If we now scale the CNDO and EHT curves additively so that the calculated potential energy surfaces reflect the energy difference between bridged and open radicals ($E\cdot = +11$ kcal mol^{-1} in Figure 1) and assume the cationic surface is similarly scaled, then one concludes that the bridged ion is 1–4 kcal mol^{-1} more stable than the open one.

In summary, neither CNDO or EHT MO calculations on the 2-phenethyl → phenonium cation give results which accord with experimental data. The deficiencies of CNDO for small ring compounds are quite serious, and its application to such problems must be approached with caution. Certainly the CNDO results quoted above must be viewed as merely suggestive and treated with reservation. For the time, at least, further information on this problem must await experimental results rather than those of calculation.

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Catalysis of Ionic Reactions by Polyelectrolytes. II. Electron Transfer between Cobalt(III) Complexes and Iron(II) in Solutions of Poly(vinylsulfonate)[1]

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Abstract: Dilute solutions of poly(vinylsulfonate) (PVS) accelerate by several orders of magnitude the reduction of $Co(NH_3)_5Cl^{2+}$, *cis*-$Co(NH_3)_4(N_3)_2^+$, and *trans*-$Co(NH_3)_4(N_3)_2^+$ by Fe^{2+}. The dependence of the reaction rate on polyion concentration, concentration of simple electrolyte, and reagent concentration is qualitatively similar to the characteristics of the previously reported polyanion-catalyzed reaction of $Co(NH_3)_5Cl^{2+}$ with Hg^{2+}. The reduction of $Co(NH_3)_4(N_3)_2^+$ is catalyzed by PVS much more powerfully with the trans isomer of the Co(III) complex, since this reaction is acid catalyzed and the complex ion bound to the polymer is in a region of high local hydrogen-ion concentration. A comparison of the PVS catalysis of $Co(NH_3)_5Cl^{2+}$ reactions with Hg^{2+} and Fe^{2+}, respectively, shows that the catalytic effect cannot be accounted for entirely by the concentration of the reagent ions in the polyion domain, but that this concentration also affects in some manner the activation process. On addition of PVS, the ΔE^* is reduced for the reaction with Hg^{2+} but increased for the reaction with Fe^{2+}.

In a previous communication from this laboratory,[2] it was demonstrated that small concentrations of polyanions may accelerate by very large factors reactions involving two cationic species. In particular, conditions were found where as little as 5×10^{-5} *N* poly(vinylsulfonate) (PVS) accelerated the Hg^{2+}-catalyzed aquation of $Co(NH_3)_5Cl^{2+}$ by a factor of 176,000.[3] It was proposed to interpret the dependence of the acceleration factor on the PVS concentration by two parameters, (a) the "effective local reagent ion concentration" in the polymer domain and (b) the product of the dissociation constants of the polyion with the two reagent ions. The second of these parameters could be evaluated by dialysis equilibrium, and the value thus obtained was in gratifying agreement with that estimated from kinetic data.

We are now extending this study to redox reactions involving Fe^{2+} as the electron donor and the species $Co(NH_3)_5Cl^{2+}$, *cis*-$Co(NH_3)_4(N_3)_2^+$, and *trans*-$Co(NH_3)_4(N_3)_2^+$ as electron acceptors.[4] In choosing these systems we had the following objectives. (1) The reactions of $Co(NH_3)_5Cl^{2+}$ with either Hg^{2+} or Fe^{2+} involve two species with a double positive charge, and it was of interest to determine whether both reactions are equally susceptible to polyanion catalysis. (2) In comparing the polyanion catalysis of the Fe^{2+} reduction of the cis and trans isomers of $Co(NH_3)_4(N_3)_2^+$, we hoped to find whether the affinity of a reagent species for the polyanion is sensitive to its dipole moment.

