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Medium Effects on the Exchange of Chlorochromium(III) Ion and Chromium(II) Ion[1]

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The exchange of chromium-51 between chromium(II) ion and chlorochromium(III) ion has been studied as a function of temperature in aqueous 5 *M* perchloric acid and in 0.010–0.20 *M* perchloric acid solutions in water–dioxane (mole fraction of dioxane (Z) = 0, 0.048, 0.12, and 0.23). In the solvents with $Z = 0.12$ and 0.23, pathways involving perchlorate ion play an important role in the exchange reaction. Activation parameters (for electrolyte-free solution) are $\Delta H^{\ddagger} = 6.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -37$ cal mol^{-1} deg^{-1} at $Z = 0$, and $\Delta H^{\ddagger} = 7.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -33$ cal mol^{-1} deg^{-1} at $Z = 0.048$.

The exchange of chromium between chlorochromium(III) ion and chromium(II) ion in solution occurs by an inner-sphere mechanism, a chloride ion bridged transition state being demanded by the absence of net aquation of chlorochromium(III) ion during exchange.[2,3] The net activation process for exchange is

$$(H_2O)_5CrCl^{2+} + Cr(OH_2)_6^{2+} = \{(H_2O)_5CrClCr(OH_2)_5^{4+}\}^{\ddagger} + H_2O$$

with a second-order rate coefficient related to the half-time for exchange by[4]

$$k = \frac{0.69a_w}{([Cr^{2+}] + [CrCl^{2+}])t_{1/2}}$$

in which a_w is the activity of the water. Since this transition state is well-defined, the reaction is an ideal one for study of medium effects. The present paper deals with studies of the dependence of the rate of exchange upon ionic strength (range I = 0.001–0.2 *M*) in solvents with Z = 0, 0.048, 0.12, and 0.23, where Z is the mole fraction of dioxane with only the solvent components taken into account. The temperature was varied at most of the concentration conditions, providing activation parameters for this reaction, which previously had been studied[2,3] only at 0°. In addition the reaction was studied in 5 *M* perchloric acid over the temperature range −15 to −37° to provide activation parameters for the reaction in this medium.

Experimental Procedures

Reagents.—Water was doubly distilled, having been passed through a Barnstead deionizing column between distillations. The second distillation was from an all-Pyrex still. Dioxane (Reagent grade, Matheson Coleman and Bell) was purified by distillation at atmospheric pressure from lithium aluminum hydride.[5] Perchloric acid solutions containing chlorochromium(III) ion as the only chromium(III) species were prepared by an ion-exchange separation of the species present in an acidic solution in which *trans*-dichlorochromium(III) ion had aquated incompletely.[6] Chromium(II) perchlorate solutions in dilute perchloric acid were prepared by dissolving high-purity chromium metal (99.999% pure; obtained from the United Mineral and Chemical Corp.) in 0.5 *M* perchloric acid.[7] Chromium-51 was obtained in the form of chromium(III) in 0.5 *M* hydrochloric acid. This was allowed to exchange with chromium(II),[8] which in turn was allowed to exchange with chlorochromium(III), which then was purified by ion exchange. Lanthanum(III) perchlorate was prepared from the oxide and perchloric acid; the salt was recrystallized from 0.1 *M* perchloric acid. Dowex 50W-X8 resin was used in all column separations of species.

Equipment.—Spectrophotometric measurements were made using a Cary Model 15 spectrophotometer. Constant-temperature baths were employed which regulated temperatures to ±0.02° above 0° and to ±0.2° below 0°. Determination of radioactivity was performed using a Packard Tri-Carb liquid-scintillation spectrometer.

Analyses.—Analysis for chromium was made by conversion to chromate ion with alkaline hydrogen peroxide; chromate ion then was determined spectrophotometrically.[9] Dioxane (at $Z \leq 0.23$) does not interfere with this analysis. Chromium(II) at low concentrations was analyzed by its reaction with chromium(VI) in acidic solution (1 *M* perchloric acid); the chromium(VI) consumed was determined from the decrease in light absorption at 348 nm. Activity due to chromium-51 was determined using liquid-scintillation techniques. The spectrometer was adjusted

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[1] (a) Based in part on the M.S. thesis (1967) and Ph.D. thesis (1969) of R. V. J. (b) Supported in part under Contract AT(11-1)-1286 between the United States Atomic Energy Commission and the University of Colorado.

