

method in being applicable only so long as the plateau region lasts: both are based on the conservation of mass and the fact that transport occurs only by sedimentation in a region where  $\partial c/\partial r = 0$ . Unfortunately there seems to be little gain in accuracy when it is used with interference<sup>15</sup> rather than schlieren optics.<sup>26,27</sup>

In addition to being precise, the present method has the advantage that the measurements and computations are simple. To find  $\Delta c$  it is necessary only to record the positions of a few fringes at either end of the column and then to count the fringes in between.<sup>4</sup>

**A New Method for Measuring Molecular Weights during the Transient Period.**—Since the slope of the plot in Fig. 1 gives  $s^2/D$ , it could be used to find  $s/D$  (and therefore  $M$ ) if  $s$  were known. This is illustrated in Table II, where predicted values of  $s$  (eq. 1) and known values of  $\bar{v}$ ,  $\rho$ , and  $\partial \ln y/\partial c$  have been combined with the present measurements of  $s^2/D$  to give  $M$ . The

TABLE II  
VALUES FOR THE MOLECULAR WEIGHT OF SUCROSE OBTAINED BY  
A NEW METHOD

$c^0$ , g./100 ml.	$M$ (obsd.)/ $M^a$
3.619	0.994 ± 0.004
4.498	0.998 ± .009
5.420	1.003 ± .004
5.579	1.001 ± .007

<sup>a</sup> Calculated from eq. 7 using known values for the sedimentation coefficient: in this case, the ones given by the extended Svedberg equation and the diffusion data of Gosting and Morris.<sup>7</sup> The experimental uncertainty indicated for  $M$  (obsd.) is that of finding the slope of eq. 7.<sup>21</sup>

agreement is quite good. This new method might be a good way of making use of the potential accuracy of interference optics in finding molecular weights from the transient period, something which has not yet been accomplished with the Archibald method (*cf.* Richards and Schachman<sup>8</sup>). It could be useful with proteins of large molecular weight which take a long time to reach sedimentation equilibrium because of low diffusion coefficients.<sup>20</sup> The procedure would be to find  $s$  from the rate of movement of a boundary at high rotor speed

(27) K. E. Van Holde, *J. Phys. Chem.*, **63**, 1574 (1959).

(inspection of the boundary shape also provides a check on the homogeneity of the material) and then to measure  $(\Delta c/c^0)$  vs.  $t$  in experiments at lower rotor speed where a freely sedimenting boundary is not formed. Then the results from the two experiments are combined to give the molecular weight.

**Factors Controlling the Time Needed to Reach Equilibrium.**—With the aid of eq. 6 we can now derive expressions for two effects noted experimentally in an earlier study<sup>4</sup> of the approach to sedimentation equilibrium. First  $\Delta c/c^0$  is almost independent of column height while the plateau region lasts. When we compare two experiments (1 and 2) at the same time and rotor speed but with different column heights, we find from eq. 6

$$\frac{\Delta c_1}{\Delta c_2} = \frac{\bar{r}_1 [1 + H_1(\omega^2 s/4)(\pi t/D)^{1/2} + \dots]}{\bar{r}_2 [1 + H_2(\omega^2 s/4)(\pi t/D)^{1/2} + \dots]} \quad (11)$$

The column height  $H$  enters only in a small correction term. There is however a definite dependence of  $\Delta c$  on the position of the mid-point  $\bar{r}$ . In principle one could hold  $\bar{r}$  constant while varying  $H$ , but in routine experiments  $\bar{r}$  would be likely to change when  $H$  is changed.

Secondly it was noted<sup>4</sup> that the rate of approach to sedimentation equilibrium is nearly independent of  $\omega^2$  during the existence of the plateau region as well as in later stages of the experiment. The departure from equilibrium may be measured by the parameter  $\epsilon$ ,<sup>4,20</sup> which is defined as

$$\epsilon \equiv 1 - \Delta c/\Delta c(\text{eq}) \quad (12)$$

When  $\Delta c(\text{eq})$  is expressed by eq. 9 and  $\Delta c$  by eq. 6, and these are substituted into eq. 11, one obtains a simple expression for  $\epsilon$  which is valid in the first part of the experiment, while the plateau region lasts. Here

$$\epsilon = 1 - 4(Dt/\pi H^2)^{1/2} [1 + (H\omega^2 s/4)(\pi t/D)^{1/2} + \dots] \quad (13)$$

$\omega^2$  appears only in the minor correction term and  $\epsilon$  depends chiefly on  $(D/H^2)$ , as is also true after the plateau region vanishes.<sup>4,20</sup>

**Acknowledgment.**—We wish to thank Dr. T. Kotaka for his discussions of the theory.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIF.]

