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The Kinetics of Oxidative Substitution in Bromopentaamminecobalt(III) Ion By Chlorine, Hypochlorous and Hypobromous Acids

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A kinetic study of the oxidative substitution reactions of bromopentaamminecobalt(III) with aqueous chlorine, hypochlorous acid and hypobromous acid has been carried out using the stopped-flow technique. For the reaction in excess hypobromous acid the rate law has the form $d[Co(NH_3)_5Br^{2+}]/dt = -k[HOBr][H^+][Co(NH_3)_5Br^{2+}]$ *where* $k = 3.2 \pm 0.2\ M^{-2}\ sec^{-1}$ *at 25 °C,* $\mu = 1.0$ *with* $\Delta H^* = 9.4 \pm 1.5$ *kcal/mol and* $\Delta S^* = -25 \pm 5$ *e.u. For the hypochlorous acid reaction* $d[Co(NH_3)_5Br^{2+}]/dt = -(k+k'[H^+])[HOCl][Co(NH_3)_5Br^{2+}]$ *with* $k = 4 \pm 1\ M^{-1}\ sec^{-1}$ *and* $k' = 100 \pm 7\ M^{-2}\ sec^{-1}$*. For the k′ step,* $\Delta H^* = 3.8 \pm 1$ *kcal/mol and* $\Delta S^* = -37 \pm 5$ *e.u. In excess aqueous chlorine the rate law has the form* $d[Co(NH_3)_5Br^{2+}]/dt = -k_2[Co(NH_3)_5Br^{2+}][Cl_2]$ *where* $k_2 = (A+B[Cl^-] + C[Cl^-]^2+D[Cl^-]^3)/(1+E[Cl^-]+F[Cl^-]^2)$*. A mechanism is proposed which is consistent with the observed rate law and with the effect of added sulfate ion upon the kinetics of the reaction.*

Introduction

Oxidation by aqueous chlorine of bromide ion coordinated in the bromopentaamminecobalt(III) complex was shown by Haim and Taube[1] to yield the chloropentaamminecobalt(III) ion quantitatively. The reaction was postulated to proceed through an intermediate of the form

$$(NH_3)_5CoBrCl^{3+}$$

which would rearrange to form the product ion. It is especially interesting that the oxidative substitution reaction is complete within seconds in saturated chlorine solution, since linkage isomerization in pentaamminecobalt(III) complexes is usually far less rapid.[2,3] We considered the kinetics of the reaction sufficiently unusual to warrant a detailed investigation. A description of the work and of a related study using the oxidizing agents hypochlorous and hypobromous acids is presented here.

Experimental Section

Materials. Doubly distilled water was used in the experiments, the second distillation having been made from basic permanganate solution. Hypochlorous and hypobromous acids were prepared by treating an excess of saturated chlorine or bromine water at 0°C with acidic silver perchlorate solution. After filtering the solutions, excess halogen was removed by bubbling with inert gas. Substitution of air for argon did not affect the results.

Concentrations of oxidizing agents were determined iodometrically. In the stopped-flow experiments with aqueous chlorine a calibrated volume of chlorine solution from the instrument's reservoir syringe was injected under the surface of the iodide solution.

Bromopentaamminecobalt(III) perchlorate was prepared by established procedures.[4] *Anal.* Calcd for $Co(NH_3)_5Br(ClO_4)_3 \cdot H_2O$: N, 15.88; Br, 18.12; Cl, 16.12; H, 3.89. Found N, 15.85; Br, 18.33; Cl, 16.27; H, 3.64.[5]

Instruments. Kinetic measurements were made using a Durrum Model D-100 stopped-flow instrument with a two centimeter optical path-length and all-Kel F flow system (Durrum Instrument Co., Palo Alto, California). Spectrophotometric measurements were made using a Cary Model 14 spectrophotometer. Temperature in the cell compartments of both instruments was controlled within ±0.5°C.