Results and Discussion

Reduction of Co(III) Complexes by Fe^{2+} in the Absence of Polyanions. Second-order rate constants for reactions of the three Co(III) complexes in the ab-

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[1] Abstracted from a Ph.D. thesis submitted by G. Gordimer to the Graduate School of the Polytechnic Institute of Brooklyn, June 1970. Financial support of this research by Research Grant No. GM 05811 of the National Institutes of Health is gratefully acknowledged.

[2] H. Morawetz and B. Vogel, *J. Amer. Chem. Soc.*, **91**, 563 (1969). This paper should also be consulted for a bibliography of related investigations.

[3] This effect is many orders of magnitude larger than the classical "kinetic salt effect" observed for reactions of ionic reagents in solutions of simple electrolytes. [See, *e.g.*, J. N. Brønsted and R. Livingston, *ibid.*, **49**, 435 (1927); A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, 17, 1167 (1949); G. Scatchard, *Nat. Bur. Stand.* (*U. S.*), *Circ.*, **500**, 185 (1953).] It should also be pointed out that the two effects are not superimposable. For instance, simple salts accelerate reactions of two cations in the absence of polyions but inhibit the catalysis of such reactions by polyanions.[2]

[4] The polyelectrolyte catalysis of redox reactions has recently been studied also by S. Brückner, V. Crescenzi, and F. Quadrifoglio, *J. Chem. Soc. A*, 1168 (1970), and by F. Quadrifoglio, V. Crescenzi, and A. Ius, *Proc. Symp. Coord. Chem., 3rd, 1970*, 1, 73 (1970).

Table I. Reduction of $\text{Co(NH}_3)_5\text{Cl}^{2+}$, *cis*-$\text{Co(NH}_3)_4(\text{N}_3)^+$, and *trans*-$\text{Co(NH}_3)_4(\text{N}_3)_2^+$ by Fe^{2+} in the Absence of Polyelectrolyte[a]

Co(III) complex	Temp, °C	$10^3k_2^0$, M^{-1} sec^{-1}
$\text{Co(NH}_3)_5\text{Cl}^{2+}$	35.9	1.06
cis-$\text{Co(NH}_3)_4(\text{N}_3)_2^+$	25.0	86.1
trans-$\text{Co(NH}_3)_4(\text{N}_3)_2^+$	5.0	7.5

[a] $[\text{Co(NH}_3)_5\text{Cl}^{2+}] = 4 \times 10^{-5}$, $[\text{Co(NH}_3)_4(\text{N}_3)_2^+] = 5 \times 10^{-6}$, $[\text{Fe}^{2+}] = 5 \times 10^{-3}$, $[\text{HClO}_4] = 10^{-3}$ *M*. The solutions were adjusted to an ionic strength of 0.0187 by addition of sodium perchlorate.

sence of added polyelectrolyte are listed in Table I. The kinetic data for $\text{Co(NH}_3)_5\text{Cl}^{2+}$ had to be corrected for the concurrent aquation, which proceeded with a rate constant of 7.1×10^{-6} sec^{-1}. With the diazido complexes, the aquation rate was negligible compared to the rate of reduction by Fe^{2+} under our experimental conditions.

Order of the Redox Reactions in Polyelectrolyte Solution. While the reaction of the Co(III) complexes with Fe^{2+} follows second-order kinetics in the absence of polyelectrolyte, deviations from this simple kinetic pattern should occur, in principle, when the reaction is catalyzed by poly(vinylsulfonate) (PVS) because of a competition between the reagents and the reaction products for the polyion domains. Such an effect was previously observed for the reaction of $\text{Co(NH}_3)_5\text{Cl}^{2+}$ with Hg^{2+}, where the triply charged reaction product $\text{Co(NH}_3)_5\text{H}_2\text{O}^{3+}$ proved to be an effective inhibitor at low PVS/Co(III) ratios.[2]