## The Reactions of Iodopentaamminecobalt(III) with Various "Two-Electron" Oxidizing Agents

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The reactions of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with  $\text{Cl}_2$  and  $\text{Br}_2$  result in quantitative yields of  $\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$  and  $\text{Co}(\text{NH}_3)_5\text{Br}^{++}$ , respectively. Similarly, the reactions of  $\text{Co}(\text{NH}_3)_5\text{Br}^{++}$  and  $\text{Cr}(\text{NH}_3)_5\text{Br}^{++}$  (in 0.10  $M$   $\text{Cl}^-$ ) with  $\text{Cl}_2$  produce quantitative yields of  $\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$  and  $\text{Cr}(\text{NH}_3)_5\text{Cl}^{++}$ , respectively. The reactions of  $\text{Co}(\text{NH}_3)_5\text{Br}^{++}$  with  $\text{HOBr}$  and  $\text{HOCl}$  and of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with  $\text{HOBr}$ ,  $\text{ICl}$ ,  $\text{O}_3$ ,  $\text{CH}_3\text{CO}_3\text{H}$ ,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{HSO}_5^-$ , and  $\text{H}_2\text{O}_2$  yield  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  quantitatively.  $\text{O}^{18}$  tracer studies on the reactions of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  indicate that 31 and 5.5%, respectively, of the oxygen in the  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  product is derived from the oxidizing agent. The reaction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with  $\text{H}_2\text{O}_2$  when  $\text{H}^+$  and  $\text{H}_2\text{O}_2$  are in excess obeys the rate law  $k_3(\text{Co}(\text{NH}_3)_5\text{I}^{++})(\text{H}_2\text{O}_2)(\text{H}^+)$  during approximately the first two half-lives, but this phase is terminated by a sharp decrease in  $(\text{Co}(\text{NH}_3)_5\text{I}^{++})$ . Iodine and iodate ion strongly accelerate the rate of disappearance of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ . The rate of reaction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  and  $\text{H}_2\text{O}_2$  is independent of  $(\text{Cl}^-)$  but as  $(\text{Cl}^-)$  is increased  $\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$  becomes an increasingly important product.  $\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$  is also formed in high yields when  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  reacts with  $\text{O}_3$  or  $\text{S}_2\text{O}_8^{2-}$  in the presence of  $\text{Cl}^-$ . The mechanisms of the reactions are discussed,

and they feature rearrangements of the type  $(\text{NH}_3)_5\text{CoIOH}^{+3}$  to  $(\text{NH}_3)_5\text{CoOI}^{+3}$  and  $(\text{NH}_3)_5\text{CoICl}^{+3}$  to  $(\text{NH}_3)_5\text{CoClI}^{+3}$ , followed in each case by loss of  $\text{I}(\text{I})$  (as  $\text{HOI}$ , for example).

The behavior of the iodopentaamminecobalt(III) ion toward various "one-electron" oxidation-reduction reagents has been reported recently.<sup>1</sup> It was demonstrated that with some of these reagents (hydroxyl and

methyl radicals, iodine atoms) reduction of the Co(III) center occurs, whereas with other reagents (ceric and cobaltic ions) the oxidation state of the Co(III) center is preserved. In the present paper we report the results obtained in a study of the reactions of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$

(1) A. Haim and H. Taube, *J. Am. Chem. Soc.*, **85**, 495 (1963).

$I^{++}$  with various "two-electron" oxidizing agents. Two important features have emerged from this investigation. First, the oxidation-reduction changes that occur in the bound iodide ion do not involve any net change in the oxidation state of the Co(III) center and, in all instances, the cobalt-containing products are Co(III) pentaammine complexes. Second, it has been possible to show in some cases that the reduced form of the oxidizing agent is retained in the coordination sphere of the Co(III) product. The very efficient capture of ligands when oxidizing agents act on  $I^-$  or  $Br^-$  bound in the coordination sphere of Co(III) which we have observed in the present work has no precedent in the numerous reactions so far reported for Co(III) complexes.

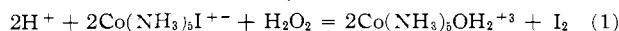
### Experimental

**Materials.**—Hypochlorous and hypobromous acids were prepared by treating an excess of saturated chlorine or bromine water at  $0^\circ$  with silver perchlorate-perchloric acid solution. The silver halide formed was filtered out and nitrogen was bubbled through the resulting solutions to remove the excess chlorine or bromine. These solutions were standardized iodometrically. Peroxyacetic acid solutions were prepared from glacial acetic acid and 30% hydrogen peroxide.<sup>2</sup> The unreacted hydrogen peroxide was titrated with Ce(IV) and the peroxyacetic acid was standardized iodometrically. Caro acid was prepared by heating sodium peroxydisulfate in 5 *M* perchloric acid.<sup>3</sup> All other chemicals were reagent grade. Ordinary distilled water was used in all experiments.

