The Halomercury(II)-assisted Aquation of the Bromopentacyanocobaltate(III) Anions

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The aquation of the bromopentacyanocobaltate(III) ion was carried out in the presence of several kinds of hard acids or halomercury(II) complexes. The hard acids(H^+, Na^+, and Mg^{2+}) had small effects, while the addition of mercury(II) halides significantly accelerated the aquation. The effect of mercury(II) halides was attributed to the monohalomercury(II) cations, which were formed in a small amount by the dissociation of the dihalomercury(II) complexes. The effect of the dihalomercury(II) complexes was also studied in the presence of an excess of sodium halide. The rate constant for halomercury(II)-assisted aquation was expressed by:

$$k_{obsd} = k_0 + k_1[HgX^+] + k_2[HgX_2], \quad X^- = Cl^-, Br^-.$$

The values of k_1 and k_2 obtained ($k_1 = 1.6 \times 10^4$ mol^{-1} dm^3 s^{-1}, $k_2 = 1.0$ mol^{-1} dm^3 s^{-1}, for $X^- = Cl^-$; $k_1 = 2.0 \times 10^4$ mol^{-1} dm^3 s^{-1}, $k_2 = 1.6 \times 10^{-1}$ mol^{-1} dm^3 s^{-1}, for $X^- = Br^-$) were compared with the stability constants for the mercury(II) complexes formed by the combination with Br^-.

The metal ion-assisted aquation of halo-cobalt(III) and chromium(III) complexes has been extensively studied, and attempts have been made to correlate the rate constants with the stability constants for the respective halo complexes of the metal ions and with the electrostatic force between the reactants.[1)] However, the mechanism of the reaction and the nature of the intermediate are not yet well characterized, and only cationic complexes have hitherto been studied, with a few exceptions.[2)] Therefore, studies of the reaction of different types are necessary in order to generalize the reaction mechanism.

In this study, the anionic complex, $[CoBr(CN)_5]^{3-}$, was allowed to aquate in the presence of such metal ions as Na^+, Mg^{2+}, and Hg^{2+} or of the halomercury(II) complexes ($HgCl^+$, $HgBr^+$, $HgCl_2$, and $HgBr_2$). The results will be discussed in the light of those obtained for the halopentaamminecobalt(III) complexes.

Experimental

Materials. *Potassium Bromopentacyanocobaltate (III)*: The complex was prepared by Adamson's method.[3)] The visible absorption spectrum of the product agreed with the published data.[3,4)] Found: C, 15.39; N, 18.82%. Calcd for $K_3[CoBr(CN)_5]$: C, 15.55; N, 18.13%.

Magnesium Perchlorate Solution: Hydrous magnesium perchlorate, a guaranteed reagent of Wako Pure Chemical Industries, Ltd., was dissolved in a perchloric acid solution ($[HClO_4] = 0.05$ mol dm^{-3}) and was used as the stock solution. The magnesium concentration of this solution was determined by direct titration with EDTA(=ethylenediaminetetraacetic acid), using EBT(=Eriochrome Black T) as the indicator.

Mercury(II) Perchlorate Solution: Mercury(II) oxide was dissolved in a 5-mol dm^{-3} perchloric acid solution, and the mercury(II) perchlorate was crystallized out by cooling. The hygroscopic crystals were dissolved in a perchloric acid solution ($[HClO_4] = 0.05$ mol dm^{-3}) and thereafter used as the stock solution. The mercury(II) concentration was determined by back titration with EDTA in the presence of excess $Mg(edta)^{2-}$(EDTA=H_4edta), using EBT as the indicator.

Mercury(II) Halides: Guaranteed reagents of E. Merck AG were used.

Solutions of Halomercury(II) Complexes: Proper amounts of mercury(II) halide and sodium halide were dissolved in a perchloric acid ($[HClO_4] = 0.05$ mol dm^{-3}) solution. The sodium halides used were guaranteed reagents of Wako Pure Chemical Industries, Ltd., and were dried at 110 °C before use.

