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Role of Solvent in Polymer "Catalysis". Polyelectrolyte Catalysis in the Aquation of Tris(oxalato)cobaltate in Binary Mixtures of Water with Dimethylformamide or Dimethyl Sulfoxide

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Received July 11, 1980

ABSTRACT: The catalytic influence of poly(ethyleniminepropionate) (PEI·PA) and other polyelectrolytes on the reaction tris(oxalato)cobaltate, $Co(C_2O_4)_3^{3-}$ (I) → $Co(C_2O_4)_2(H_2O)_2^-$ (II) (step A) → products (Co^{2+}, $H_2C_2O_4$, H_2O, and CO_2) (step B) was studied in binary mixtures of dimethylformamide or dimethyl sulfoxide with water. The first-order rates of the reactions I → products and II → products dramatically increased with decreasing water content. Furthermore, the rate-determining step of the aquation shifted from step A to step B by the addition of the organic solvents. These results supported a significant "dehydration" effect of the activated complex ions and hydronium cations in the two reactions. The enhanced reactions were retarded by PEI·PA addition, which clearly demonstrated the role of the "hydration" (selective water absorption) by the polymer. These "dehydration" and "hydration" effects were also supported by fluorescence, NMR, and light scattering measurements. In pure water, reaction of I was sharply accelerated by PEI·PA, whereas cationic polymers such as poly(4-vinyl-*N*-ethylpyridinium bromide) decelerated the reaction. The latter observation was explained by the so-called "primary salt effect" of the macroions.

Intensive studies on the rate enhancement and retardation effects of polyelectrolytes have been carried out hitherto.[1-6] Recently, we reported a pronounced role of solvent in polyelectrolyte catalysis in cyanoethylation of amino acids in dimethyl sulfoxide (Me_2SO) + H_2O systems and in esterolysis in hexanol + H_2O systems.[7] The role of solvent in polyelectrolyte-catalyzed interionic reaction was clearly demonstrated by our recent work on the influence of high pressure on rate constants.[8] In this report, the solvation effect of polyelectrolytes on the aquations of tris(oxalato)cobaltate and its reaction intermediate in dimethylformamide (DMF) + H_2O and Me_2SO + H_2O mixtures is further studied.

Experimental Section

Materials. The tris(oxalato)cobalt complex $K_3Co(C_2O_4)_3$ was synthesized by the method of Bunton et al.[9] The stable reaction intermediate of $K_3Co(C_2O_4)_3$, $Co(C_2O_4)_2(H_2O)_2^-$, was obtained from $K_2C_2O_4$, CoC_2O_4, and H_2O_2.[10] Poly(ethylenimine) (PEI) was kindly donated by Nippon Shokubai Co., Tokyo (degree of polymerization 100). Purification was carried out by ion exchange through columns of Amberlite IRA-400 and IR-120B. The propionate of PEI (PEI·PA) was obtained from PEI and an equivalent amount of propionic acid. Polybrene (3,6-Ionene polymer, 1,5-dimethyl-1,5-diazaundecamethylene polymethobromide) was purchased from Aldrich Chemical Co. This polymer was purified by repeated precipitation, using a H_2O + acetone mixture. The details of the preparation of poly(4-vinyl-*N*-ethylpyridinium bromide) (C2PVP) were described in a preceding paper.[11] Brij 35, $C_{12}H_{25}(OCH_2CH_2)_{23}OH$, and cetyltrimethylammonium bromide (CTABr) were commercially available and used without further purification. 8-Anilino-1-naphthalenesulfonic acid (ANS) was commercially available and used after repeated recrystallization from water. DMF and Me_2SO were of spectral grade. Water was deionized and distilled for solution preparation.