**Preparation of Complexes.**— $[Co(NH_3)_5I](ClO_4)_2$ ,  $[Co(NH_3)_5Br](ClO_4)_2$ ,  $[Co(NH_3)_5OH_2](ClO_4)_3$ , and  $[Co(NH_3)_5Cl]Cl_2$  were synthesized as described earlier.<sup>1</sup> Since some experiments required a very precise knowledge of the extinction coefficients of the chloro and aquo complexes at various wave lengths,  $[Co(NH_3)_5OH_2](ClO_4)_3$  and  $[Co(NH_3)_5Cl]Cl_2$  were purified by recrystallizing them four times from aqueous solution.  $[Cr(NH_3)_5OH_2](NO_3)_3 \cdot NH_4NO_3$  was prepared according to the procedure described by Mori.<sup>4</sup> Treatment with hydrochloric or hydrobromic acid yielded  $[Cr(NH_3)_5Cl]Cl_2$  and  $[Cr(NH_3)_5Br]Br_2$ , respectively.

**Stoichiometric Experiments.**—Solutions of the complex ion under study and of other reagents required were pipetted into volumetric flasks. The oxidizing agent was then added ( $O_3$  and  $Cl_2$  as gases and other oxidizing agents in solution) and any volume defect was made up by adding solvent. After the reactions had proceeded to completion, the solutions were treated in the following manner. For the experiments with  $Cl_2$ ,  $Br_2$ , and  $O_3$ , the excess oxidant was removed by bubbling nitrogen through the solutions. For the experiments with HOCl and HOBr, the excess oxidant was reduced with sodium bromide and the bromine formed was removed by a stream of nitrogen. For the experiments with ICl,  $H_2O_2$ ,  $S_2O_3^{2-}$ ,  $HSO_3^-$ , and  $CH_3CO_3H$ , the iodine formed was extracted with carbon tetrachloride and the aqueous layer was centrifuged to clarify it. After treating the product solutions as described, aliquots were withdrawn and examined spectrophotometrically to determine the nature of the cobalt species present in solution.

**Kinetics of the  $Co(NH_3)_5I^{++}-H_2O_2$  Reaction.**—Solutions of  $Co(NH_3)_5I^{++}$  and all other reagents except the  $H_2O_2$  were pipetted into a volumetric flask which was placed in a constant temperature bath at  $25 \pm 0.1^\circ$ . After temperature equilibrium had been reached, the  $H_2O_2$  was added, and the solution was made up to volume and rapidly transferred to a spectrophotometric cell. The cell was placed in the thermostated ( $25 \pm 0.1^\circ$ ) cell holder of a Cary spectrophotometer, and a recording of optical density *vs.* time at the desired wave length was obtained. All experiments were performed at 388  $m\mu$ ; at this wave length  $Co(NH_3)_5I^{++}$ ,  $Co(NH_3)_5OH_2^{+3}$ , and  $I_2$  have extinction coefficients of 2700, 11, and 100, respectively. In all experiments the concentration of  $Co(NH_3)_5I^{++}$  was less than 1% that of  $H_2O_2$ . Pseudo-first-order rate constants  $k_1$  were obtained from the slopes of plots of  $\log(D_t - D_\infty)$  *vs.* time;  $D_t$  and  $D_\infty$  are the optical densities of the solution at *t* and after reaction is complete, respectively;  $D_\infty$  could not be measured experimentally because even after all the  $Co(NH_3)_5I^{++}$  has reacted, the optical density at 388  $m\mu$  continues to decrease because  $H_2O_2$  oxidizes iodine to iodate. Therefore, values of  $D_\infty$  were calculated from the initial concentration of the  $Co(NH_3)_5I^{++}$  reactant and the extinction coefficients of the  $Co(NH_3)_5OH_2^{+3}$  and  $I_2$  products assuming that the stoichiometry of the reaction is given by eq. 1.



(2) W. C. Smit, *Rec. trav. chim.*, **49**, 675 (1930).

(3) I. M. Kolthoff and I. K. Miller, *J. Am. Chem. Soc.*, **73**, 3055 (1951).

(4) T. Moeller, *Inorg. Syn.*, **5**, 131 (1957).