In the present study, we found no deviation from second-order kinetics in the reaction of $\text{Co(NH}_3)_5\text{Cl}^{2+}$ with Fe^{2+} even at PVS concentrations as low as 1.5×10^{-5} *N* (with 5×10^{-6} *M* Co(III) and 5×10^{-5} *M* Fe^{2+}). The triply charged Fe^{3+} would be expected to be very effective in displacing Fe^{2+} from the domains of the polyanion, leading to a decrease in the catalytic efficiency with the progress of the reaction. However, Fe^{3+} is extensively hydrolyzed under our experimental conditions. Using for $K_H = [\text{FeOH}^{2+}][\text{H}^+]/[\text{Fe}^{3+}]$ the value of 6.7×10^{-3} obtained by Milburn[5] at 25° and at low ionic strength, we may estimate that only 13% of the Fe(III) formed at pH 3 escapes complexation with hydroxyl ion. Thus, when the reaction has run half to completion, the system contains more than 150 doubly charged reagent ions for each Fe^{3+}. It is not surprising that the inhibitory effect of Fe^{3+} is not detectable under these conditions.

The polyanion-catalyzed reaction of the two singly charged $\text{Co(NH}_3)_4(\text{N}_3)_2^+$ species with Fe^{2+} would be expected to be more sensitive to inhibition by multiply charged reaction products than the reaction of the doubly charged $\text{Co(NH}_3)_5\text{Cl}^{2+}$. In fact, a slight downward curvature of second-order plots of the kinetic data was observed with polyanion concentrations up to 1.5×10^{-4} *N*. At higher PVS concentrations the inhibitory effect of the reaction products (Co^{2+} and FeOH^{2+}) was no longer detectable. In any case, whereever such deviations from second-order kinetics occurred, the initial apparent rate constant is considered, in our further discussions, the significant quantity.

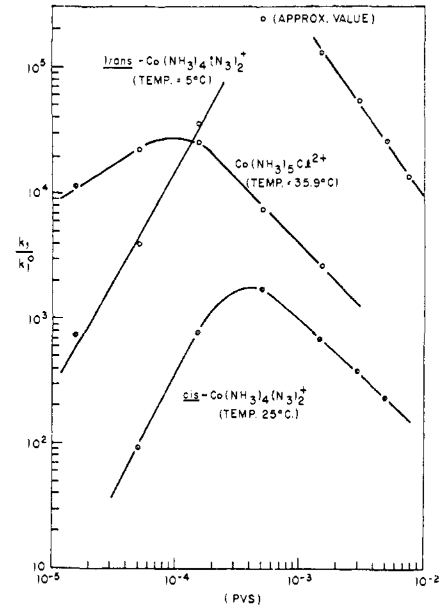

Figure 1. PVS catalysis of the reduction of Co(III) complexes by Fe^{2+}; 5×10^{-6} *M* Co(III), 5×10^{-5} *M* Fe^{2+}, 10^{-3} *M* H^+.

Dependence of Polyion Catalysis on PVS Concentration. Addition of small concentrations of sodium poly(vinylsulfonate) leads to a dramatic acceleration of the reduction of all three Co(III) complexes by Fe^{2+}. A double logarithmic plot of k_1/k_1^0, the ratio of the first-order rate constants obtained in the presence and absence of PVS, respectively,[6] against the normality of the polyion is given in Figure 1. The following points may be made.

(1) The general shape of the curves is similar to those observed previously in the polyion-catalyzed reaction of $\text{Co(NH}_3)_5\text{Cl}^{2+}$ with Hg^{2+}.[2] Thus, the reaction rate increases with polyion concentration when that concentration is low, passes through a maximum, and falls off on further PVS addition. This behavior was previously interpreted as follows. As long as the sum of the normalities of the two reagent ions is in large excess over the normality of the polyions, only a small fraction of the reagent ions is held in the polyion domains, where their high local concentration increases their mutual collision frequency and the resulting reaction rate. The increase of the catalytic effect on polyion addition in the dilute-concentration range reflects then the increasing fraction of bound reagent ions. However, at higher polyion concentrations virtually all the reagent ions are captured, and further increase in the polyelectrolyte concentration will distribute the reagent ions over a larger number of polymer domains. This will decrease their local concentration in these domains and the rate will, therefore, drop off. A simple model which assumed (a) that the distribution of the reagent ions could be assigned two values characteristic of the regions inside and outside the polyion domains and (b) that the polyion–reagent ion interaction could be characterized by an association constant at low coverage of the binding sites, led to the following interpretation of k_1/k_1^0 at very low and very high polyion

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(5) R. M. Milburn, *J. Amer. Chem. Soc.*, **79**, 537 (1957).