Kinetic Runs. The rate of the absorbance change was measured at 35 °C for the solutions containing the complex (4.5×10^{-4} mol dm^{-3}) and the other salts. The change in absorbance was observed at 290 nm for all the solutions except for those containing tribromo- and tetrabromomercurate(II) ions, which were measured at 360 nm because of the strong absorption in the ultraviolet region.

A Hitachi 200-10 spectrophotometer was used for the slow reactions (with half-lives greater than 1 min) and a UNION RA-1300 stopped-flow spectrophotometer for the fast reactions (with half-lives less than 10 s).

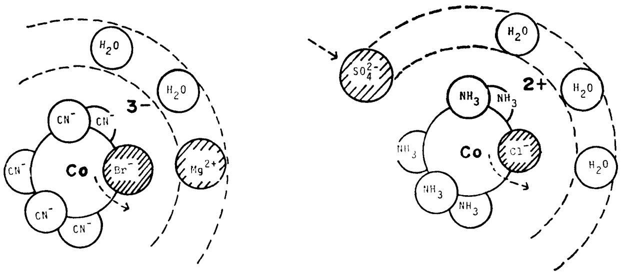
The rates were determined by plotting $\ln(D_t - D_\infty)$ against the time, t, D_t, and D_∞ being the absorbances at the time t and at an infinite time respectively. The slope of this plot gives the pseudo-first-order rate constant, k_{obsd}.

Results and Discussion

Catalysis by Hard Acids. We first studied the effects of hard acids, such as protons, sodium ions, and magnesium ions, on the aquation rate of the bromopentacyanocobaltate(III) anion. The results given in Table 1 show that protons and sodium ions (ionic strength) have little effect, whereas magnesium ions slightly retard the aquation. This effect can be explain-

TABLE 1. EFFECT OF HARD ACIDS ON THE RATE OF THE AQUATION OF $[CoBr(CN)_5]^{3-}$

Run	Medium (concentrations/mol dm^{-3})	$k_{obsd} \times 10^4$/s^{-1}
1	$HClO_4$ (0.084)	1.05
2	NH_4ClO_4(0.05)-NH_3(0.05) buffer pH *ca.* 9	1.12
3	NaOH (0.10)	1.09
4	$NaClO_4$ (0.14)	1.03
5	$NaClO_4$ (0.34)	1.02
6	$NaClO_4$ (0.54)	1.03
7	$NaClO_4$ (0.74)	1.02
8	$NaClO_4$ (0.97)	1.00
9	$Mg(ClO_4)_2$ (0.14)	0.85
10	$Mg(ClO_4)_2$ (0.28)	0.81



a) $CoBr(CN)_5{}^{3-}\cdot Mg^{2+}$ b) $CoCl(NH_3)_5{}^{2+}\cdot SO_4{}^{2-}$

Fig. 1. Structures of ion-pairs.

ed on the basis of the postulate that the spontaneous aquation of the complex proceeds by means of the "D mechanism"[5] and that the formation of ion-pairs between the complex anion and magnesium cations suppresses the dissociation of the bromide ion (Fig. 1a). It is interesting to compare this slight retardation with the appreciable acceleration of the aquation of the pentaamminechlorocobalt(III) cation caused by ion-pairing with sulfate ions.[6] The latter reaction is also known to proceed dissociatively. When a multivalent anion associates with the complex cation, it will preferentially occupy a site opposite to the chloride ligand as a result of electrostatic repulsion, and will effectively push the chloride ion out of the complex (Fig. 1b). In the present reaction systems, however, all the ligands attached to the cobalt(III) are anionic, and so little preference is shown by the magnesium ion as to the site of association with the complex anion. Thus, the effect of magnesium ions on the complex anion spreads over all the ligands, resulting in only a slight retardation of the dissociation of the bromide ligand.

Interactions with Mercury(II) Ions. Bromopentacyanocobaltate(III) anions form a pale yellow precipitate with mercury(II) cations. This reaction appears to include a mercury(II)-assisted aquation, but the follow-up of the aquation was prevented by the formation of a precipitate even if the stopped-flow technique was used. An elemental analysis of this precipitate gave a composition suggesting a mixture of $Hg[Co(OH_2)(CN)_5]$ and $Hg_3[CoBr(CN)_5]_2$.