Although  $I_2$  is oxidized to  $IO_3^-$ , the calculation of  $D_\infty$  on the basis of eq. 1 is a sufficiently good approximation. During the time when useful kinetic data can be obtained  $D_\infty$  is only 2.2–5% of  $D_t$  and 88–95% of the  $I_2$  corresponding to eq. 1 is formed.

**Stoichiometry of the  $Co(NH_3)_5I^{++}-H_2O_2$  Reaction in the Presence of  $Cl^-$ .**—Solutions of  $Co(NH_3)_5I^{++}$ ,  $HClO_4$ , and  $HCl$  of known concentrations were pipetted into volumetric flasks. The desired quantity of  $H_2O_2$  was then added and any volume defect was made by adding solvent. After the reaction had proceeded to completion, the iodine was extracted with carbon tetrachloride, the aqueous layer was centrifuged, and the optical densities at 507 and 550  $m\mu$  were measured. At 507  $m\mu$ ,  $Co(NH_3)_5Cl^{++}$  and  $Co(NH_3)_5OH_2^{+3}$  have an isosbestic point with extinction coefficient 45.2, and therefore this wave length is useful in establishing that the chloro and aquo complexes were the only two cobalt-containing products. Furthermore, any large (>2%) difference between experimental and calculated optical density at 507  $m\mu$  was adopted as a criterion to reject experiments (7 out of 44 experiments were rejected on this basis). At 550  $m\mu$  the extinction coefficients of  $Co(NH_3)_5Cl^{++}$  and  $Co(NH_3)_5OH_2^{+3}$  are 47.2 and 20.8, respectively; thus this wave length was useful in calculating the concentration of the  $Co(NH_3)_5Cl^{++}$  product.

**$O^{18}$  Tracer Experiments.**— $Co(NH_3)_5I^{++}$  was dissolved in  $O^{18}$ -enriched water containing the perchloric acid. The oxidizing agent was added and after reaction had proceeded to completion the solution was cooled to  $0^\circ$  and  $[Co(NH_3)_5OH_2]Br_3$  was precipitated by addition of an excess of concentrated HBr. The removal of the bound water and subsequent equilibration with  $CO_2$  were performed as described by Posey and Taube.<sup>5</sup> The mass spectrometric analyses were performed by the courtesy of Dr. John W. Harbaugh of the Geology Department.

**Spectrophotometric Measurements.**—Absorption spectra were obtained with a Cary Model 14 recording spectrophotometer fitted with a thermostated cell holder and cell compartment.

All experiments with  $Co(NH_3)_5I^{++}$  were performed in semi-darkness to avoid photochemical decomposition. The results obtained for the reactions of  $Co(NH_3)_5I^{++}$  have been corrected for the amount of  $[Co(NH_3)_5OH_2](ClO_4)_3$  originally present in the  $[Co(NH_3)_5I](ClO_4)_3$  preparation.<sup>2</sup> All stoichiometric experiments were performed at room temperature.

### Results

In Table I we present a summary of the experiments designed to determine the identity of the cobalt(III) products formed in the reactions of  $Co(NH_3)_5I^{++}$ ,  $Co(NH_3)_5Br^{++}$ , and  $Cr(NH_3)_5Br^{++}$  with various oxidants. Columns 5 and 6 of Table I list the positions of the maxima and the optical densities at the maxima, respectively, of the solutions resulting from the various reactions. Column 7 lists the optical densities calculated for quantitative formation of the products indicated in the last column. The excellent agreement between the values in columns 6 and 7, and also between the values in column 5, with those expected for the formation of the corresponding products, demonstrates that the major products of the reactions are indeed the ones listed in the last column of Table I. In addition to the wave lengths listed in column 5, other wave lengths at which the various possible reaction products display a larger difference in extinction coefficients were examined, and it is estimated that the reaction products indicated in Table I are formed in >95% yield, except where otherwise indicated. The agreement referred to above shows that Co(II) is not an important reaction product. In addition, the absence of Co(II) was demonstrated for experiments 1, 2, 6, and 8 by examining the absorption of the corresponding solutions in 9.6 *M* HCl at 692  $m\mu$  (where Co(II) has a maximum with extinction coefficient 522). Since no absorption could be detected, it is concluded that less than 0.5% Co(II) is formed in these reactions.

Experiments 2, 10, and 11 of Table I show that the reaction of  $Co(NH_3)_5I^{++}$  and  $Co(NH_3)_5Br^{++}$  with  $Cl_2$  yield  $Co(NH_3)_5Cl^{++}$ , even when as in 0.010 *M*  $H^+$  the hydrolysis of  $Cl_2$  is appreciable. In contrast, the reaction of  $Cr(NH_3)_5Br^{++}$  with  $Cl_2$  in 1.0 *M*  $H^+$  yields principally the  $Cr(NH_3)_5OH_2^{+3}$  ion (*cf.* expt. 15). However, in 1.0 *M*  $H^+$  and 0.10 *M*  $Cl^-$  (*cf.* expt. 16)

(5) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).

