CHEMISTRY LETTERS, pp. 693-694, 1980. © The Chemical Society of Japan 1980

ELECTROSTATIC AND HYDROPHOBIC EFFECTS OF 1-1 ELECTROLYTES ON THE REACTIONS BETWEEN CHLOROCOBALT(III) COMPLEXES AND MERCURY(II) IONS

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The Hg^{2+}-assisted aquation of *cis*-$[CoCl(OH_2)(phen)_2]^{2+}$ was retarded by sodium methanesulfonate and benzenesulfonate(0.5-1.0 mol dm^{-3}), while they accelerated a similar reaction of $[CoCl(NH_3)_5]^{2+}$. The unusual retardation effect has been attributed to the hydrophobic interaction of the complex ion and the organic sulfonate ions.

Most of the metal ion-assisted aquations of halo-cobalt(III) and chromium(III) complexes are the reactions between cations and, therefore, with the addition of inorganic electrolytes the acceleration according to the primary salt effect can be expected.[1)] It is interesting that while long-chained alkane sulfonates and polyalkane sulfonates drastically accelerate the Hg^{2+}-assisted aquation of $[CoCl(NH_3)_5]^{2+}$, they have a much smaller effect on the electron-transfer reaction between $[Co(phen)_3]^{2+}$ and $[Co(phen)_3]^{3+}$.[2-4)] No studies have been reported, however, for the effect of simple organic electrolytes on these reactions. A relevant study seems to give an important basis for clarifying the driving force for the catalytic actions of the polysulfonate anions. The present paper reports the study of the specific effects of simple organic sulfonate ions on the Hg^{2+}-assisted aquation of *cis*-$[CoCl(OH_2)(phen)_2]^{2+}$ comparing it with the effect of these anions on a similar reaction of $[CoCl(NH_3)_5]^{2+}$.

Crystals of *cis*-$[CoCl(OH_2)(phen)_2](ClO_4)_2$ were prepared by the method of Hancock *et al.*.[5)] A 1.0×10^{-3} mol dm^{-3} solution of this salt was allowed to react with a 1.1×10^{-2} mol dm^{-3} $Hg(ClO_4)_2$ solution at 25 °C and pH 2. The spectrum of the system changed with isosbestic points at 513 and 445 nm, and the final spectrum agreed with that of the *cis*-$[Co(OH_2)_2(phen)_2]^{3+}$. This shows that side reactions can be neglected. Therefore, the reaction can be written as: $MCl^{2+} + Hg^{2+} \longrightarrow MOH_2^{3+} + HgCl^{+}$, where $M = Co(NH_3)_5$ or $Co(OH_2)(phen)_2$, and $[Hg^{2+}] >> [complex]$. The pseudo-first-order rate constants, k_{obsd}, were obtained from $\ln(D_t - D_\infty)$ vs. t plots, where D_t and D_∞ are the absorbances at time t and at an infinite time, respectively. The absorbances were measured at 290 nm for $[CoCl(NH_3)_5]^{2+}$-Hg^{2+} system and at 410 nm for *cis*-$[CoCl(OH_2)(phen)_2]^{2+}$-$Hg^{2+}$ system. No pH dependency was detected in the pH range of 1.7-2.3, where all the reactions were carried out.

Figures 1 and 2 show the effects of various 1-1 electrolytes and nonelectrolytes on the reaction rates in the two systems. Two facts should be noted before discussing the results. The first is that methane- and benzene-sulfonic acids are completely dissociated in the experimental pH range. The second is that no indication of the