In order to gain further information, the infrared spectrum of the precipitate was compared with that of the reactant, $K_3[CoBr(CN)_5]$. The bromo complex has a strong absorption maximum at 2140 cm^{-1} assigned to the terminal C≡N stretching, while the precipitate exhibits two absorption maxima, at 2200 cm^{-1} (strong) and 2140 cm^{-1} (medium), assigned respectively to the bridging and to the terminal C≡N stretching. In the lower-frequency region, the bromo complex exhibits Co–C stretching bands at 550 and 570 cm^{-1} (shoulder) and a precipitate at 625 cm^{-1}. This shift can be attributed to the conversion of the terminal C≡N into the bridging C≡N.[7]

These infrared results show that mercury(II) ions reacted with both cyano and bromo ligands to form cyano-bridged and partially aquated polymers. This kind of bridging polymerization of the cyano complexes by heavy metals is well known in the formation of $KFe^{III}Fe^{II}(CN)_6$, $KFe^{II}Cr^{III}(CN)_6$, *etc.*[8]

Interactions with Chloromercury(II) Complexes. On the addition of mercury(II) chloride to a dilute perchloric acid solution containing bromopentacyanocobaltate(III) ions ($[HClO_4]=0.05$ mol dm^{-3}), a rapid change in the spectrum of the complex occurred, with isosbestic points at 340 nm and 400 nm. This spectral change can reasonably be associated with the aquation of bromopentacyanocobaltate(III) ions, forming aquapentacyanocobaltate(III) ions and no other cobalt complexes. The absorbance change at 290 nm was observed by means of the stopped-flow technique and was found to follow a pseudo-first-order law in the presence of a large excess of mercury(II) chloride(more than ten times the concentration of the cobalt(III) complex). At low concentrations of mercury(II) chloride near that of the cobalt(III) complex, the $\ln(D_t-D_\infty)$ *vs.* t plots showed deviations from linear relationships. Therefore, under such conditions, the linear portions of the plots were used to obtain the rate constants. The observed pseudo-first-order rate constants, k_{obsd}, depend on the $HgCl_2$ concentration (Table 2).

TABLE 2. EFFECT OF MERCURY(II) CHLORIDE ON THE RATE OF THE AQUATION OF $[CoBr(CN)_5]^{3-}$

$[CoBr(CN)_5{}^{3-}]=4.5\times10^{-4}$ mol dm^{-3}, $[HClO_4]=0.05$ mol dm^{-3}, ionic strength $=1.0$ mol dm^{-3} ($NaClO_4$).

$[HgCl_2]$/ mol dm^{-3}	$[HgCl^+]$/ mol dm^{-3}	$[HgCl_3{}^-]$/ mol dm^{-3}	k_{obsd}/s^{-1}
1.00×10^{-1}	2.35×10^{-4}	8.45×10^{-5}	3.00
4.98×10^{-2}	1.51×10^{-4}	3.29×10^{-5}	2.15
2.99×10^{-2}	1.12×10^{-4}	1.60×10^{-5}	1.96
9.94×10^{-3}	6.12×10^{-5}	3.26×10^{-6}	0.956
4.96×10^{-3}	4.27×10^{-5}	1.17×10^{-6}	0.668
2.47×10^{-3}	3.00×10^{-5}	4.16×10^{-7}	0.410

TABLE 3. DEPENDENCE OF THE RATE ON THE IONIC STRENGTH FOR THE MERCURY(II) CHLORIDE-ASSISTED AQUATION OF $[CoBr(CN)_5]^{3-}$

$[CoBr(CN)_5{}^{3-}]=4.5\times10^{-4}$ mol dm^{-3}, $[HClO_4]=0.05$ mol dm^{-3}, $[HgCl_2]=0.01$ mol dm^{-3}, at 35 °C.