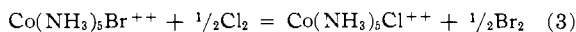
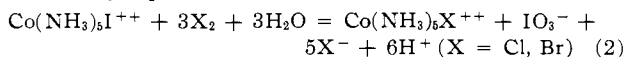
TABLE I

SPECTROPHOTOMETRIC IDENTIFICATION OF THE Co(III) PRODUCTS FORMED BY THE REACTIONS<sup>a</sup> OF Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup>, Co(NH<sub>3</sub>)<sub>5</sub>Br<sup>++</sup>, AND Cr(NH<sub>3</sub>)<sub>5</sub>Br<sup>++</sup> WITH VARIOUS OXIDANTS

Expt.	Complex, <i>M</i> × 10 <sup>3</sup>	Oxidant, <i>M</i>	(H <sup>+</sup> ), <i>M</i>	λ <sub>max</sub> , mμ	<i>D</i> <sub>max</sub>	<i>D</i> <sub>max</sub> , calcd. <sup>b</sup>	Co(III) product
1	Co(NH <sub>3</sub> ) <sub>5</sub> I <sup>++</sup> , 3.30	Br <sub>2</sub> , 0.050	0.010	550 <sup>c</sup>	0.170	0.176 <sup>d</sup>	Co(NH <sub>3</sub> ) <sub>5</sub> Br <sup>++</sup>
2	Co(NH <sub>3</sub> ) <sub>5</sub> I <sup>++</sup> , 3.20	Cl <sub>2</sub> , bubbling	0.010	532 <sup>e</sup>	.157	.160 <sup>d</sup>	Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>++</sup>
				363 <sup>e</sup>	.155	.151 <sup>d</sup>	
3	Co(NH <sub>3</sub> ) <sub>5</sub> I <sup>++</sup> , 1.05	HOBr, 0.020	1.0	492 <sup>f</sup>	.490	.500	Co(NH <sub>3</sub> ) <sub>5</sub> OH <sub>2</sub> <sup>+3</sup>
				345 <sup>f</sup>	.460	.470	
4	Co(NH <sub>3</sub> ) <sub>5</sub> I <sup>++</sup> , 1.14	ICl, 0.10	1.0	492 <sup>f</sup>	.544	.541	Co(NH <sub>3</sub> ) <sub>5</sub> OH <sub>2</sub> <sup>+3</sup>
				345 <sup>f</sup>	.525	.509	
5	Co(NH <sub>3</sub> ) <sub>5</sub> I <sup>++</sup> , 9.00	CH <sub>3</sub> CO <sub>2</sub> H, 0.065	0.010	492 <sup>g</sup>	.420	.425	Co(NH <sub>3</sub> ) <sub>5</sub> OH <sub>2</sub> <sup>+3</sup>
				345 <sup>g</sup>	.396	.400	
6	Co(NH <sub>3</sub> ) <sub>5</sub> I <sup>++</sup> , 0.89	O <sub>3</sub> , bubbling	0.010	492 <sup>f</sup>	.427	.422	Co(NH <sub>3</sub> ) <sub>5</sub> OH <sub>2</sub> <sup>+3</sup>
				345 <sup>f</sup>	.401	.396	
7	Co(NH <sub>3</sub> ) <sub>5</sub> I <sup>++</sup> , 5.36	S <sub>2</sub> O <sub>8</sub> <sup>-2</sup> , 0.20	1.0	492 <sup>h</sup>	.250	.254	Co(NH <sub>3</sub> ) <sub>5</sub> OH <sub>2</sub> <sup>+3</sup>
				345 <sup>h</sup>	.230	.239	
8	Co(NH <sub>3</sub> ) <sub>5</sub> I <sup>++</sup> , 5.48	H <sub>2</sub> O <sub>2</sub> , 0.50	1.0	492 <sup>f</sup>	.258	.260	Co(NH <sub>3</sub> ) <sub>5</sub> OH <sub>2</sub> <sup>+3</sup>
				345 <sup>f</sup>	.240	.243	
9	Co(NH <sub>3</sub> ) <sub>5</sub> I <sup>++</sup> , 6.50	HSO <sub>5</sub> <sup>-</sup> , 0.020	1.0	492 <sup>h</sup>	.310	.308	Co(NH <sub>3</sub> ) <sub>5</sub> OH <sub>2</sub> <sup>+3</sup>
				345 <sup>h</sup>	.300	.290	
10	Co(NH <sub>3</sub> ) <sub>5</sub> Br <sup>++</sup> , 5.40 <sup>i</sup>	Cl <sub>2</sub> , bubbling	0.010	532 <sup>e</sup>	.277	.278	Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>++</sup>
				363 <sup>e</sup>	.256	.261	
11	Co(NH <sub>3</sub> ) <sub>5</sub> Br, 5.20	Cl <sub>2</sub> , bubbling	1.0	532 <sup>e</sup>	.265	.267	Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>++</sup>
				363 <sup>e</sup>	.252	.251	
12	Co(NH <sub>3</sub> ) <sub>5</sub> Br, 0.91	HOBr, 0.020	1.0	492 <sup>f</sup>	.426	.431	Co(NH <sub>3</sub> ) <sub>5</sub> OH <sub>2</sub> <sup>+3</sup>
				345 <sup>f</sup>	.395	.405	
13	Co(NH <sub>3</sub> ) <sub>5</sub> Br, 3.04	HOCl, 0.020	1.0	492 <sup>f</sup>	.140	.144	Co(NH <sub>3</sub> ) <sub>5</sub> OH <sub>2</sub> <sup>+3</sup>
				345 <sup>f</sup>	.139	.135	
14	Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>++</sup> , 6.25	HOCl, 0.020	1.0	532 <sup>e</sup>	.326	.322 <sup>i</sup>	...
				363 <sup>e</sup>	.303	.302 <sup>i</sup>	
15	Cr(NH <sub>3</sub> ) <sub>5</sub> Br <sup>++</sup> , 5.90	Cl <sub>2</sub> , bubbling	1.0	492 <sup>j,k</sup>	.191	.190	$\left\{ \begin{array}{l} 9\% \text{ Cr(NH}_3)_5\text{Cl}^{++} \\ 91\% \text{ Cr(NH}_3)_5\text{OH}_2^{+3} \end{array} \right\}$
				367 <sup>j,k</sup>	.188	.187	
16	Cr(NH <sub>3</sub> ) <sub>5</sub> Br <sup>++</sup> , 2.86	Cl <sub>2</sub> , bubbling <sup>l</sup>	1.0	513 <sup>k</sup>	.510	.512	Cr(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>++</sup>
				376 <sup>k</sup>	.538	.540	