Kinetic Measurements. The reactions of $Co(C_2O_4)_3^{3-}$ (I) and $Co(C_2O_4)_2(H_2O)_2^-$ (II) were followed by the absorption decrease at 425 nm, using a high-sensitivity spectrophotometer (SM-401, Union Engineering Co., Osaka-fu) and a stopped-flow spectrophotometer (RA-1100, Union Engineering). The molar extinction coefficients of I and II were 209 and 168 M^{-1} cm^{-1}, respectively, at 425 nm.

Fluorescence Measurements. A fluorescence spectrophotometer (FS-401, Union Engineering) was used for the fluorescence measurements of ANS.

Nuclear Magnetic Resonance Measurements. Chemical shifts of protons of water molecules in DMF + H_2O and Me_2SO + H_2O mixtures were determined by using an NMR spectrometer (JNM-PMX60, JEOL Ltd., Tokyo).

Results and Discussion

A. Reactions of I and II in Water, DMF + H_2O, and Me_2SO + H_2O.

The aquation reaction of $Co(C_2O_4)_3^{3-}$ (I) in both aqueous and organic media is believed to proceed via an intermediate, $Co(C_2O_4)_2(H_2O)_2^-$ (II), as given in eq 1.[9,10,12] The absorption spectra I and II in water gave two clear peaks at 425 and 605 nm and at 420 and 600 nm, respectively. The molecular extinction coefficients of the peaks (10^2 order) coincided with the literature values.[10] New absorption peaks appeared around 500 nm when PEI·PA was added to solutions containing I or II, due to the production of complexes of Co^{2+} with PEI. A typical example of the time dependence of the absorption spectra of a solution of I in the presence of PEI·PA is seen in Figure 1. The absorption spectra of I and II in DMF or Me_2SO in the presence of a small amount of water were quite similar to those in water. However, the peaks were slightly red-shifted (2–5 nm) in the organic solvents. The rate constants of I → products and II → products in the presence of the polymer were obtained from the absorption decrease at 425 or 600 nm. For several cases, the rate constants thus obtained were compared with those ob-

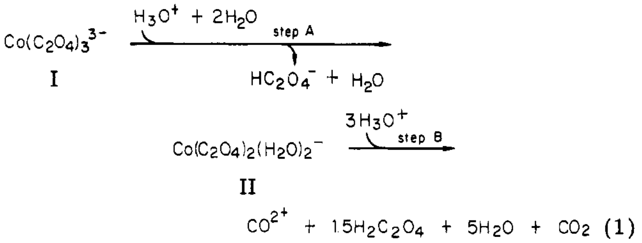


Table I
Thermodynamic Parameters for the Reactions of Compounds I and II in the Absence or Presence of PEI·PA at 35 °C[a]

		I				II			
solvent	[PEI·PA], M	k, s^{-1}	$\Delta G^{\ddagger}$, kcal·mol^{-1}	$\Delta H^{\ddagger}$, kcal·mol^{-1}	$\Delta S^{\ddagger}$, eu	k, s^{-1}	$\Delta G^{\ddagger}$, kcal·mol^{-1}	$\Delta H^{\ddagger}$, kcal·mol^{-1}	$\Delta S^{\ddagger}$, eu
H_2O	0	8.0×10^{-6}	25.4	31.1	19	3.07×10^{-3}	21.8	22.6	2
DMF + H_2O (0.1 M)	0	0.42	18.6	12.9	−18	0.061[b]	19.8[b]	35.4[b]	51[b]
Me_2SO + H_2O (0.1 M)	0	0.060	19.8	22.3	8	0.071	19.7	29.1	31
H_2O	1	2.63×10^{-3}	21.7	10.3	−37	3.41×10^{-3}	21.5	10.4	−36
DMF + H_2O (0.1 M)	1	1.40×10^{-4}	23.7	21.5	−7				
Me_2SO + H_2O (0.1 M)	1	4.39×10^{-5}	24.4	15.9	−27	5.0×10^{-5}	24.3	8.1	−52

[a] [I] = [II] = 4×10^{-4}, [$HClO_4$] = 6×10^{-3} M. [b] [H_2O] = 5.28 M.