$[NaClO_4]$/ mol dm^{-3}	Ionic strength /mol dm^{-3}	k_{obsd}/s^{-1}
0	0.05	1.89
0.20	0.25	1.48
0.40	0.45	1.15
1.00	1.05	0.96

The rate constant also depends on the ionic strength, as is shown in Table 3. This suggests that the reactions occur between the ions of opposite signs and, therefore that $HgCl^+$, produced through the dissociation of $HgCl_2$, may participate in the reaction rather than the $HgCl_2$ molecule. While the formation of chloromercury(II) complexes has been studied by many workers, the stability constants obtained by Sillén *et al.*[9] at 25 °C and at an ionic strength of 0.5 are adopted here:

$$Hg^{2+} + Cl^- \rightleftharpoons HgCl^+ \qquad \log K_1 = 6.74,$$

$$HgCl^+ + Cl^- \rightleftharpoons HgCl_2 \qquad \log K_2 = 6.48,$$

$$HgCl_2 + Cl^- \rightleftarrows HgCl_3^- \qquad \log K_3 = 0.85,$$
$$HgCl_3^- + Cl^- \rightleftarrows HgCl_4^{2-} \qquad \log K_4 = 1.00.$$

The correction of these values to the present condition of $I=1.0$ and 35 °C was made as follows.

According to the results of Scaife and Tyrrell[10] and of Vasil'kevich and Shilov[11] for halomercury(II) complexes, the logarithm of the formation constant decreased by 0.1 unit with the rise in temperature from 25 °C to about 35 °C. Therefore, the values at 35 °C were estimated to be Sillén's values minus 0.1. The resulting values were then corrected to the ionic strength of 1.0 by using the Davies equation:

$$\log y_i = -0.521 z_i^2\left(\frac{\sqrt{I}}{1+\sqrt{I}}-0.3I\right),$$

where y_i is the activity coefficient of the i ion; z_i, its charge number, and I, the ionic strength. The corrected values are $\log K_1'=6.77$, $\log K_2'=6.45$, $\log K_3'=0.75$, and $\log K_4'=0.83$. Using these values, one can calculate the concentrations of the halomercury(II) complexes existing in the mercury(II) chloride solutions. Among them, Hg^{2+} and $HgCl_4^{2-}$ are present only in trace amounts and can be neglected.

Table 2 shows the calculated concentrations of each chloromercury(II) complex and the observed rate constants. Whereas the values of k_{obsd} show an apparent dependence on $[HgCl_2]$ to the 0.6 power, their dependence on $[HgCl^+]$ is approximately linear.

In view of the fact that reaction rates of the first order with respect to the metal-ion concentrations have been observed in many metal-ion-assisted aquations,[12] the present results can be taken as suggesting that the catalyst in the present reaction system is actually $HgCl^+$.

In order to substantiate this view, the aquation was examined in solutions containing mercury(II) chloride and an excess of sodium chloride. The concentrations of the respective chloromercury(II) complexes were calculated for each run by the use of four equilibrium constants, K_1', K_2', K_3', and K_4'. In order to see how k_{obsd} depends on the concentration of each chloromercury(II) complex, $\log(k_{obsd}-k_0)$ is plotted against $\log[HgCl_n^{2-n}]$ (n=1—4) in Fig. 2. The observed value of 1.0×10^{-4} s^{-1} was used for the spontaneous aquation rate constant, k_0. Figure 2 shows that the $\log(k_{obsd}-k_0)$ values have no simple correlations with the $\log[HgCl_n^{2-n}]$ values in any case except for n=2. This can be taken as evidence that only $HgCl_2$ molecules effectively assisted the aquation in these runs. Therefore, the results were analyzed by using this equation:

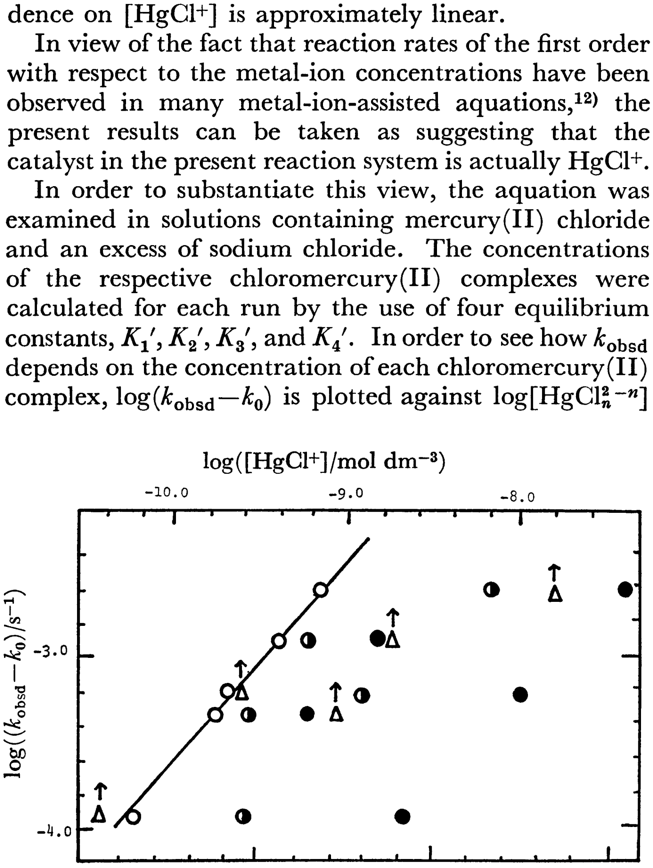


Fig. 2. Effect of chloromercury(II) complexes on the aquation rate of $[CoBr(CN)_5]^{3-}$.
$HgCl_4^{2-}$: ●, $HgCl_3^-$: ◑, $HgCl_2$: ○, $HgCl^+$: △.

$$k'_{obsd} = k_0 + k_2[HgCl_2]$$

(in solutions containing mercury(II) chloride and an excess of sodium chloride)

which gave $k_2=(1.0\pm0.1)$ $mol^{-1}\,dm^3\,s^{-1}$. This value of k_2 shows that the contribution of $HgCl_2$ to the reaction can be neglected when mercury(II) chloride reagent is added. Therefore, from Table 2 the second-order rate constant, k_1, of the $HgCl^+$-assisted reaction was found to be $(1.6\pm0.2)\times10^4$ $mol^{-1}\,dm^3\,s^{-1}$. Thus, the pseudo-first-order rate constant for the chloromercury(II)-assisted aquation can be expressed by this equation:

$$k_{obsd} = k_0 + k_1[HgCl^+] + k_2[HgCl_2].$$

An additional term, $k[Hg^{2+}]$, may be included when $[Hg^{2+}]$ is present in an appreciable concentration; however, this term could not be well characterized because of the strong interaction of the mercury(II) ions with the cyano ligands.

Interactions with Bromomercury(II) Complexes. The addition of mercury(II) bromide also accelerated the aquation of $[CoBr(CN)_5]^{3-}$, but to a smaller degree than in the case of mercury(II) chloride. This is reasonable if $HgBr^+$, by analogy with $HgCl^+$, acts as a virtual reacting species, since the dissociation constant of $HgBr_2$ is much smaller than that of $HgCl_2$. The $\ln(D_t-D_\infty)$ *vs.* t plot was not linear, not even at $HgBr_2$ concentrations as high as 1.0×10^{-2} mol dm^{-3}, nearly the highest one experimentally attainable. (The solubility is 2.2×10^{-2} mol dm^{-3} at 35 °C). Therefore, the rate constant was not obtained directly, but from the analysis of the results according to the following reaction scheme:

$$CoBr(CN)_5^{3-} + HgBr^+ \xrightarrow[\text{slow}]{k_{1(Br)}} Co(CN)_5^{2-} + HgBr_2 \qquad (1)$$
$$\xrightarrow[\text{fast}]{} Co(OH_2)(CN)_5^{2-} + HgBr_2$$

$$HgBr^+ + Br^- \overset{K_{2(Br)}}{\rightleftarrows} HgBr_2 \qquad (2)$$

$$HgBr_2 + Br^- \overset{K_{3(Br)}}{\rightleftarrows} HgBr_3^- \qquad (3)$$

where $\log K_{2(Br)}=8.28$ and $\log K_{3(Br)}=2.41$ (I=0.5), as has been reported by Sillén.[13]

The reaction rate can be expressed by

$$-\frac{d[CoBr]}{dt} = k_{1(Br)}[CoBr][HgBr^+], \qquad (4)$$

where $CoBr(CN)_5^{3-}$ is abbreviated as CoBr.