Stoichiometry of the $Co(NH_3)_5Br^{2+}$ *-* Cl_2*, HOCl Reaction.* The methods of Haim and Taube[1] were used in collecting and analyzing the spectrophotometric data. Solutions containing $Co(NH_3)_5Br^{2+}$,hydrochloric, perchloric and/or sulfuric acids at the proper ionic strength (lithium perchlorate) were made up in volumetric flasks and mixed by injection, with rapid stirring, with solutions of HOCl, Cl_2, $HClO_4$ and HCl. The Br_2 and/or Cl_2 present in the product solutions were eliminated by bubbling with water-saturated argon after the addition of lithium chloride to consume any remaining hypohalous acid. From the measured absorbance of solutions containing $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5OH_2^{3+}$ as the only chromophores, the total cobalt(III) could be determined using $\varepsilon_{507} = 45.2\ M^{-1}\ cm^{-1}$ at the isosbestic point for the two species. The measured absorbance at 550 nm, where the molar

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(1) A. Haim and H. Taube, *J. Am. Chem. Soc.*, *85*, 3108 (1963).
(2) B. Adell, *Z. Anorg. u. Allgem. Chem.*, *271*, 49 (1952).
(3) F. Basolo and R.G. Pearson, « Mechanisms of Inorganic Reactions », second ed., John Wiley and Sons, Inc., New York, N.Y., 1967, pp. 291-4.
(4) A. Haim and H. Taube, *J. Am. Chem. Soc.*, *85*, 495 (1963).
(5) Microanalysis performed by the Stanford Microanalytical Laboratory, Stanford Universit.

absorbances of the two species cited above are, respectively, 47.2 and 20.8 M^{-1} cm^{-1}, was used to calculate the per cent yield of the chloride-containing product. The method was checked by the use of ion exchange separations and was shown to yield satisfactory results. Ion exchange separation was also used to identify the products of the oxidative substitution reaction in the presence of sulfate ion. In agreement with he results of Haim and Taube it was found that, within an error of four per cent in the total cobalt determination, no cobalt(III) was lost in the reactions. Further, application of a test for Co^{II} as $Co(NCS)_4^{2-}$ showed no cobalt(II).[6] The lower limit of detection by the test is about three per cent of the total cobalt used in the stoichiometric experiments.

Treatment of Data. The observed pseudo first-order rate constants were calculated as the negatives of the slopes of plots of ln $|A_\infty - A_t|$ *vs* t, where A_t is the measured absorbance at time t. Under the normal conditions of a tenfold or greater excess of the oxidizing agent the plots were linear over at least three half lives.

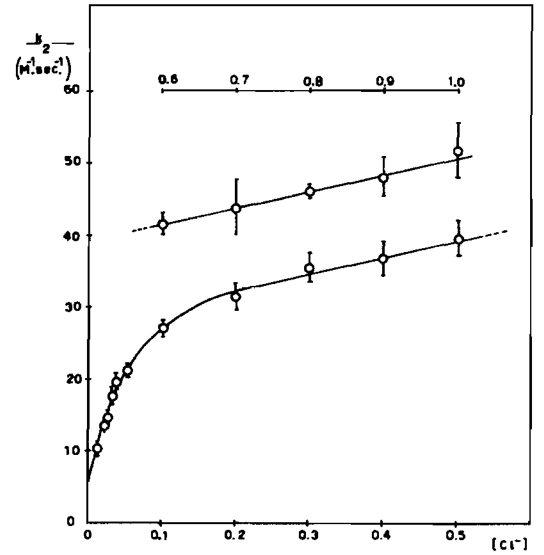

Figure 1. Dependence of k_2 upon the chloride ion concentration. Curve calculated using eq 2. (Higher range of value refers to upper abscissa). $[H^+] = 1.0$ M, $\mu = 1.0$ (ACl, $HClO_4$), 25°C.

The experimentally obtained curve for the chloride dependence of k_2 in the bromopentaamminecobalt(III)-chlorine reaction (Figure 1, *vide infra*) was cast in the mathematical form given in eq. 2 in the following way. The curve was resolved as the algebraic sum of two functions: function (i), a line whose slope is equal to the limiting slope which is evident in Figure 1 at high $[Cl^-]$ and whose ordinate intercept is the value of k_2 at $[Cl^-] = 0$, and function (ii), a new curve which was obtained by subtracting the values given by line (i) from each value of k_2 in Figure 1. The advantage in the procedure is that curve (ii) attains a constant value of k_2 at high $[Cl^-]$ and is easily fitted. It was found that the simplest function which generates curve (ii) has the form

$$y=(a[Cl^-]+b[Cl^-]^2)/(1+c[Cl^-]+d[Cl^-]^2) \quad (1)$$

Since eq. 1 is a ratio of polynomials, the factor of unity in the denominator was chosen arbitrarily. All the coefficients are positive and each term is significant to the curve. The final form of the dependence, eq. 2, was obtained by adding eq. 1 algebraically to the expression $y' = u[Cl^-]+v$, which defines the line (i).