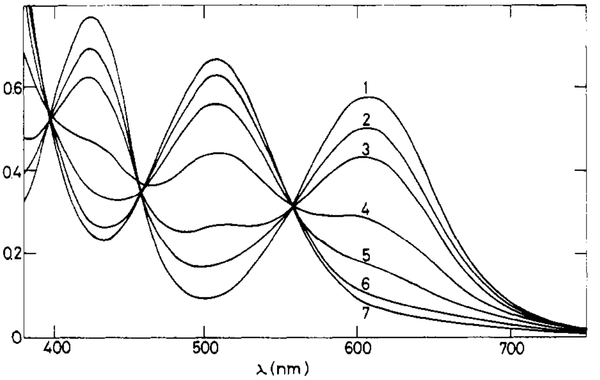


Figure 1. Absorption spectra of reaction mixtures of I in the presence of PEI·PA and in water at 43 °C: (1) 0 min after mixing; (2) 1 min; (3) 2 min; (4) 5 min; (5) 10 min; (6) 20 min; (7) 3 h. [PEI·PA] = 0.1 M, [I] = 4×10^{-3} M, [$HClO_4$] = 6×10^{-3} M.

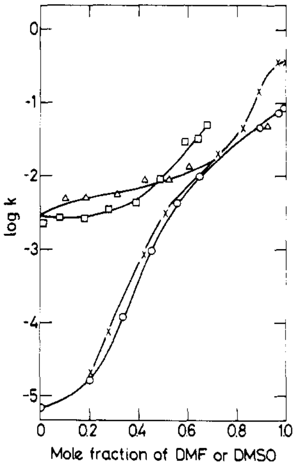


Figure 2. Reaction rates of I and II in DMF + H_2O and Me_2SO + H_2O mixtures at 35 °C: (○) I in Me_2SO + H_2O; (×) I in DMF + H_2O; (△) II in Me_2SO + H_2O; (□) II in DMF + H_2O. [I] = [II] = 4×10^{-4} M, [$HClO_4$] = 6×10^{-3} M.

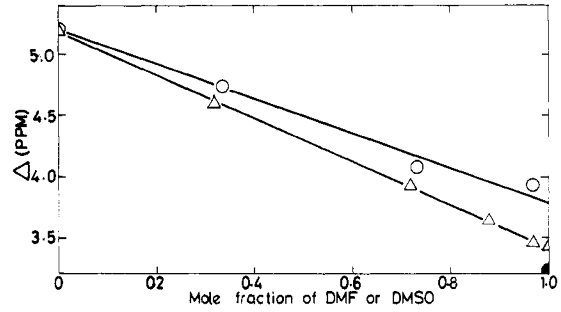


Figure 3. Chemical shifts of protons in the DMF + H_2O (△) and Me_2SO + H_2O (○) mixtures at 35 °C. (●) In Me_2SO, taken from ref 17.

tainable simultaneously from the increase at 500 nm and were found to agree with each other.

The rate constants of the reactions of I and II are shown as a function of the content of the organic solvents in Figure 2. The first-order rate constant, k, of I increased very sharply with increasing content of the organic solvent, and the largest acceleration was on the order of 10^5. A simple interpretation for this rate enhancement is that the reactant ions, including hydronium cations, are dehydrated in the water-poor organic solvents. Some researchers have reported a similar enhanced reactivity of dehydrated hydronium cations[13] and nucleophiles.[8,14,15] Another reason for the rate acceleration would be the enhanced reactivity of water due to the breaking of the hydrogen bonds between water molecules by the organic solvents.[16] This is supported by NMR measurements, which show that the chemical shifts, Δ, clearly decrease with increasing content of DMF or Me_2SO, as seen in Figure 3. The filled circle in the figure indicates the literature value in pure Me_2SO.[17]

The rate enhancement of II by the addition of the organic solvents was much smaller compared with that of I, and this is due to dehydration of the activated complex in reaction step B in eq 1, as described later.