The expressions for Equilibria 2 and 3 are

$$K_{2(Br)} = \frac{c_{HgBr_2}}{[HgBr^+][Br^-]}, \qquad (5)$$

$$K_{3(Br)} = \frac{[HgBr_3^-]}{c_{HgBr_2}\cdot[Br^-]}, \qquad (6)$$

where c_{HgBr_2} represents the analytical concentration of $HgBr_2$ and is practically equal to its actual concentration at any stage of the reaction. At time 0, the following expression should hold in order for the system to be electrically neutral:

$$[HgBr^+]_0 = [Br^-]_0 + [HgBr_3^-]_0.$$

At time t this becomes

$$[HgBr^+] = [Br^-] - [CoBr]_0 + [CoBr] + [HgBr_3^-]. \quad (7)$$

Equations 6 and 7 are combined to give

$$[Br^-] = \frac{[HgBr^+]+[CoBr]_0-[CoBr]}{1+K_{3(Br)}c_{HgBr_2}}.$$

By substituting this expression for $[Br^-]$ in Eq. 5, one obtains

$$K_{2(Br)}[HgBr^+]^2 + K_{2(Br)}([CoBr]_0-[CoBr])[HgBr^+] - (K_{3(Br)}c_{HgBr_2}+1)c_{HgBr_2} = 0. \quad (8)$$

The elimination of $[HgBr^+]$ from Eqs. 4 and 8 gives a differential equation with respect to [CoBr]. From this equation, a reasonable $k_{1(Br)}$ value can be determined so as to fit the experimental results. The $K_{2(Br)}$ and $K_{3(Br)}$ values given for $I=0.5$, 25 °C were corrected to the present conditions in the same way as has been described above for the case of chloro complexes; then, with the corrected $K'_{2(Br)}$ and $K'_{3(Br)}$ values and an arbitrarily chosen $k_{1(Br)}$ values, the concentration of $[CoBr(CN)_5]^{3-}$ denoted by [CoBr] was calculated as a function of the time for each system. The best fit to the experimental values was obtained when $k_{1(Br)}$ was assumed to be 2.5×10^4 mol^{-1} dm^3 s^{-1} (Fig. 3). The calculations were carried out on a FACOM 270-20 computer for the two systems, with $[CoBr]_0=4.5\times10^{-4}$ mol dm^{-3} and $c_{HgBr_2}=7.63\times10^{-3}$ and 3.81×10^{-3} mol dm^{-3}.

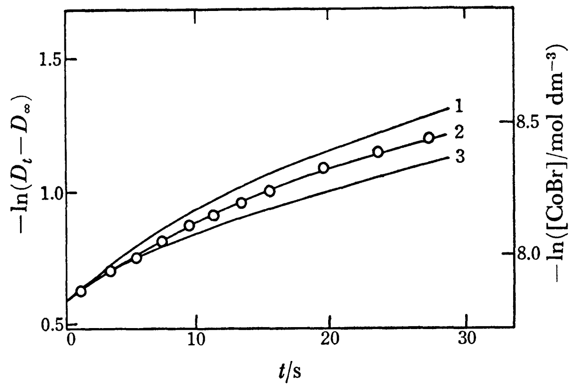


Fig. 3. Comparison of the experimental results(○) and the computational ones(—, scaled on the right-hand oridinate). $c_{HgBr_2}=7.63\times10^{-3}$ mol dm^{-3}. $[CoBr(CN)_5^{3-}]_0=4.5\times10^{-4}$ mol dm^{-3}, at 35 °C. $k_{1(Br)}$ was assumed to 3.0×10^4 mol^{-1} dm^3 s^{-1} (curve 1), 2.5×10^4 mol^{-1} dm^3 s^{-1}(curve 2), and 2.0×10^4 mol^{-1} dm^3 s^{-1} (curve 3).