The error limits quoted for the constants in eq. 2 were calculated as the minimum changes required to give a significant deviation from the plot in Figure 1. A significant deviation was considered to be one falling outside the error bars shown. The error bars give the average deviation of at least three independent rate measurements at each concentration of chloride ion.

Results

Kinetics of Oxidative Substitution by Aqueous Chlorine. An investigation of the chlorine-bromopentaamminecobalt(III) reaction in excess aqueous chlorine (pseudo first-order conditions, $1.7\times10^{-3} \leqslant [Cl_2] \leqslant 2.7\times10^{-2}$ M) was carried out. The specific rate of formation of aqueous Br_2 (or BrCl), measured at 435 nm, was observed to be the same as that for consumption of the $Co(NH_3)_5Br^{2+}$ species, monitored at 550 and 310 nm. No evidence for observable concentration of any intermediate was found. The rate law was shown to be of the form

$$\frac{-d[Co(NH_3)_5Br^{2+}]}{dt} = k_2[Cl_2][Co(NH_3)_5Br^{2+}]$$

The rate of the reaction was independent of $[H^+]$ in the range 0.05-1.0 M.

A significant dependence of the specific rate, k_2, upon the chloride ion concentration was discovered. The dependence was rigorously investigated in the concentration range $0.01 < [Cl^-] < 1.0$ M yielding the observed variation of k_2 with $[Cl^-]$ which is shown in Figure 1. The points in the figure were determined by experiment. The curve corresponds to the function

$$k_2=\frac{A+B[Cl^-]+C[Cl^-]^2+D[Cl^-]^3}{1+E[Cl^-]+F[Cl^-]^2} \quad (2)$$

Elimination of any of the terms in eq. 2 causes the plot to deviate substantially from the form shown in the figure. The actual values of the parameters in eq. 2 are of course, set by an arbitrary choice of unity as the first term in the denominator. The values are A: 7 ± 1.0, B: $(4\pm0.6)\times10^2$, C: $(9\pm1.5)\times10^3$, D: $(7\pm1)\times10^3$, E: 13 ± 1.5, F: $(3\pm0.4\times10^2$.

To see whether the dependence of the rate upon $[Cl^-]$ would be extended to other anions, the sulfate dependence of k_2, which is given in Table I, was in-

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[6] E.R. Kantrowitz, M.Z. Hoffman, and J.F. Endicott, *J. Phys. Chem.*, *75*, 1914 (1971).

Table I. Effect of Sulfate and Bisulfate Ions on the Rate of Reaction between Cl_2 and $Co(NH_3)_5Br^{2+}$ [a].

Run	$10^2[Cl_2]$ M	$10^4[RBr^{2+}]$ [c] M	$[Cl^-]$ M	$[H^+]$ M	$[SO_4^{2-}]$ M	$[HSO_4^-]$ M	k_{obs} [b] sec^{-1}	$k_{obs}/[Cl_2]$ $M^{-1}sec^{-1}$
1	1.80	7.8	0.5	0.05	—	—	0.77	43
2	1.70	6.4	.0.5	0.05	.02	.005	0.82	49
3	2.01	7.5	0.5	0.03	.07	.016	1.09	54
4	1.76	7.7	0.5	0.03	.136	.024	1.12	64
5	2.33	7.2	0.05	1.0	—	—	0.506	22
6	2.44	10.3	0.05	0.04	.048	.012	0.71	29
7	2.73	6.5	0.05	0.04	.141	.024	1.16	42
8	3.03	12.	0.05	0.016	.287	.033	1.83	61
9	1.85	8.1	0.5	0.9	.02	.130	0.85	46
10	2.50	4.0	0.5	0.9	.05	.300	1.29	52

[a] μ = 1.0 ($LiClO_4$); Data taken at 550 and 435 *nm*, 25°C. [b] k_{obs} for bisulfate catalysis corrected for effect of sufate ion. [c] R is experiments 1-8, HOBr for experiments 9-15.

Table II. Kinetic Data Obtained for the Reactions of HOCl and HOBr with $Co(NH_3)_5Br^{2+}$.