(6) While the polymer solutions contained no simple electrolyte other than the reagent ions and 10^{-3} *M* HClO_4, the polyion-free solutions were adjusted by addition of NaClO_4 to an ionic strength of 0.0187 to allow comparison of present results with those of Morawetz and Vogel.[2]

concentrations.[2]

$$k_1/k_1^0 = 2c_{\mathrm{max}}c_{\mathrm{p}}/(\overline{K})^2 \qquad \text{very low } c_{\mathrm{p}} \qquad (1)$$

$$k_1/k_1^0 = 2c_{\mathrm{max}}/c_{\mathrm{p}} \qquad \text{very high } c_{\mathrm{p}} \qquad (2)$$

Here c_{max} represents the maximum effective local concentration of the reagent ions when their charge in the polymer domain is equivalent to the charge of the polyions, c_{p} is the normality of the polyions, and $(\overline{K})^2$ is the product of the dissociation constants of the polyion with the two reagent ions. Equations 1 and 2 would be expected to apply when c_{p} is very low or very high, respectively, as compared with the normality of the reagent ions. We should note that this interpretation of the experimentally observed behavior does not specify whether the reagent ions are "site-bound" by ion-pair formation with the ionized groups of the polyion or are merely held in the vicinity of the polyion by long-range coulombic forces.

(2) There is a striking difference in the susceptibility of the redox reaction of the two isomeric $Co(NH_3)_2(N_3)_2^+$ to polyanion catalysis. With the trans isomer, the rate was accelerated by factors as high as 2.4×10^5, while the largest acceleration factor observed with the cis isomer was only 1.7×10^3.[7] This difference is, in our opinion, a consequence of the fact that the reduction of the trans isomer is acid catalyzed. According to Haim,[8] the cis isomer forms with Fe^{2+} a doubly bridged transition state, while in the trans isomer the N_3^- trans to the bridging N_3^- has a site available for proton attachment, and the movement of the trans-N_3^- away from the Co center as electron transfer occurs is facilitated by protonation. Thus, whereas the polyanion catalyzes the reaction of *cis*-$Co(NH_3)_4(N_3)_2^+$ with Fe^{2+} merely by concentrating the two reagents in its vicinity, it favors the corresponding reaction of the trans isomer also by the high concentration of hydrogen ions surrounding the polyanion, so that the Co(III) complex is efficiently converted to its highly reactive conjugate acid. The difference in the behavior of the *cis*- and *trans*-$Co(NH_3)_4(N_3)_2^+$ resulting from the susceptibility of one of them to acid catalysis obscured, unfortunately, any effect which might have originated from the interaction of the dipole of the cis derivative with the polyion.

(3) It may be noted that the polyion concentration at which the catalytic effect is maximized is higher for the reduction of the two singly charged $Co(NH_3)_4(N_3)_2^+$ species than for the doubly charged $Co(NH_3)_5Cl^{2+}$. This is what might have been expected, since the singly charged reagent ions have a lower affinity for the polyion, so that their capture would be completed only at higher polyion concentrations. If we compare the reaction of $Co(NH_3)_5Cl^{2+}$ and *cis*-$Co(NH_3)_4(N_3)_2^+$ (where we need not consider complications due to acid catalysis), we find that in the limit of high PVS concentration the reaction of the diazido complex is catalyzed somewhat less efficiently. This may be due to the fact that the Na^+ and H^+ counterions compete effectively with the singly charged diazido complex so that we never approach complete binding of this species to the polyion.