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to bracket the 0.323-MeV radiation of this nuclide. A solubilizer (Bio-Solve, obtained from Beckman Instruments) was used to make the aqueous solutions studied soluble in the toluene-rich scintillation liquid.

The Binding of Dioxane to Chromium(III).—To check on the possible binding of dioxane to chromium(III), a perchloric acid (0.1 M) solution of chromium(III) perchlorate with a 0.23 mole fraction of dioxane was heated for 3 days at 60°. Ion-exchange procedures at 0° similar to those employed in other studies[10] were used to separate free solvent from chromium(III). Analysis of eluted chromium(III) showed no bound dioxane (moles of bound dioxane/mol of chromium(III) <0.05). It is possible that a dioxane–chromium(III) species formed in the mixed solvent, with complete aquation of this species occurring during the rinsing procedure. It has been demonstrated, however, that the other metal ions do not coordinate appreciably to dioxane in water–dioxane mixtures.[11]

Exchange Reaction Studies.—The exchange reaction was studied in a manner similar to that employed previously.[2,3] The concentrations of chromium(II) ion and chlorochromium(III) ion were varied in the range 2×10^{-4} to 1.2×10^{-3} M. During the course of a run, four to six portions of reaction mixture were blown from the reaction vessel by nitrogen pressure into a quenching solution in which chromium(II) was oxidized (usually with hydrogen peroxide but iron(III) was used in some experiments). The chlorochromium(III) ion of charge 2+ in the quenched solution was separated from other chromium species (all of charge $\geq 3+$) by column ion-exchange procedures. The specific activity of the separated chlorochromium(III) ion was then determined. An infinity-time ($>10t_{1/2}$) sample was taken; its specific activity was compared with that expected on the basis of the stoichiometric composition of the solution. In obtaining $t_{1/2}$ from the data, the integrated rate equation $-\ln (1 - f) = kt([\mathrm{CrCl}^{2+}] + [\mathrm{Cr}^{2+}])/a_{\mathrm{w}} - \ln (1 - f_0)$ was used in which the extent of exchange at zero time was allowed to be an adjustable parameter; that is, the plot of log $(1 - f)$ *vs.* time (where f is the fraction of exchange) was not forced through the origin. From the slope of these plots the second-order rate coefficient for exchange was calculated; since a water molecule is split out from aquochromium(II) ion in forming the activated complex, an inverse dependence of the rate upon the activity of water is incorporated into the rate law. In the solvent composition range studied, deviations from Raoult's law are slight,[12] and replacing a_{w} with $(1 - Z)$ does not introduce an appreciable error. The factor a_{w} was not introduced into the rate law for exchange in 5 M perchloric acid. The activity of water in the solution at temperatures below 0° is not known, and more important, the inner-sphere coordination of chromium(II) by perchlorate ion[13] introduces uncertainty.

Since chromium(II) catalyzes the aquation of halochromium(III) ions at low acidity,[14] it was necessary to demonstrate that this side reaction did not interfere in the present studies. In both water and a solvent with $Z = 0.23$ at perchloric acid concentrations small (6×10^{-3} M) compared to those employed in the exchange studies, the rate of the chromium(II)-catalyzed aquation was shown to be negligible. It was shown in the earlier study[3] in aqueous solution that variation in the concentration of hydrogen ion (0.054–0.97 M at $I = 1.0$ M) does not influence appreciably the rate of exchange.

Results[15]