Another indirect way of obtaining the second-order rate constant, $k_{1(Br)}$, is to carry out the aquation in the presence of an excess of $HgBr^+$ and Hg^{2+}. Under such conditions, the decrease in the concentration of $HgBr^+$, accompanies by the progress of the reaction can be neglected, and the $\ln(D_t-D_\infty)$ *vs.* t plots give straight lines. Since this disproportionation reaction:[13]

$$2\ HgBr^+ \overset{K}{\rightleftarrows} HgBr_2+Hg^{2+} \quad (\log K=-0.83 \text{ at } I=0.5)$$

occurs, the rate constant for the $HgBr^+$-assisted aquation cannot be estimated independently of the effect of Hg^{2+}. As has been described above, Hg^{2+} interferes with the measurement of aquation by forming a precipitate. However, if $HgBr^+$ is present in excess of Hg^{2+}, the stopped-flow technique enables us to observe the aquation before the precipitation begins. Table 4 shows the results. In order to obtain the first-order rate constant, $k_{1(Br)}$, a certain magnitude of the relative effect of Hg^{2+} on the aquation has to be assumed. If Hg^{2+} has no effect, $k_{1(Br)}$ will be 1.8×10^4 mol^{-1} dm^3 s^{-1}, and if Hg^{2+} has an effect as large as that of $HgBr^+$, $k_{1(Br)}$ will be 1.3×10^4 mol^{-1} dm^3 s^{-1}. These values are somewhat smaller than that obtained from the other experiment described above (2.5×10^4 mol^{-1} dm^3 s^{-1}), but are comparable to that for $HgCl^+$. Therefore, the rate constant due to $HgBr^+$ can be $k_{1(Br)}=(2.0\pm0.5)\times10^4$ mol^{-1}dm^3 s^{-1}.

Table 4. Rapid aquation of $[CoBr(CN)_5]^{3-}$ in the presence of $HgBr^+$ (with Hg^{2+} and Br^- added in equal analytical concentrations)

[Hg(II)]/mol dm^{-3}	k_{obsd}/s^{-1}
9.83×10^{-3}	92.5
4.91×10^{-3}	41.9
1.96×10^{-3}	22.5

Table 5. Effect of bromomercury(II) complexes on the rate of aquation of $[CoBr(CN)_5]^{3-}$

$[HgBr_4^{2-}]$/ mol dm^{-3}	$[HgBr_3^-]$/ mol dm^{-3}	$[HgBr_2]$/ mol dm^{-3}	$(k_{obsd}-k_0)$/ s^{-1}
7.54×10^{-3}	1.09×10^{-2}	1.29×10^{-3}	2.28×10^{-4}
5.70×10^{-3}	3.95×10^{-2}	1.81×10^{-3}	2.66×10^{-4}
2.11×10^{-2}	2.58×10^{-2}	2.24×10^{-3}	3.50×10^{-4}

The effect of $HgBr_2$ was also examined in a manner similar to that described for the case of $HgCl_2$. Table 5 gives the results, from which the second-order rate constant, $k_{2(Br)}=(1.6\pm0.2)\times10^{-1}$ mol^{-1} dm^3 s^{-1}, was obtained.

The pseudo-first-order rate constant for the bromomercury(II)-assisted aquation can, then, be expressed by

$$k_{obsd}^{(Br)} = k_0 + k_{1(Br)}[HgBr^+] + k_{2(Br)}[HgBr_2].$$

Comparisons of $k_{1(Br)}$ and $k_{2(Br)}$ with $'k_1$ and k_2 show that the effect of $HgBr^+$ is comparable to that of $HgCl^+$ and that $HgCl_2$ is a somewhat better catalyst than $HgBr_2$.