(4) At low polyion concentration, the acceleration factor of the reactions of the two diazido complexes with Fe^{2+} increased much more rapidly than in proportion to c_{p}, as predicted by eq 1. For instance, when c_{p} was tripled from 5×10^{-5} to 15×10^{-5}, k_1/k_1^0 for the reaction of the trans isomer increased more than ninefold, from 3.8×10^3 to 3.6×10^4. This behavior is accounted for by the unequal charge of the two reagent ions competing for the polyion. As long as the polyion normality is lower than that of Fe^{2+}, this ion will effectively displace the cobalt complex from the polyion domain. However, as the concentration of free Fe^{2+} approaches exhaustion, the binding of the singly charged diazido complex increases rapidly, leading to a corresponding rapid rise in the reaction rate.

Effect of Simple Electrolytes on Polyion Catalysis. As would be predicted from eq 1, addition of simple electrolyte reduces strongly the catalytic effect of the polyion if the polyion concentration is low, since the shielding of the polyion charge by an increasing concentration of counterions reduces the electrostatic attraction for the reagent ions. On the other hand, if the polyion concentration is high, eq 2 predicts that the catalytic effect is determined by c_{max}, which does not depend on the counterion atmosphere, and simple electrolyte addition is, in fact, without influence on the magnitude of the catalytic efficiency.

The addition of $NaClO_4$ depressed the polyion-catalyzed rate more strongly than addition of $HClO_4$. For instance, the reaction rate of 5×10^{-6} M $Co(NH_3)_5Cl^{2+}$ with 5×10^{-5} M Fe^{2+} in the presence of 5×10^{-4} N PVS was decreased only by a factor of 1.5 when the $HClO_4$ concentration was increased from 10^{-3} to 10^{-2} M, but when 9×10^{-3} M $NaClO_4$ was added to 10^{-3} M $HClO_4$, the rate dropped by a factor of 2.4. This difference is undoubtedly due to the fact that the counterions with the smaller hydrated radius are bound more strongly to polysulfonates,[9] and a similar effect has been noted previously in the relative efficiency with which different alkali ions inhibit catalysis by PVS[2] or by alkylsulfonic acid micelles.[10]

Dependence of Reaction Rate on Fe^{2+} Concentration. In Figure 2 the reaction rate of $Co(NH_3)_5Cl^{2+}$ is plotted as a function of the Fe^{2+} concentration at two concentrations of PVS. The following features of the results should be noted.

(1) As the Fe^{2+} concentration is increased, the reaction is accelerated, but the rate eventually passes through a maximum and decreases on further Fe^{2+} addition. A similar effect has been noted previously in the polyanion-catalyzed Hg^{2+}-induced aquation of $Co(NH_3)_5Cl^{2+}$.[2] It is clearly the result of the gradual displacement of the cobalt complex from the polyanion domain by the second cationic reagent.

(2) At low Fe^{2+} concentration, the reaction is faster at the lower PVS concentration, while an increase in the polyion concentration leads to an acceleration at high concentrations of Fe^{2+}. This behavior is a corollary

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(7) Because of this large difference in the efficiency with which PVS catalyzed the reactions of these two reagents, it was impracticable to study them at the same temperature. We should note, however, that the ratios k_1/k_1^0 would be expected to have a relatively small temperature coefficient, so that the difference in the temperature at which the PVS catalysis of the reduction of the cobalt complexes was studied can have made only a relatively small contribution to the large differences illustrated in Figure 1.

(8) A. Haim, *J. Amer. Chem. Soc.*, **85**, 1016 (1963).

(9) N. Ise and T. Okubo, *J. Phys. Chem.*, 72, 1361, 1366 (1968).

(10) L. R. Ronsted, R. B. Dunlap, and E. H. Cordes, *ibid.*, 71, 4581 (1967).

of the results represented in Figure 1, as discussed above. When the reagent ion concentration is low, *i.e.*, the polymer binding sites are in excess, an increase in the PVS concentration leads to a decrease of the concentration of reagent ions in the polyion domains. Conversely, when the reagent ions are in large excess over the polyion binding sites, their local concentration in the polymer domains depends only little on the polymer concentration, and the reaction rate increases with the concentration of these domains.