Expt. [a]	$[H^+]$ M	T °C	$10^2[HOX]$ [b] M	$10^4[RBr^{2+}]$ M	k_{obs} sec^{-1}	$k_{obs}/[HOX]$ $M^{-1}sec^{-1}$
1	1.0	13.0	3.80	8.2	2.93	77.2
2	1.0	13.0	1.64	2.9	1.34	82.0
3	1.0	13.0	0.33	3.0	0.225	67.0
4	0.05	24.5	1.72	7.0	0.143	8.3
5	0.30	25.0	2.75	25.0	9.03	32.8
6	1.0	24.5	1.64	2.9	1.70	103.
7	1.0	8.5	1.64	2.9	1.24	75.1
8	1.0	38.5	1.64	2.9	2.53	154.
9	1.0	25.0	0.51	4.8	1.52	2.99
10	1.0	25.1	2.05	4.1	6.36	3.10
11	0.90	24.6	1.03	5.9	2.94	2.86
12	0.55	24.5	1.80	14.8	3.07	1.71
13	0.10	25.0	1.80	14.8	0.603	0.335
14	1.0	6.2	2.23	8.0	2.16	0.98
15	1.0	35.8	1.70	6.0	9.30	5.50

[a] μ = 1.0 ($LiClO_4$). Data taken at λ = 550 *nm* for runs 1-8, at 550 and 435 *nm* for experiments 9-15. [b] HOX is HOCl for experiments 1-8, HOBr for experiments 9-15.

vestigated. The presence of sulfate ion was found to increase the rate of the reaction significantly. At both high (0.50 *M*, expts. 1-4, Table I) and low (0.050 *M*, expts. 5-8) chloride concentrations an additional term, $k_3[SO_4^{2-}]$, was developed in the rate law, with k_3 equal to $1.4\pm0.1\times10^2$ M^{-2} sec^{-1} at 25 °C. The dependence of the rate on bisulfate ion concentration was also investigated (expts. 1, 9 and 10). The rate constant, k_4, for the bisulfate-dependent term is 33 ± 3 M^{-2} sec^{-1}.

Kinetics of Oxidative Substitution by Hypochlorous and Hypobromous Acids. Oxidation of cordinated bromide in bromopentaamminecobalt(III) by hypochlorous and hypobromous acids was shown by Haim and Taube[1] to produce aquopentaamminecobalt(III) in quantitative yield. Our study of the kinetics of those reactions yielded the data given in Table II. The reaction rates were measured by the stopped-flow technique employing at least a tenfold excess of the oxidizing agent. In the HOBr reaction the formation of bromine (measured at 435 nm) was observed to occur at the same rate as the consumption of bromopentaamminecobalt(III). In the HOCl reaction the absorbance change at 435 nm was hardly measurable, indicating that in this case bromine is not a primary product of the reaction. No evidence for observable concentration of any intermediate was found in either the hypochlorous or hypobromous acid reactions.

Plots of k_{obsd} *vs* [HOX] showed that the reactions follow first order rate dependence upon concentrations of the oxidants in the ranges studied: $(3.3\text{-}38.)\times10^{-3}$ *M* in [HOCl] and $(5.0\text{-}22.3)\times10^{-3}$ *M* in [HOBr]. From a plot of $k_{obs}/[HOCl]$ *vs* $[H^+]$ the form of the rate law for the oxidation of cobalt-coordinated bromide by hypochlorous acid was found to be

$$\frac{-d[Co(NH_3)_5Br^{2+}]}{dt}=(k+k'[H^+])[HOCl][Co(NH_3)_5Br^{2+}]$$

with $k = 4\pm1$ M^{-1} sec^{-1} and $k' = 100\pm7$ M^{-2} sec^{-1} at 25°C. For the k' path the temperature dependence study gave $\Delta H^* = 3.8\pm1$ kcal/mole, $\Delta S^* = -37\pm5$ e.u.

In oxidative substitution by hypobromous acid the k term analogous to that in the rate law given above did not contribute significanly to the rate. The dependence of the rate of the HOBr reaction on temperature gave $\Delta H^* = 9.4\pm1.5$ kcal/mole and $\Delta S^* = -25\pm5$ e.u. with $k' = 3.2\pm0.2$ M^{-2} sec^{-1} at 25°C.