<sup>a</sup> The reactions are complete on mixing except in experiments 7 (*t*<sub>1/2</sub> 3 min. at 0.05 *M* S<sub>2</sub>O<sub>8</sub><sup>-2</sup>), 8 (rate reported on elsewhere in this paper), and 14 (no reaction in 10 min.). <sup>b</sup> Optical density calculated for formation of the product indicated in the last column. <sup>c</sup> λ<sub>max</sub> for Co(NH<sub>3</sub>)<sub>5</sub>Br<sup>++</sup> is 550 mμ. <sup>d</sup> Corrected for the Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> originally present in the [Co(NH<sub>3</sub>)<sub>5</sub>I](ClO<sub>4</sub>)<sub>2</sub> preparation. <sup>e</sup> λ<sub>max</sub> for Co(NH<sub>3</sub>)<sub>5</sub>Cl<sup>++</sup> are 532 and 363 mμ. <sup>f</sup> λ<sub>max</sub> for Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> are 492 and 345 mμ. <sup>g</sup> λ<sub>max</sub> for Co(NH<sub>3</sub>)<sub>5</sub>OCOCH<sub>3</sub><sup>++</sup> are 510 and 353 mμ. <sup>h</sup> λ<sub>max</sub> for Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub><sup>+</sup> are 515 and 355 mμ. <sup>i</sup> Calculated for no reaction. <sup>j</sup> λ<sub>max</sub> for Cr(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> are 480 and 361 mμ. <sup>k</sup> λ<sub>max</sub> for Cr(NH<sub>3</sub>)<sub>5</sub>Cl<sup>++</sup> are 512 and 375 mμ. <sup>l</sup> 0.10 *M* Cl<sup>-</sup> present.

the dominant reaction product becomes Cr(NH<sub>3</sub>)<sub>5</sub>Cl<sup>++</sup>. The iodometric titer of the solutions resulting from experiments 1, 2, 10, and 11 of Table I was determined after the excess chlorine or bromine had been removed. For the reactions of Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup>, the titer corresponded to oxidation of I<sup>-</sup> to IO<sub>3</sub><sup>-</sup>.<sup>6,7</sup> In contrast, the solutions derived from the experiments with Co(NH<sub>3</sub>)<sub>5</sub>Br<sup>++</sup> did not display any oxidizing capacity after the volatile oxidizing agents were removed. The stoichiometries of these reactions are therefore described by eq. 2 and 3.