As is clear from Figure 2 the rate constant for I in water was dramatically smaller than that for II. This means that step A is rate determining in water. However, the two rates assume similar values when the content of DMF or Me_2SO is increased, which suggests that step A is remarkably enhanced in the organic solvents and the rate-determining step shifts from A.

The activation parameters for the reactions of I and II in H_2O, DMF + H_2O, and Me_2SO + H_2O are compiled in Table I. It is clear that (1) the striking rate enhancement of I in the organic solvents is due to the decrease of enthalpy terms, whereas (2) the rate acceleration of II is exclusively caused by an increase of activation entropy. Result 1 is ascribed to the dehydration and the enhanced reactivity of the reactant ions, including hydronium ions. Observation 2 is due to the dehydration of the activated complex in step B.

B. Polyelectrolyte Influences upon the Reactions of I and II in Water. The reaction rates of I in water are plotted as a function of the concentrations of the polymers added in Figure 4. As is clear from this figure, the reaction was greatly enhanced by PEI·PA but was not enhanced by C2PVP and Polybrene. The reaction rate of II was, however, not sensitive to polymer addition (graphical presentation omitted). These results support the reaction

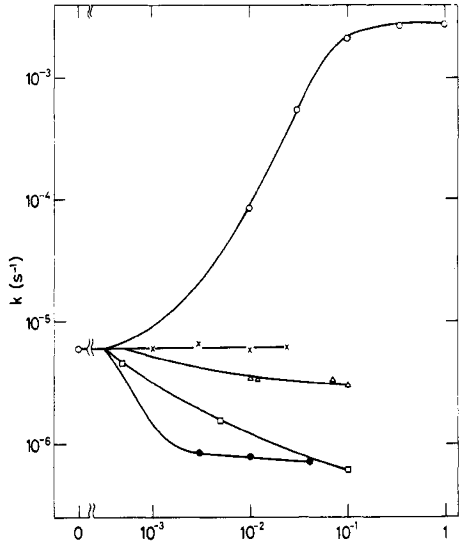
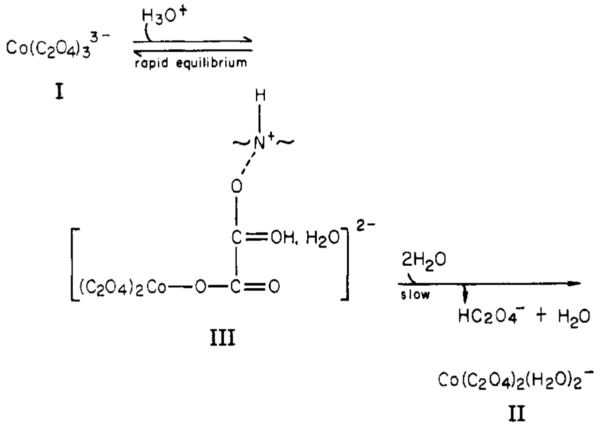


Figure 4. Reaction rates of I in the presence of PEI·PA (○), Brij 35 (×), CTABr (△), Polybrene (□), and C2PVP (●) in water at 35 °C. [I] = 4×10^{-4} M, [$HClO_4$] = 6×10^{-3} M.

scheme proposed by Fendler et al.;[12] PEI·PA facilitates the formation of III in eq 2 by the hydrogen bonding between the ammonium ions of the polymer and the oxygen atoms of III, although the catalyst used by Fendler et al. is not the same as ours. The reason C2PVP and Polybrene did not enhance the reaction of I as is shown in Figure 4 is that the nitrogens of these polymers are quaternized and surrounded by bulky hydrocarbon groups. We believe that this situation must be unfavorable for hydrogen bonding with III, although it is not conclusive at present because the gegenions of C2PVP and Polybrene (Br^-) are different from those of PEI. A more detailed study is now in progress. The retardation of the reaction of I by C2PVP, Polybrene, and CTABr may be explained by the fact that step A is the rate-determining step of the aquation and is an interionic equilibrium between oppositely charged species, $Co(C_2O_4)_3^{3-}$ and H_3O^+.[3,5,6] The equilibrium would shift toward the reactant (I) side in the presence of the polymers according to the secondary salt effect. Insensitivity of the reaction of I to the addition of the neutral surfactant Brij 35 is also well understood.