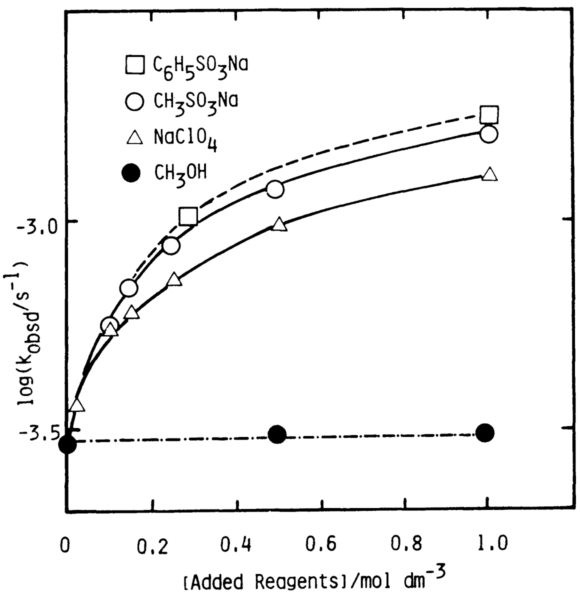

Fig. 1. Medium effects for $[CoCl(NH_3)_5]^{2+}$- Hg^{2+} system.

[complex]=1.0x10^{-3} mol dm^{-3}, [Hg(ClO$_4$)$_2$]= 1.19x10^{-2} mol dm^{-3}, pH 2.0±0.2, at 25 °C

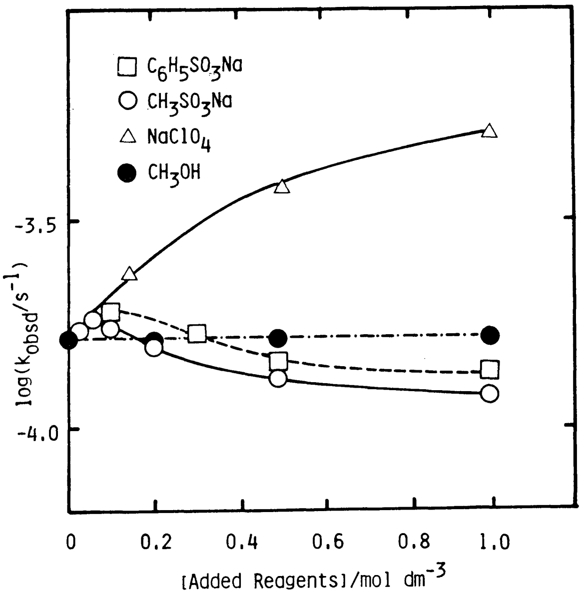

Fig. 2. Medium effects for cis-$[CoCl(OH_2)(phen)_2]^{2+}$-$Hg^{2+}$ system.
[complex]<1.0x10^{-3} mol dm^{-3}, [Hg(ClO$_4$)$_2$]= 1.19x10^{-2} mol dm^{-3}, pH 2.0±0.2, at 25 °C

coordination of these sulfonate ions to the cobalt(III) ion was detected in the course of the reactions.

Figures 1 and 2 show the obvious results that the effects of sodium perchlorate are similar in the two reaction systems while those of the organic sulfonates differ between them. The effects of sodium perchlorate on both of the reactions and those of sulfonates on the $[CoCl(NH_3)_5]^{2+}$-Hg^{2+} reaction system can be interpreted as of essentially electrostatic nature, while the anomalous effect of the sulfonates on the *cis*-$[CoCl(OH_2)(phen)_2]^{2+}$-$Hg^{2+}$ system may be attributed to the hydrophobic interaction between the organic sulfonate ions and the coordinated phenanthrolines. The addition of methanol showed no substantial effect on the reaction. Thus the effect of the sulfonate ions cannot be due to a simple hydrophobic interaction, but can be expected to arise from cooperative hydrophobic and electrostatic interactions. The electrostatic interaction promotes the formation of the *cis*-$[CoCl(OH_2)(phen)_2]^{2+}$-sulfonate$^-$ ion-pair, but is not sufficiently strong for the association of a second sulfonate ion to yield a neutral aggregate, which may be formed with the assistance of the hydrophobic interaction. Although the neutral aggregate, compared with the positively charged complex ion or ion-pair, is more easily approached by Hg^{2+}, but the negatively charged large sulfonate groups of the aggregate more or less block Hg^{2+} from its attacking the chloride ligand. This can be an explanation for why the deceleration effect of the sulfonate occurs in the *cis*-$[CoCl(OH_2)(phen)_2]^{2+}$-$Hg^{2+}$ system but not in the $[CoCl(NH_3)_5]^{2+}$-Hg^{2+} system.

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(Received April 24, 1980)