(3) Given the above interpretation, the curves shown in Figure 2 are surprisingly flat. For instance, with 5×10^{-5} *N* PVS and 1.5×10^{-3} *M* Fe^{2+}, the observed rate constant was 5.7×10^{-4} sec^{-1}, as compared with a maximum rate constant of 12.8×10^{-4} sec^{-1} with $[Fe^{2+}] = 10^{-4}$ *M*. Thus, a 60-fold excess of Fe^{2+} over the polyion binding sites led to a reduction of the reaction rate by only a factor of 2.2. It must be concluded that Fe^{2+} is quite ineffective in competing with $Co(NH_3)_2Cl^{2+}$ for the polyanion.

Comparison of the Polyion Catalysis of $Co(NH_3)_5Cl^{2+}$ with Hg^{2+} and with Fe^{2+}. The reactions of $Co(NH_3)_5Cl^{2+}$ with Hg^{2+} and with Fe^{2+} both involve two doubly positive species, and they should, therefore, be equally susceptible to acceleration by PVS, if the effect is entirely accountable for by concentration of the reagent ions in the polyion domains in response to coulombic forces.

Table II. Effect of PVS on the Activation Energy in the Reaction of $Co(NH_3)_5Cl^{2+}$ with Fe^{2+} [a]

10^5[PVS], *N*	Temp, °C	k_2, M^{-1} sec^{-1}	ΔE^*, kcal/mol
0	26.1	2.12×10^{-3}	
0	35.9	4.49×10^{-3}	
0	47.5	10.3×10^{-3}	14.4 ± 1.2
1.5	26.1	5.0	
1.5	35.9	11.96	
1.5	47.5	33.0	17.2 ± 0.3
15	26.1	9.72	
15	35.9	26.4	
15	47.5	79.8	18.6 ± 1.6
150	35.9	2.42	
150	41.9	4.18	
150	47.5	7.08	18.2 ± 0.7

[a] The reagent concentrations were 1.49×10^{-3} *M* $Co(NH_3)_5Cl^{2+}$ and 0.491 *M* Fe^{2+} at an ionic strength of 1.7 in the absence of polyelectrolyte and 5×10^{-6} *M* $Co(NH_3)_5Cl^{2+}$ and 5×10^{-5} *M* Fe^{2+} in the presence of PVS. All solutions contained 10^{-3} *M* $HClO_4$.

In this context, it is of special interest to determine the effect of the polyion on the activation energy of the ionic reactions under study. Table II lists the experimental data for the $Co(NH_3)_5Cl^{2+}$–Fe^{2+} system, and it may seem that addition of PVS increases generally the activation energy of the redox reaction with the effect becoming somewhat more pronounced at the higher polyion concentrations. This is in sharp contrast to the behavior of the $Co(NH_3)_5Cl^{2+}$–Hg^{2+} reaction, which was characterized by ΔE^* values of 19.6, 13.3, and 15.7 kcal/mol in solutions containing no polyanion, 5×10^{-5} *N*, and 3×10^{-3} *N* PVS, respectively. In view of the fact that polyelectrolyte catalysis has a different effect on the activation energies of the two reactions, a comparison of the catalytic efficiency at any given temperature is of only limited significance. Such a comparison for the reaction of $Co(NH_3)_5Cl^{2+}$ with Fe^{2+} or Hg^{2+} at 5° is presented in Table III, and it may be seen that the catalytic efficiency of PVS is higher for the Hg^{2+} reaction by factors of 8 and 15 at low and high polyanion concentrations, respectively. Since the k_1/k_1^0 ratio increases with increasing temperature for the Fe^{2+} reaction, while it decreases for the reaction involving Hg^{2+}, the catalytic efficiency of PVS would be more nearly equal if the comparison were carried out at a higher temperature.