(2)

C. Polyelectrolyte Influences upon the Reactions of I and II in DMF + H_2O and Me_2SO + H_2O Mixtures. Now we examine the polyelectrolyte influences in the organic solvent–water mixtures. At lower organic solvent content, the reaction of I was much enhanced by PEI·PA, as seen in Figure 5, whereas that of II was not so much accelerated. These results have already been discussed. On the other hand, at higher DMF or Me_2SO content the reactions of both I and II were strikingly retarded by PEI·PA. This observation supports the notion that PEI·PA absorbs water molecules strongly and selectively from the mixtures of DMF + H_2O and Me_2SO + H_2O. Thus, the anionic reactants of I and II would again be stably "hydrated" around the polymer, and the reactivities of water molecules and the complex ions would be lowered. A similar retarding action of polyelectrolyte by a hydration effect was recently observed by us.[8] Preferential hydration of polyelectrolytes in organic solvent–water mixtures has been also reported.[18-20] Another factor for the retardation is the electrostatic repulsive action of PEI macrocations upon the hydronium ions as catalyst for the aquation reaction. However, the observed retarding action of PEI·PA in Figure 5 seems to be too great to be explained quantitatively by this effect only, and, moreover, it was shown in Figure 4 that the repelling effect was negligible, as seen from the CTABr data. Thus, we believe that the hydration effect is the predominant one for the retardation.

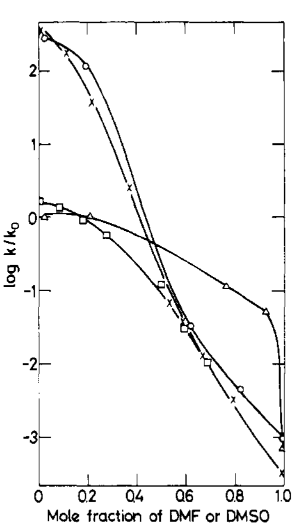


Figure 5. Acceleration and deceleration factors of PEI·PA for the reactions of I and II in the DMF + H_2O and Me_2SO + H_2O mixtures at 35 °C: (○) I in Me_2SO + H_2O; (×) I in DMF + H_2O; (△) II in Me_2SO + H_2O; (□) II in DMF + H_2O. [PEI·PA] = 0.1 M in Me_2SO + H_2O, 0.8 M in DMF + H_2O. [I] = [II] = 4×10^{-4} M, [$HClO_4$] = 6×10^{-3} M.

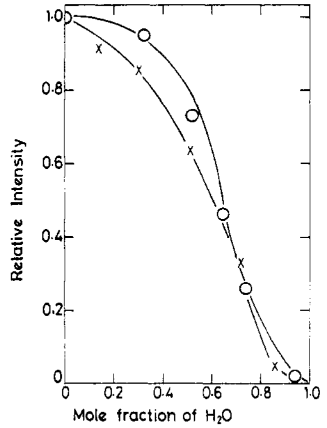


Figure 6. Changes in fluorescence intensities of ANS as a function of H_2O content in the DMF + H_2O (○) and Me_2SO + H_2O (×) mixtures at 25 °C. [ANS] = 5×10^{-6} M.

