefold for the dipositive complexes and sixfold for the tripositive complexes,[6b] but should not seriously alter the relative values within each charge group. The acceleration factors, although large, are well below those found in the aquations,[3a] again reflecting, at least in part, the higher concentrations of electrolyte used in this study.[10]

As expected, the acceleration factors exhibited by the tripositive complexes are, as a group, greater than those for the dipositive, which, in turn, exceed those for the unipositive. Complexes having a basic nitrogen (derivatives II, III, VI, and the *p*-aminobenzoato complex) have, in consideration of their estimated pK_A values,[5a,b] been taken to exist prodominantly in the tripositive forms shown, and the observed high values of the acceleration factors confirm this. Sulfonated complexes, featuring the strongly acid $-SO_3H$ group, are assumed to exist almost wholly in their deprotonated forms (*e.g.*, VIII and IX); the relatively low acceleration factors for these complexes fit this picture.

Among the tripositive complexes, there is no apparent correlation between the magnitude of polyelectrolyte acceleration and reaction mechanism. Acceleration factors for the N-coordinated pyridine complexes (including VI), and for the DMF complex, each of which is reduced *via* an outer-sphere mechanism,[6b] fall into the same range as those for the O-coordinated carboxylatopyridine derivatives (I, II, III, and V), which are reduced through carboxylato bridges.[5a,11]

Perhaps the most surprising feature here encountered is the wide variation in acceleration factors among reactions having both a common charge type and a common mechanism. The observed trends reflect, in large part, the distribution of charge within the Co(III) complex. Acceleration is very marked for N-coordinated pyridine derivatives; with these, the 3+ charge on cobalt is partially dispersed by coordination to the six donor nitrogens, but there is no mechanism for distributing it to the periphery of the complex. In the O-bound pyridinecarboxylato complexes, the charge on cobalt in the oxidant is partially neutralized by the negative carboxylato group, but an additional positive charge is introduced elsewhere in the complex by the tetracovalent nitrogen. When that nitrogen lies near

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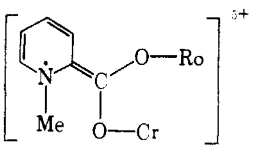
(10) The action of Cr^{2+} is complicated by its dual role in these systems. When it acts as a reagent, an increase in its concentration must increase the rate of reaction, but at high concentrations it may compete with the Co(III) complex for sites on the polyanion, thus reducing the acceleration factor. The superposition of these two effects should lead to a kinetic order less than unity if experiments are carried out over a wide range of Cr(II) concentrations, but no serious departures from first-order behavior were noted in these experiments. Typically, specific rates for the reduction of complex II were found to be 194 and 183 M^{-1} sec^{-1} at Cr(II) concentrations of 0.00030 and 0.00046 *M*, respectively.

(11) A desirable extension of the present study to include examples of two other mechanistic variations, electron transfer with chelation and remote attack through extended conjugated systems,[5c] would be complicated by the circumstance that reactions in many such cases are strongly acid dependent. Since hydrogen ion activities for polyelectrolyte solutions have not been unambiguously defined, medium effects would be superimposed on acidity effects of unknown magnitude.

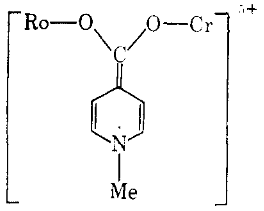
the Co(III) (*e.g.*, complexes I and II), the accelerating action stemming from the highly negative electrostatic potential of the polyanion is most pronounced. As the distance between the two positive centers is increased, acceleration is less marked; it becomes least effective when nitrogen and Co(III) lie on opposite ends of the ligand (*e.g.*, complex VI).[12]