Since this exchange reaction involves positively charged reactant ions and transition state, it is appropriate to check effects upon the rate due to varying the concentration of perchlorate ion. For this purpose, experiments were done at 20° in solvent mixtures with constant ionic strength. The adjustment of perchlorate ion concentration at constant ionic strength was accomplished by use of lanthanum(III) perchlorate. In calculation of the ionic strength, it is assumed tacitly that the principal electrolytes present (perchloric acid and lanthanum perchlorate) are completely dissociated. In solutions with $Z = 0.048$ (ϵ 63.6 at 20°),[16] there is no appreciable dependence of k upon the concentration of perchlorate ion at the highest ionic strength studied ($I = 0.10$ M). At 0.097 M $\mathrm{ClO_4^-}$, $k = 5.0 \pm 0.3$ M^{-1} sec^{-1}, and at 0.049 M $\mathrm{ClO_4^-}$, $k = 4.6 \pm 0.4$ M^{-1} sec^{-1}. In solutions with $Z = 0.12$ (ϵ 46.0 at 20°),[16] there is no appreciable dependence of k upon the concentration of perchlorate at ionic strength 0.049 M: $k = 1.6 \pm 0.2$ M^{-1} sec^{-1} at 0.049 M $\mathrm{ClO_4^-}$ and $k = 1.7 \pm 0.1$ M^{-1} sec^{-1} at 0.027 M $\mathrm{ClO_4^-}$; at ionic strength 0.10 M in this medium ($Z = 0.12$), however, there is a dependence of k upon the concentration of perchlorate ion: $k = 3.1 \pm 0.1$ M^{-1} sec^{-1} at 0.097 M $\mathrm{ClO_4^-}$ and $k = 2.3 \pm 0.3$ M^{-1} sec^{-1} at 0.054 M $\mathrm{ClO_4^-}$. At $Z = 0.23$ (ϵ 28.5 at 20°),[16] the value of k depends upon the concentration of perchlorate at each ionic strength at which this variable was studied. At $I = 0.10$ M, $k = 1.8 \pm 0.1$ M^{-1} sec^{-1} at 0.10 M $\mathrm{ClO_4^-}$ and $k = 0.83 \pm 0.02$ M^{-1} sec^{-1} at 0.051 M $\mathrm{ClO_4^-}$. At $I = 0.051$ M, $k = 1.14 \pm 0.07$ M^{-1} sec^{-1} at 0.051 M $\mathrm{ClO_4^-}$ and $k = 0.66 \pm 0.001$ M^{-1} sec^{-1} at 0.028 M $\mathrm{ClO_4^-}$. The reported uncertainty is average deviation from the mean.

These observations indicate that an activated complex involving perchlorate ion is important in the solvents of low polarity. In the solvent with $Z = 0.23$, the second-order rate constant is directly proportional to the stoichiometric concentration of perchlorate ion indicating that an activated complex containing no perchlorate ion is relatively unimportant in this solvent at formal ionic strengths ≥ 0.05 M. It would be appropriate, therefore, to express the rate in this solvent in terms of a third-order rate law

$$R = k'[\mathrm{CrCl}^{2+}][\mathrm{Cr}^{2+}][\mathrm{ClO_4}^-]a_{\mathrm{w}}^{-1}$$

with values of the third-order rate coefficient being for 20°: $I = 0.10$ M, $k' \cong 17$ M^{-2} sec^{-1}; $I = 0.051$ M, $k' \cong 23$ M^{-2} sec^{-1}.

Variation of the concentration of perchlorate ion at constant ionic strength was not attempted at lower ionic strength in this solvent because of the resulting lowered concentration of acid. Experiments at 0.010 M perchloric acid gave a second-order rate coefficient, $k = 0.6 \pm 0.2$ M^{-1} sec^{-1}, which becomes a third-order rate coefficient, $k' = 60 \pm 20$ M^{-2} sec^{-1}, if the second-order rate coefficient is divided by the con-

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(15) Detailed tables of data are available as Document No. NAPS-00865 from ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. Price is $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

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TABLE I

ACTIVATION PARAMETERS FOR THE EXCHANGE OF CHLOROCHROMIUM(III) ION AND CHROMIUM(II) ION

Solvent Z	Temp studied, °C	I range, M	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	B, M^{-1}	$k(0°)$,[c] M^{-1} sec^{-1}
0.048[a]	10 to 30	0.01–0.10	7.87 ± 0.6[e]	−33.0 ± 2[e]	−4.20 ± 0.2[e]	0.18[d]
0[a]	0 to 35	0.01–0.20	6.19 ± 0.3	−37.2 ± 1	−1.88 ± 0.1	0.50[d]
0[d]	7 to 35	0.20	7.99 ± 0.7	−27.1 ± 2	. . .	2.8
0[b]	−37 to −15	5	8.2	−21	. . .	45