In Table I, thermodynamic parameters in the presence of PEI·PA are compiled. In water, the polymer clearly decreased the $\Delta G^{\ddagger}$ of the reactions of I and II, whereas the opposite was true in the organic media. These results

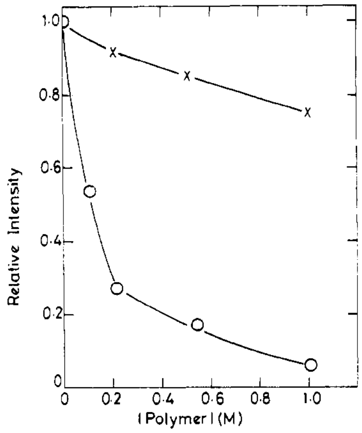


Figure 7. Changes in fluorescence intensities of ANS as a function of the concentration of PEI·PA in the DMF + H_2O (5.03 M) (○) and Me_2SO + H_2O (6.92 M) (×) mixtures at 25 °C.

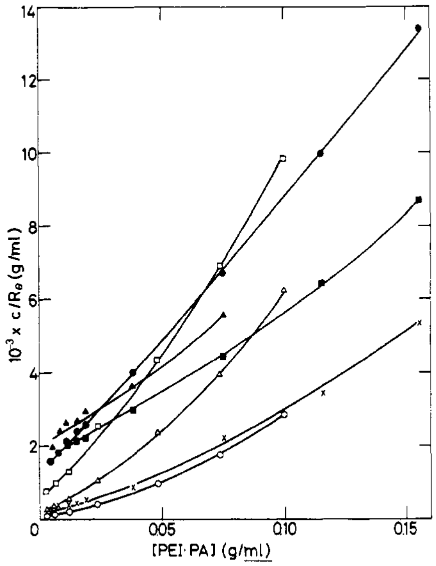


Figure 8. Light scattering of PEI·PA in the Me_2SO + H_2O mixtures at 25 °C: (○) mol % Me_2SO = 0; (×) 6.0; (△) 10.0; (□) 30.0; (●) 50.3; (▲) 82.7; (■) 92.5. [ANS] = 5 × 10^{-6} M.

correspond to the rate-enhancing and -reducing effects of the polymer in pure water and organic media, respectively. Furthermore, the increase of $\Delta H^\ddagger$ by the addition of DMF or Me_2SO in the polymer-containing systems can be ascribed to the "hydration" of the reactants described above.

To confirm the preferential hydration effect of PEI·PA, we conducted fluorescence measurements with ANS as a fluorescent probe. From the decrease in the fluorescence intensity with addition of water (see Figure 6), ANS was found to be an excellent hydrophobic probe in mixtures containing DMF or Me_2SO.[21,22] These fluorescences were dramatically weakened by the addition of PEI·PA (see Figure 7). This clearly shows that the polymers preferentially absorb water molecules around themselves.

Light scattering measurements were conducted in order to confirm that the sharp retarding action of PEI·PA upon the reactions of I and II is not a result of change in conformation and/or aggregation of PEI·PA. Figure 8 shows plots of c/R_θ vs. c for PEI·PA in Me_2SO + H_2O mixtures, where R_θ is the Rayleigh factor at scattering angle θ = 5.9° and c is the concentration of PEI·PA in g/mL. The plots show that there are no large jumps of c/R_θ when c is changed. Therefore, there exists no drastic change in conformation and/or aggregation of the polymer under the experimental conditions studied.

Finally, a few words appear to be necessary in our interpretation on the mechanism of the reaction. As is customarily the case in the study of polymer catalysis, we assumed that the reaction mechanism was the same, irrespective of the presence of macroions. Whether correct or not, the assumption is inevitable because the local concentration of reactants in the vicinity of macroions cannot be determined quantitatively. Similar ambiguity is also associated with the local solvent composition in the neighborhood of the macroions. Qualitatively, one can talk about the water-rich or -poor atmosphere on the basis of the fluorescence data, but quantitative argument is formidable at present. We stress that the local reactant concentration or solvent composition can be quantitatively discussed only when the corresponding volume element is well-defined from the experimental point of view. Unfortunately, this is not the case.

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