The sulfonated unipositive complexes follow the reverse pattern. Here, the "extra" charge is a negative one, and the acceleration factor is greatest when the centers of charge within the complex are farthest apart. The negative $-SO_3^-$ group on the ligand may be considered to facilitate reduction by lowering the electrostatic barrier between the positive reaction centers, with intramolecular electrostatic acceleration most effective when the negative center is close to the reaction site (the *o*-sulfo derivative and complex IX). The role assumed by this substituent is thus much the same as that of the added polysulfonate. The trend within the unipositive series indicates the two accelerating actions to be complementary when polysulfonate is added; *i.e.*, the intermolecular action is greatest when a minimum share of its role has been usurped by the intramolecular action.[13]

The very high rate for the *N*-methylpyridine-2-carboxylato complex (I) in the presence of polyelectrolyte deserves comment; this value is significantly greater than that for the 3-carboxylato analog (V), under the same conditions, although reduction of I would be expected to be subject to steric retardation. It is suggested that the pyridine ring in I facilitates reduction by conjugative stabilization of an activated complex having the character of radical cation XI; structure XI is analogous to XII, which has been invoked to account for the high rate of reduction of the N-methylated 4-carboxy analog in the absence of polyelectrolyte.[5a] This accelerative action with the 2-carboxy derivative is generally overshadowed by electrostatic retardation but comes to light when this retardation is minimized in the presence of polysulfonate.[14] A structure analogous either to XI or XII cannot be drawn for the 3-carboxy analog.



XI



XII

Note finally that among the complexes listed in Table III there are more than 50 inversions, *i.e.*, pairs of complexes for which relative reactivities are reversed when the reactions are carried out in 0.003 *N* poly(vinylsulfonate) rather than in 1.0 *M* $LiClO_4$ with polymer absent. Although many of these involve comparison of complexes of differing charge types and are therefore not expected, 14 result from the comparisons of complexes of equal charge. Moreover, a somewhat different order of reactivities for reductions carried out in a different concentration (say 0.001 *N*) of this polyelectrolyte, or with a different polyanion, would not be unexpected. Taken as a group, such inversions serve as a reminder that any attempted correlation of redox rates with thermodynamic or molecular properties of reactants and products must, if it is to apply to real systems, make provision for peculiarities of the reaction medium as well.

Acknowledgments. The author is grateful to Professors Herbert Morawetz and Frank Millich, and to Dr. David Breslow for valuable discussions.

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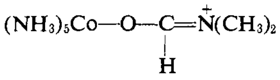
(12) The much greater rate for complex II than for the 2,4,6-trimethylbenzoato complex in PVS solution is in accord with earlier suggestions[5b,6a] that reduction is being shielded electrostatically with II but sterically with the methylated species; addition of polyanion helps to offset the electrostatic but not the steric effect. The acceleration factor for reduction of the dimethylformamido complex lies appreciably below those for the pyridine and dimethylpyridine derivatives, suggesting partial dispersal of positive charge through the amide linkage in the oxidant, as may be represented by structure X.



$$(\mathrm{NH_3})_5\mathrm{Co{-}O{-}}\underset{\substack{|\\ \mathrm{H}}}{\mathrm{C}}\mathrm{{=}}\overset{+}{\mathrm{N}}(\mathrm{CH_3})_2$$

X

(13) The final two entries within the dipositive group in Table III hint a similar complementarity of action. Both of these *o*-oxy-substituted benzoato complexes are reduced significantly faster than other ortho-substituted benzoato complexes in the absence of polyelectrolyte. Although the accelerating action of the oxy substituent is not yet understood, the kinetic advantage that these complexes enjoy is lowered appreciably in the polyelectrolyte medium.

(14) A structure similar to XI receives additional support from the recent observation (S. A. Kazmi, Ph.D. Thesis, Kent State University, 1970) that if Cr^{2+} is replaced as a reductant by Cu^+, which is less demanding sterically and suffers less electrostatic repulsion, complex I is reduced almost 20 times as rapidly in the absence of polyelectrolyte as is the benzoatopentaammine derivative under the same conditions.