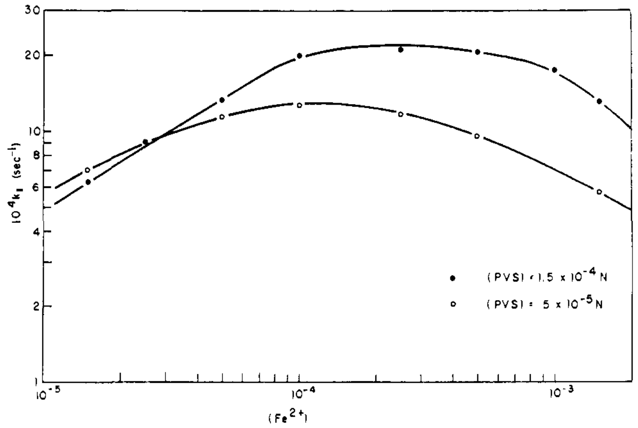

Figure 2. Reaction of $Co(NH_3)_5Cl^{2+}$ with Fe^{2+}. Dependence of the reaction rate on the Fe^{2+} concentration in the presence of PVS; 5×10^{-6} *M* $Co(NH_3)_5Cl^{2+}$, 10^{-3} *M* $HClO_4$, 35.9°.

Table III. Relative Efficiency of PVS at 5° in Catalyzing the Reaction of $Co(NH_3)_5Cl^{2+}$ with Fe^{2+} and with Hg^{2+} [a]

10^5[PVS], *N*	k_1/k_1^0	
	Fe^{2+} [b]	Hg^{2+} [c]
1.5	2100	17,000
150	1300	19,000

[a] 5×10^{-6} *M* Co(III), 5×10^{-5} *M* Fe^{2+} (or Hg^{2+}), 10^{-3} *M* $HClO_4$, 10^{-2} *M* $NaClO_4$. [b] Calculated from experimental data obtained in this investigation at 35.9° and the activation energies in Table II. [c] Data from ref 2.

It is clear from these results that long-range electrostatic interactions cannot account quantitatively for polyelectrolyte catalysis of ionic reactions. In particular, if concentration of the ionic reagents in the polyion domain were the only cause of the phenomenon, no change in the activation energy would be observed in the limit of high polyelectrolyte excess, ensuring the capture of virtually all reagent ions irrespective of temperature. The results imply then that the nature of the polymer domain affects in some specific manner the reaction under consideration. Bifano and Link have noted[11] that rates of Hg^{2+} induced aquations of various chloro complexes of Co(III) do not correlate with the rates of the reductions of these compounds by Fe^{2+}, suggesting important differences in the mechanism of the two processes. It seems probable that the Hg^{2+} reaction with $Co(NH_3)_5Cl^{2+}$ involves $Co(NH_3)_5{}^{3+}$ as a reaction intermediate,[12] while the reduction with Fe^{2+} probably involves a transition state in which the chloride acts as a bridging group.[13] Thus, the Hg^{2+}-induced

(11) C. Bifano and R. G. Link, *Inorg. Chem.*, 7, 908 (1968).
(12) F. A. Posey and H. Taube, *J. Amer. Chem. Soc.*, 79, 255 (1957).
(13) J. H. Espenson, *Inorg. Chem.*, 4, 121 (1965).

aquation would be expected to have a more polar transition state, which would be subject to greater stabilization by the polyion. This would explain why concentration of the reagents in the polyion domain leads to more efficient catalysis in the case of the Hg^{2+}-induced aquation.