Stoichiometry of the Oxidation of Coordinated Bromide in $Co(NH_3)_5Br^{2+}$ by Mixed Aqueous HOCl

Table III. Distribution of Products on Oxidation of Bromopentaamminecobalt(III) by Aqueous Mixtures of Chlorine and Hypochlorous Acid.

$[H^+]$ *M*	$10^2[Cl^-]$ *M*	$10^2[Cl_2]$ [a] *M*	$10^3[RBr^{2+}]$ [b] *M*	$10^3[RCl^{2+}]$ *M*	% ROH_2^{3+} found	% ROH_2^{3+} calcd
0.1	0.75	2.23	3.05	1.33	56	50
0.1	1.45	2.23	3.21	2.16	67	66
0.1	3.0	1.9	2.80	2.35	84	85
0.1	6.0	1.9	2.88	2.72	94	94
1.0	0.35	1.8	3.28	1.28	39	38
1.0	1.0	2.2	2.9	2.2	76	74
1.0	2.6	2.2	1.04	0.92	89	88
1.0	5.0	2.2	0.66	0.62	94	92
1.0	7.5	2.2	0.76	0.71	94	97

[a] total $[Cl_2]+[HOCl]$. [b] originally present.

and Cl_2. At low $[H^+]$ and low $[Cl^-]$ (0.01 *M*) the rapid disproportionation of aqueous chlorine produces significant amounts of hypochlorous acid. We have shown that, under these experimental conditions, HOCl reacts with the ion $Co(NH_3)_5Br^{2+}$ at a specific rate comparable to that of the oxidative substitution by chlorine. Neither oxidant appears to react with the product chloropentaamminecobalt(III) ion. Therefore, when solutions of the bromopentaamminecobalt(III) complex are exposed to aqueous Cl_2-HOCl mixtures, a calculable yield of the $Co(NH_3)_5OH_2^{3+}$ ion is expected in addition to the chloride-substituted product. The yields obtained in a series of such experiments are presented in Table III along with predicted yields based on the specific rates of the two competing reactions. Agreement is excellent. In calculating the percent yield of the aquo-substituted product the quotient[7] $K = 3.4\times10^{-4}$ M^2 was used to determine the degree of disproportionation of aqueous chlorine.

Stoichiometry in the Presence of Sulfate Ion. The effect of added sulfate ion upon the stoichiometry of the reaction with chlorine was investigated. Under the conditions $[Cl^-] = 0.5$ *M*, $[Cl_2]_T = 3.02\times10^{2-}$ *M*, $[H^+] = 0.05$ *M* and $[SO_4^{2-}] = 0.17$ *M*, the reaction yielded $[Co(NH_3)_5Cl^{2+}] = 4.9\times10^{-3}$ *M* and $[Co(NH_3)_5OH_2^{3+}] = 0.9\times10^{-3}$ *M*. All the initial Co^{III} was recovered in these two products. In another experiment, under the conditions $[H^+] = 0.05$ *M*, $[Cl^-] = 0.05$ *M*, $[Cl_2]_T = 2.37\times10^{-2}$ *M*, $[SO_4^{2-}] = 0.33$ *M* the yields and products were, respectively, 3.5×10^{-3} *M*, $[Co(NH_3)_5Cl^{2+}]$, 2.02×10^{-3} *M* $[Co(NH_3)_5OH_2^{3+}]$, and 0.79×10^{-3} *M* $[Co(NH_3)_5SO_4^+]$. The small yields of the sulfate-containing product are significant because in the two experiments, respectively, thirty and sixty percent of the Cl_2 oxidation reactions are known from the kinetic data to proceed *via* the sulfate-catalyzed pathway.