[a] Data over a range of temperature and ionic strength correlated with the equation $\log k = \log (kT/h) + \Delta S^{\ddagger}/2.3R - \Delta H^{\ddagger}/2.3RT + 8A\sqrt{I}/(1 + \sqrt{I}) + BI$. [b] Data over a range of temperature at a particular ionic strength correlated with the equation $\log k = \log (kT/h) + \Delta S^{\ddagger}/2.3R - \Delta H^{\ddagger}/2.3RT$. [c] For ionic strength 1 M at 0° values of k reported previously are 8.3 M^{-1} sec^{-1} [2] and 9.1 M^{-1} sec^{-1}.[3] [d] This is the calculated value of k at zero ionic strength. [e] Reported uncertainties are standard deviations obtained from a least-squares treatment of the data.

centration of perchlorate ion. It seems likely that the pathway involving perchlorate ion may contribute appreciably at this lowest ionic strength studied.

The data for the solutions with $Z = 0.12$ and $I = 0.10$ M suggest that activated complexes with zero and with one perchlorate ion are important. At $Z = 0.12$ and $I = 0.05$ M, at $Z = 0.048$ and $I = 0.10$ M, and, presumably, at lower concentrations of electrolyte, only the activated complex with zero perchlorate ions is important.

The data for each of the two solvents of highest polarity ($Z = 0$ and 0.048) were correlated with the three-parameter equation

$$\log k = \log \frac{kT}{h} + \frac{\Delta S^{\ddagger}}{2.3R} - \frac{\Delta H^{\ddagger}}{2.3RT} + \frac{8A\sqrt{I}}{1 + \sqrt{I}} + BI$$

The adjustable parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ describe the temperature dependence of the rate at zero ionic strength in the solvent considered. These quantities may also be used in discussions of the temperature dependence at other ionic strengths since the precision of the data does not warrant calculation of additional parameters at each ionic strength. Values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and B (assumed to be independent of temperature), determined by the method of least squares, are summarized in Table I. The average difference between the experimentally observed values of k and values calculated using this three-parameter equation is 11.6% for the 59 experiments at $Z = 0$ ($I = 0.010$–0.20 M and 273.2–308.2°) and 10.1% for the 29 experiments at $Z = 0.048$ ($I = 0.010$–0.10 M and 283.2–303.2°). These differences are only slightly larger than the average difference between experimentally observed values in duplicate runs and the average of the values obtained in such runs (9.4%). The data obtained in 5 M perchloric acid at temperatures below 0° (−15.7 to −37.1°) were treated independently to obtain values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, also given in Table I. The average difference between the value of k calculated using these values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ and the observed values (19 values) is 10.6%.

Discussion

If the threefold change in k at 0° and zero ionic strength in going from water ($\epsilon \sim 88$) to a water–dioxane solvent with $Z = 0.048$ ($\epsilon \sim 69$)[17] is interpreted in terms of the simple double-sphere activated complex theory,[18] one obtains 7 ± 2 Å as the radius of the activated complex.[19] This value is comparable to values calculated for other simple reactions; *e.g.*, a radius of 5.6 Å is obtained from the dependence upon dielectric constant of the rate of the bromoacetate–thiosulfate reaction.[18] Recently it has been suggested that such correlations with dielectric constant are inappropriate; rather it is proposed that correlation of the medium dependence of an ionic equilibrium in water–dioxane mixtures (or other mixtures containing water and a poorly solvating component) with the molar concentration of water yields the number of water molecules involved in the equilibrium.[20] Applying this view to the present system gives 20 ± 6 as the number of water molecules involved as reactant in the net activation process if the correlation involves the activity of water; if the molarity of water is used, the number of water molecules involved becomes 5 ± 2. It would be expected that formation of an activated complex of charge 4+ from two ions of charge 2+ would result in preferential outer-sphere solvation of the activated complex by the more polar solvent component. Whether there is real physical meaning in either the derived radius of the activated complex (∼7 Å) or the number of extra water molecules solvating the activated complex (∼20 or ∼5, depending on the basis of the correlation), obtained in quantitative application of the two theories, is open to question. (It must be admitted that a more reasonable value for the number of water molecules involved is obtained in the correlation involving the molarity of water.[21])

The effect of electrolyte concentration upon the rate at 0° is enormous, 1 M lithium perchlorate raising

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the rate by a factor of ~18 and 5 *M* perchloric acid raising the rate by a factor of ~90.