Whatever the detailed interpretation of the difference in the susceptibility of these two reactions to catalysis by polyions, we must conclude that the concept of "effective local concentration" as used in 1 and 2 has a more complicated significance than previously[2] believed. It represents the ratio of the reaction rate of reagents A and B in the polyion domain to the rate which would be observed if the same number of reagents A were placed in a molar solution of reagent B. It reflects, therefore, not only the spatial distribution of the reagents in the vicinity of the polyion, but also medium effects which may modify the intrinsic reactivity of the interacting species. A similar conclusion was arrived at recently in studies of Crescenzi and his associates.[4]

Experimental Section

Polymer. The sodium salt of poly(vinylsulfonic acid) was prepared as described by Breslow and Kutner.[14] The polyelectrolyte was purified by twice precipitating 25% aqueous solutions into methanol and was dried *in vacuo* at 80° for 15 hr. The specific viscosity of a 1% solution in water at 25° was 0.56 dl/g, corresponding to a viscosity-average molecular weight of 40,000.[12] *Anal.* Calcd: C, 18.46; S, 24.65; Na, 17.67. Found: C, 19.73; S, 22.81; Na, 17.20.

Cobalt Complexes. *cis*- and *trans*-diazidotetraamminecobalt(III) perchlorate were prepared from carbonatotetraamminecobalt(III) chloride,[15,16] and the diaquotetraamminecobalt(III) chloride[16] intermediate was prepared by the method of Linhard, *et al.*[17] The uv spectrum of the cis isomer was characterized by λ_{max} 303 nm, ϵ_{max} 1.14×10^4, while the corresponding values for the trans isomer were λ_{max} 337 nm, ϵ_{max} 1.44×10^4. These data are in good agreement with literature values.[18]

Chloropentaamminecobalt(III) perchlorate, prepared by the method of Hynes, *et al.*,[19] was obtained from Dr. B. Vogel. The uv spectrum had λ_{max} 229 nm, ϵ_{max} 1.77×10^4.

Iron(II) perchlorate solutions were prepared from solid $Fe(ClO_4)_2 \cdot 6H_2O$ (G. F. Smith Co.) and treated with iron powder to reduce traces of Fe(III). Prepurified nitrogen was bubbled through the ferrous solutions for at least 8 hr. The stock solution of iron(II) perchlorate was stored under prepurified nitrogen in contact with iron powder and standardized with 0.1 *N* ceric sulfate.[20]

Nitrogen. Prepurified nitrogen gas was deoxygenated by passage through two scrubbing towers partially filled with chromous solution in contact with amalgamated zinc.[21]

Apparatus and Procedures. Visible and uv spectra were obtained on a Cary Model 14 recording spectrophotometer. A Beckman Research Model pH meter was used for pH measurement. Reaction rates were followed spectroscopically using a Beckman DU-2 spectrophotometer. A water-jacketed cell of 55-ml capacity thermostated to within ±0.05° with fused silica windows and an optical path length of 10 cm was used. After filling it with the solution containing all reagents except the ferrous ion, the prepurified nitrogen was bubbled through for 30 min and the reaction was started by adding the ferrous solution to the stirred solution with a microsyringe. The disappearance of $Co(NH_2)_5Cl^{2+}$, *cis*-$Co(NH_3)_4(N_3)_2^+$, and *trans*-$Co(NH_3)_4(N_3)_2^+$ was followed by changes in optical density at 229, 303, and 337 nm, respectively. Infinity readings were measured after ten half-lives. With some of the slower systems, the solution was heated until a constant optical density was obtained. In separate experiments, it was proven that air oxidation of the ferrous solution was negligible under the conditions employed.

Treatment of Data. Second-order rate constants, k_2, were calculated from $\ln [(1 - bx/a)/(1 - x)] = (a - b)k_2t$, where a and b are the initial reagent concentrations and $x = (D_0 - D_t)/(D_0 - D_\infty)$, with D_0, D_t, and D_∞ the optical densities at zero time, at time t, and at infinity. Wherever necessary, the rate of the redox reaction was corrected for the simultaneous aquation. First-order rate constants, k_1, were defined by $k_1 = k_2[Fe^{2+}]$.

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(14) D. S. Breslow and A. Kutner, *J. Polym. Sci.*, 27, 295 (1958).

(15) G. G. Schlessinger, *Inorg. Syn.*, 3, 173 (1960).

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