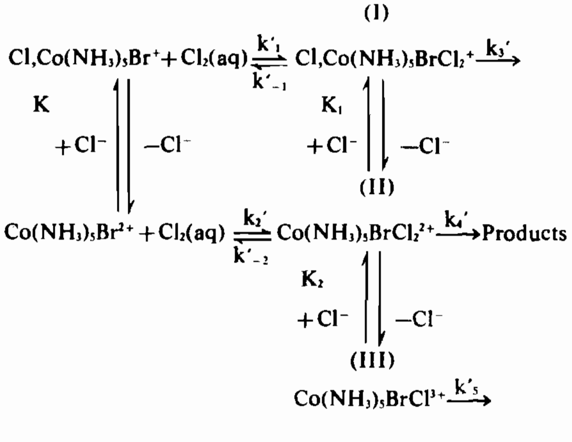
Discussion

Stoichiometry of the Cl_2 - HOCl - $Co(NH_3)_5Br^{2+}$ Reaction. The observations presented in Table III show that, under conditions of low chloride ion concentration, hypochlorous acid competes effectively against aqueous chlorine to react with bromopentaamminecobalt(III). The result disagrees with an earlier observation[1] that, even at relatively low $[H^+]$ and $[Cl^-]$, this does not occur. However, the $[H^+]$ dependence of the hypochlorous acid reaction at least partly explains that early observation since oxidative substitution by hypochlorous acid is kinetically disfavored at lower hydrogen ion concentrations.

The majority of the kinetic experiments in the chlorine-bromopentaamminecobalt(III) study were perfermed at $[Cl^-]\geqslant0.06$ *M*. Under this condition the chloride-substituted product is formed in at least ninety-five per cent yield. The rate constants presented in this work which were measured at lower chloride ion concentration have been corrected for the parallel hypochlorous acid reaction.

Kinetics of the Cl_2 - $Co(NH_3)_5Br^{2+}$ Reaction. The observations regarding this reaction are as follows. (1) The rate is proportional to the first power of the concentrations of the cobalt complex and of aqueous chlorine. The rate is independent of the hydrogen ion concentration. (2) The specific rate varies in a complex but defined way (eq. 2) with the chloride ion concentration. (3) No evidence was found for the observable concentration of any intermediate. (4) The reaction rate is increased by added sufate ion and to a lesser extent by bisulfate ion. The effect of sulfate is a catalytic one in that very little sulfatopentaamminecobalt(III) ion appears as a product.

A mechanism for the chloride ion catalyzed reaction which is consistent with the foregoing observations is the following.



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[7] G. Zimmerman and F.C. Strong, *J. Am. Chem. Soc., 84*, 1355 (1962).

The first equilibrium, the K-step, describes formation of an ion pair, a process which should be very rapid.[9] Subsequently, chlorine is postulated to react with coordinated bromide in either the free or the ion-paired cobalt complex to give the coordinated trihalide species (intermediates I and II) shown above. Since trihalides generally exist in labile[10] equilibria with the corresponding halogens, intermerdiate III, a coordinated interhalogen, is included in the mechanism. This third species is the one which was originally postulated by Haim and Taube.[1] Following those authors we consider the charge distribution in the reactive, coordinated interhalogen to approach the configuration

$$(NH_3)_5Co(III)Br^+Cl^-$$

in which negative charge is drawn toward the more electronegative end of the interhalogen. We postulate that intermediate III reacts either by linkage isomerization to yield the product ion, $Co(NH_3)_5Cl^{2+}$, or by internal electron transfer to form the reactants. Intermediates I and II, in labile equilibrium with III, are considered capable of analogous reactions.

If the steady-state approximation is made with respect to the concentration of the intermediates, one obtains the rate expression:

$$k_{obsd}/[Cl_2] = \frac{(k_5' + k_4'K_2[Cl^-] + k_3'K_1K_2[Cl^-]^2)(k_2' + k_1'K[Cl^-])}{k_5' + (k'_{-2} + k_4)K_2[Cl^-] + (k'_{-1} + k_3')K_1K_2[Cl^-]^2} \tag{3}$$

The form of this expression in $[Cl^-]$ is equivalent to that which was found by experiment (eq. 2) for the dependence of k_2 upon the chloride ion concentration. This close correspondence constitutes, in our view, strong evidence for the proposed mechanism.

Catalysis by bisulfate and sulfate ions can be understood in terms of the existence of ion-pairing equilibria, analogous to the K-step in the mechanism given above.[11] It seems reasonable, on an electrostatic basis, that oxidation of the bromide ion in the cobalt complex would be facilitated when the complex is associated with a negative ion. That the doubly negative sulfate ion should be a more effective catalyst than bisulfate ion, or chloride ion (catalytic activity at high $[Cl^-]$ judged from the slope of Figure 1) is consistent with this interpretation.