It is noteworthy that the reactions of Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> with CH<sub>3</sub>CO<sub>2</sub>H (expt. 5), S<sub>2</sub>O<sub>8</sub><sup>-2</sup> (expt. 7), and HSO<sub>5</sub><sup>-</sup> (expt. 9) do not yield acetato or sulfato complexes but Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> as the only cobalt-containing reaction product. It is not surprising that the reactions of O<sub>3</sub> (expt. 6) and H<sub>2</sub>O<sub>2</sub> (expt. 8) with Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> yield Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup>; additional insight into these reactions is provided by O<sup>18</sup>-tracer experiments which are described below. The reactions of HOBr with Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> and Co(NH<sub>3</sub>)<sub>5</sub>Br<sup>++</sup> (expt. 3, 12) and of HOCl with Co(NH<sub>3</sub>)<sub>5</sub>Br<sup>++</sup> (expt. 13) are rapid and Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> is the final product in all instances.

(6) This reaction has been exploited to analyze iodine in Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> salts.

(7) See R. G. Yalman, *J. Am. Chem. Soc.*, **75**, 1842 (1953), and ref. 1.

No reaction occurs between Co(NH<sub>3</sub>)<sub>5</sub>Cl<sup>++</sup> and HOCl in 10 min. at room temperature (expt. 14). Finally, the reaction between Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> and ICl (expt. 4) yields only Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup>.

**Kinetics of the Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup>-H<sub>2</sub>O<sub>2</sub> Reaction.**—This reaction was studied in detail and proved to be fairly complicated. Although only some general features of the reaction have been uncovered, they appear to us to be of such interest as to justify a report at the present time. First, as already indicated, the only cobalt-containing product (in the absence of anions other than ClO<sub>4</sub><sup>-</sup>) is Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup>. With regard to the iodine-containing products, I<sub>2</sub> is a reaction product, but under the experimental conditions (high H<sup>+</sup> and H<sub>2</sub>O<sub>2</sub> concentrations), I<sub>2</sub> is ultimately oxidized to IO<sub>3</sub><sup>-</sup>.<sup>8</sup> The other features of the reaction are best considered in relation to the kinetic studies summarized in Table II and Fig. 1. The pseudo-first-order rate constants *k*<sub>1</sub> listed in column 7 of Table II were obtained from the initial slopes in plots of log (*D*<sub>t</sub> - *D*<sub>∞</sub>) vs. time. It was necessary to use initial slopes because the plots for all kinetic experiments displayed deviations from linearity between the second and third half-lives.<sup>9</sup> This is

(8) For a review of work on the IO<sub>3</sub><sup>-</sup>, I<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> system see J. H. Baxendale in "Advances in Catalysis," Vol. IV, Academic Press, Inc., New York, N. Y., 1952, p. 31.

(9) The deviations from a simple pseudo-first-order behavior were dramatically displayed in the optical densities vs. time curves obtained with the spectrophotometer. Such curves are concave upward for 3-4 half-lives when suddenly an inflection point occurs and the optical density rapidly decreases.

TABLE II  
 KINETICS OF THE  $\text{Co}(\text{NH}_3)_5\text{I}^{++}-\text{H}_2\text{O}_2$  REACTION; IONIC STRENGTH, 0.94; TEMPERATURE, 25°

Expt.	$(\text{Co}(\text{NH}_3)_5\text{I}^{++}),$ $M \times 10^4$	$(\text{H}^+),^a$ $M$	$(\text{H}_2\text{O}_2),$ $M$	$(\text{Cl}^-),$ $M$	$(\text{I}_2),$ $M \times 10^4$	$k_1, \text{min.}^{-1}$	$k_2,$ $M^{-2} \text{min.}^{-1}$
1	5.11	0.935	0.097	...	...	0.0262	0.288
2	5.20	.935	.096	...	5.0	.0254	.282
3	0.68	.935	.097	...	...	.0198	.218
4	7.20	.935	.19	...	...	.0604	.340
5	4.86	.935	.38	...	...	.113	.318
6	4.24	.935	.36	...	...	.110	.328
7	4.86	.935	.38	...	...	.110	.310
8	4.86	.935	.38	...	10.0	.104	.293
9	4.86	.935	.38	...	0.20 <sup>b</sup>	.102	.292
10	0.50	.935	.36	...	...	.079	.235
11 <sup>c</sup>	4.80	.0935	.38	...	...	.0045	.126
12 <sup>d</sup>	4.35	.935	.36	...	...	.077	.229
13	4.90	.935	.97	...	...	.265	.294
14 <sup>e</sup>	4.98	.0748	.97	...	...	.017	.24
15	5.20	.937	.096	0.0124	...	.020	.22
16	5.06	.930	.097	.124	...	.0205	.227
17	4.96	.930	.096	.124	5.0	.023	.26
18	5.20	.936	.38	.0124	...	.088	.248
19	3.40	.935	.36	.036 <sup>f</sup>	...	.081	.240
20	5.10	.935	.38	.075	...	.083	.234
21	5.20	.935	.38	.125	...	.081	.227
22	5.00	.935	.38	.125	5.0	.082	.230
23 <sup>g</sup>	5.21	1.23	.87	.50	...	.337	.282
24	4.57	0.81 <sup>h,i</sup>	.37	.024 <sup>i</sup>	...	.116	.273 <sup>j</sup>
25	4.86	0.93 <sup>h,i</sup>	.37	.12 <sup>i</sup>	...	.292	.288 <sup>j</sup>