Table 6 summarizes the results obtained for the present systems as well as for the $CoBr(NH_3)_5^{2+}$–Hg^{2+} system.[14] The last column shows the stability constants for the mercury(II) complexes formed by the combination with Br^-. The constant for HgClBr has not been directly obtained, so we estimated it in the following manner.

These equilibria

$$Hg^{2+} + Br^- \rightleftarrows HgBr^+ \qquad \log K'_{1(Br)} = 9.08 \qquad (9)$$

$$HgBr^+ + Br^- \rightleftarrows HgBr_2 \qquad \log K'_{2(Br)} = 8.22 \qquad (10)$$

TABLE 6. HALOMERCURY(II)-ASSISTED AQUATION OF BROMOCOBALT(III) COMPLEXES
Ionic strength = 1.0 mol dm^{-3} (NaClO$_4$), at 35 °C.

Complex		log k_i/k_0	log K_i'
$[CoBr(NH_3)_5]^{2+}$	Hg^{2+}	6.51a)	9.08
$[CoBr(CN)_5]^{3-}$	$HgCl^+$	8.18	9.1b)
	$HgBr^+$	8.3b)	8.22
	$HgCl_2$	4.00	—
	$HgBr_2$	3.30	2.31

a) Unpublished result. Brønsted and Livingston obtained log $k_i/k_0 = 6.28$ at the ionic strength of 0.03 and at 25 °C.14) b) These values may contain larger errors than the others.

$$Hg^{2+} + Cl^- \rightleftharpoons HgCl^+ \qquad \log K_1' = 6.77 \qquad (11)$$

$$HgCl^+ + Cl^- \rightleftharpoons HgCl_2 \qquad \log K_2' = 6.44 \qquad (12)$$

$$\frac{1}{2}HgCl_2 + \frac{1}{2}HgBr_2 \rightleftharpoons HgClBr$$

$$\log K' = 0.6^{15)} \qquad (13)$$

were considered.

From Eqs. 9 and 11,

$$\frac{[HgBr^+][Cl^-]}{[HgCl^+][Br^-]} = \frac{K'_{1(Br)}}{K_1'}. \qquad (14)$$

From Eqs. 10, 12, and 13,

$$\frac{[HgClBr]}{[HgCl^+][Br^-]}\ \frac{[HgClBr]}{[HgBr^+][Cl^-]}K'_{2(Br)}{}^{-1}K_2'^{-1} = (K')^2. \quad (15)$$

Eliminating the $[HgBr^+][Cl^-]$ term in Eqs. 14 and 15, one obtains

$$\frac{[HgClBr]}{[HgCl^+][Br^-]} = K'K_2'^{1/2}K'_{2(Br)}{}^{1/2}K'_{1(Br)}{}^{1/2}K_1'^{-1/2} = 10^{9.1}.$$

The results listed in Table 6 show a roughly linear relation between the ratios of the second-order rate constant for each assisted aquation to the first-order rate constant for the spontaneous aquation (k_i/k_0) and the related stability constants (K_i').

The ratios of the rate constants for $CoBr(CN)_5{}^{3-}$ are significantly larger than that for $CoBr(NH_3)_5{}^{2+}$ in spite of the similar magnitudes of the stability constants. This difference may be attributed partially to the opposite sign of the electrostatic long-range interactions between the reactants and partially to the dissimilar short-range interactions; the latter is to be expected, since the two complexes differ greatly in their dipolar properties.

Two molecular species, $HgCl_2$ and $HgBr_2$, also showed appreciable effects on the rate of aquation of $[CoBr(CN)_5]^{3-}$. Although these effects are much smaller than those of $HgCl^+$ and $HgBr^+$, the present results show rare cases in which the effects of $HgCl_2$ and $HgBr_2$ on the aquations of metal complexes were experimentally detected. In these cases, the values of k_i/k_0 were greater than would be expected from the related equilibrium constants, K_i'. This also suggests that there exists a kind of short-range interaction between $[CoBr(CN)_5]^{3-}$ and dihalomercury(II) complexes.

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