Although the proposed mechanism and the rate law are in agreement we add the qualification that activity effects must be considered constant in order for the full kinetic development to apply to the data presened in Figure 1. The question is an extremely fundamental one and cannot be resolved completely. However, we would like to indicate that below 0.3 *M* chloride ion concentration, where relatively little perchlorate ion has been replaced by chloride, k_{obs} is probably less sensitive to medium effects at constant ionic strength and that, even in this limited region, the form of Figure 1 requires the rate law expressed by eq. 2.

The fact that no intermediates could be directly observed in this study indicates that the linkage isomerization process does not present the principal barrier encountered in the course of the oxidative substitution reaction. Assuming that the specific rate of isomerization is at least ten times larger than the highest observed rate (k_{obsd}) of the Cl_2 oxidation process ($k_{obsd} = 1.2$ sec^{-1} at $\mu = 1.0$, $[Cl_2] = 2.3 \times 10^{-2}$ *M*, 25°C), a lower limit for the specific rate of the linkage isomerization reaction can be estimated as *ca.* 12 sec.$^{-1}$. This value can be compared with $k_{isom} = 1.7 \times 10^{-5}$ sec^{-1} for the nitrito-nitro isomerization in $Co(NH_3)_5(ONO)_2{}^+$.[2]. The comparatively rapid isomerization which must occur in the oxidative substitution reaction is consistent with a strong repulsion between the cobalt(III) metal center and the coordinated (Br^+) end of the interhalogen or intertrihalide ligand.

On the basis of the foregoing discussion we conclude that the highest activation barrier in the chlorine-bromopentaamminecobalt(III) oxidative substitution reaction is presented by the oxidation step. This is certainly a consequence of the increased stability against oxidation which is expected of bromide ion when it has become coordinated to a positively charged metal center such as pentaamminecobalt(III).

Oxidative Substitution in Bromopentaamminecobalt(III) Ion by Hypohalous Acids. At $[H^+]$ equal to 0.1 *M*, and at higher concentrations, the dominant pathway in the oxidative substitution reactions involving hypochlorous and hypobromous acids is dependent upon the proton concentration. Although it has not been proved, the only reasonable site for protonation is at oxygen in HOX. The probable function of the proton is to augment the oxidizing power of the HOX species. If attack of the cobalt(III) coordinated bromide is at oxygen in hypochlorous acid, as the results of Haim and Taube[1] strongly indicate, the proton may also have the function of labilizing oxygen in the HOCl molecule to substitution. The question of the point of attack in HOBr has not been answered.

There exists good evidence that the oxidation of the aqueous Cr^{II} [12] and Fe^{II} [13] ions by hypochlorous acid takes place at least partly by two-electron transfer. A comparison of the rates of the HOCl and HOBr oxidations of the bromopentaamminecobalt(III) ion suggests that these reactions also proceed *via* two-electron pathways. The relative rates and activation enthalpies for oxidation by HOCl and HOBr show a rather large difference, with HOCl being considerably more reactive. If one considers the almost equal driving force[14] which the two oxidants could exert in a one-electron oxidation, the difference in reactivity is surprising. For two-electron oxidations the diffe-

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(8) The rate of disproportionation of aqueous chlorine (M. Eigen and K. Kustin, *J. Am. Chem. Soc.*, *84*, 1355 (1962)) is at least ten times larger than the rates of reaction of aqueous chlorine or of hypochlorous acid with bromopentaamminecobalt(III) under the conditions of this work.

(9) M. Eigen, *Z. Elektrochem.*, *64*, 115 (1960).

(10) O.E. Myers, *J. Chem. Phys.*, *28*, 1027 (1958).

(11) M.T. Beck, *Coord. Chem. Revs.*, 3, 91 (1968).

(12) M. Ardon and R.A. Plano, *J. Am. Chem. Soc.*, *81*, 3197 (1959).

(13) T.J. Connochioli, E.J. Hamilton, and N. Sutin, *J. Am. Chem. Soc.*, *87*, 926 (1965).

(14) For the Cl_2 - HOCl couple, $E^\circ = -1.63$ V; for the Br_2 - HOBr couple, $E^\circ = -1.59$ V. However, the X^- - HOX couples are calculated to be -1.49 and -1.33 V, respectively, for chlorine and bromine, W.M. Latimer, « Oxidation Potentials », second ed., Prentice-Hall, Inc., Englewood Cliffs, N.J., 1952, Chap. 5.

rence in driving force favors the HOCl reaction.

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