With the activation parameters evaluated for the reaction of chromium(II) ion with chlorochromium(III) ion, one can make a direct comparison of these quantities with those evaluated for the reaction of mercury(II) ion with chlorochromium(III) ion. Espenson and Birk[22] evaluated $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the latter reaction to be 18 kcal mol^{-1} and -5 cal mol^{-1} deg^{-1}, respectively, for solutions with ionic strength 1.0 *M*. Although the difference in ionic strength makes the comparison somewhat uncertain, the rather dramatic differences are not obscured by this uncertainty. The activation energy is much greater for the mercury(II) reaction, but the entropy of activation is much less negative. There is evidence that the reaction of mercury(II) with chlorochromium(III) ion produces pentaaquochromium(III) ion as an intermediate;[23] it seems that a reaction producing this unstable intermediate would have a high activation energy. In each of the reactions, however, the aquometal ion of charge 2+ (mercury(II) and chromium(II)) must lose a water molecule before forming the activated complex, so the differences of the values of $\Delta H^{\ddagger}$ also reflect differences in the enthalpy of formation of these species from the stable aquometal ions. Corresponding differences between the activation parameters for formation of the two analogous activation complexes $\{(H_3N)_5CoBrHg^{4+}\}^{\ddagger}$ and $\{(H_3N)_5CoBrCr^{4+}\}^{\ddagger}$ have been discussed by Ogard and Taube[24] and by Taube.[25]

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Exchange of Chromium between Chromium(II) and Fumaratochromium(III) and Related Reactions

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The reactions of chromous ion with fumaratopentaaquochromium(III), *cis*-fumaratoaquotetraamminecobalt(III), and *cis*-fumaratoaquobis(ethylenediamine)cobalt(III) have been studied. For the last complex the rate law has the form $-d[Cr^{2+}]/dt = (k_{-h}'[H^+]^{-1} + k_o + k_h'[H^+])[Cr^{2+}][Oxid]$, while for the first two complexes, the k_{-h}' and k_o terms suffice to express the variation of rate with $[H^+]$ in the range 0.1–1.0 *M*. The values of k_o at 25° for the three complexes, respectively, are ~3, 61, and 9.1 M^{-1} sec^{-1}. The relative insensitivity of rate to change in identity of the oxidizing agent is taken as indicating a stepwise mechanism for electron transfer. It is inferred that the activated complex corresponding to the k_{-h}' term is doubly bridged with OH^- and the adjacent carboxyl of the fumarate serving as bridging groups. The role of the proton in the k_h' term is interpreted as that of stabilizing the radical intermediate derived from the fumarate. This interpretation does not make obvious, however, why the k_h' term appears for one cobalt complex but not the other.

Comparisons[1] of the rate of reduction by chromous ion of isonicotinamidepentaamminecobalt(III) and isonicotinamidepentaaquochromium(III) have suggested that in these systems the electron transfers by a radical ion or stepwise mechanism. It seemed to us worthwhile to extend the comparison to other ligands featuring conjugated bond systems. We selected fumarate ion because considerable work has already been devoted to it with pentaamminecobalt(III) as the acceptor center[2-5] and because basic issues having to do not only with the mechanism of electron transfer but also with the configuration of the activated complex remain unresolved. Whereas with isonicotinamide as ligand, the latter issue can be settled by determining the identity of the immediate products of the reaction, with fumarate this direct method fails because the ligand is symmetrical. The ligand deserves attention also because the rate of reduction of acid fumaratopentaamminecobalt(III) by chromous ion shows a term first order in $[H^+]$ and the role of the proton in the activated complex is not understood. In making comparisons between acceptor centers we have not limited ourselves to studies with pentaaquochromium(III) but have extended the investigation to aquotetraamminecobalt(III) and aquobis(ethylenediamine)cobalt(III).

Experimental Section

Materials.—Stock lithium perchlorate solutions were prepared from two sources, commercial lithium perchlorate obtained from G. F. Smith Co. and that obtained by adding small portions of Baker Analyzed reagent grade lithium carbonate to 6 *F* perchloric acid solutions. The product obtained from both sources was recrystallized twice from aqueous solution before final dilution. An oxidizing component is often present in perchlorate solutions, but the conservation of chromous ion in the exchange experiments shows that this complication was not a factor in the present work.

Chromium(III) perchlorate was prepared by dissolving Mal-

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