<sup>a</sup> Added as  $\text{HClO}_4$  and  $\text{HCl}$ . <sup>b</sup> This is the concentration of added  $\text{IO}_3^-$ . <sup>c</sup> Ionic strength 0.094. <sup>d</sup> Measured at 460  $\text{m}\mu$ . <sup>e</sup> Ionic strength adjusted with  $\text{NaClO}_4$ . <sup>f</sup> Added as  $\text{NaCl}$ . <sup>g</sup> Ionic strength 1.23. <sup>h</sup> Added as  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$ . <sup>i</sup>  $(\text{H}^+)$  and  $(\text{SO}_4^{2-})$  calculated using a value of 0.15 for the dissociation constant of  $\text{HSO}_4^-$ . <sup>j</sup> After subtracting from the total rate that given by the function  $4.7(\text{Co}(\text{NH}_3)_5\text{I}^{++})(\text{H}_2\text{O}_2)(\text{H}^+)(\text{SO}_4^{2-})$ .

exemplified for expt. 7 of Table II by the curve A in Fig. 1. The other experiments summarized in Fig. 1 were designed to uncover the factors that cause the deviations from first-order behavior. A comparison of curves A and B of Fig. 1 shows that although addition of  $1.0 \times 10^{-3} M \text{I}_2$  does not appreciably change the initial slope, it brings about the rapid disappearance of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  at shorter times. Similarly, expt. 1 and 2 of Table II show that addition of an amount of  $\text{I}_2$  equal to *ca.* twice the iodine in the  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  reactant does not appreciably change the value of  $k_1$  (0.0262 and 0.0254  $\text{min.}^{-1}$ , respectively). Curves C and D of Fig. 1 serve to demonstrate that either addition of  $2 \times 10^{-3} M \text{IO}_3^-$  alone or  $2 \times 10^{-3} M \text{IO}_3^-$  and  $1 \times 10^{-3} M \text{I}_2$  tremendously increases the rate of disappearance of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ . As noted above, both iodine and iodate are formed in this reaction, and therefore the autocatalytic nature of the reaction is ascribed to the accumulation of these two products. Direct evidence bearing on the question of iodate formation was obtained from expt. 12 performed at 460  $\text{m}\mu$ ; at this wave length the extinction coefficients of  $\text{I}_2$ ,  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ , and  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  are 746, 272, and 37.7, respectively. In this experiment, the optical density of the solution first increases, reaches a maximum at 19 min., and then decreases, demonstrating that  $\text{I}_2$  is both formed and consumed during the course of the reaction. At the maximum optical density, it is estimated that 96% of the iodine content of the  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  consumed is present as  $\text{I}_2$ . Furthermore, the smaller rate constant at 460  $\text{m}\mu$ <sup>10</sup> as compared to those

(10) The rate constant was obtained from the initial slope of a plot of  $\log(D_\infty - D)$  vs. time ( $D$  is the measured optical density at 460  $\text{m}\mu$ ;  $D_\infty$  is the optical density calculated if the stoichiometry of the reaction were that given by eq. 1). It must be noted that the slope of  $\log(D_\infty - D)$  vs. time does not give the rate of formation of  $\text{I}_2$ , since it can be shown that

$$D_\infty - D = \frac{\epsilon_{\text{I}_2}}{2} C_T (1 - A) +$$

$$(\text{Co}(\text{NH}_3)_5\text{I}^{++}) \left[ \epsilon_{\text{ROH}_2} - \epsilon_{\text{RI}} + \frac{\epsilon_{\text{I}_2}}{2} A \right]$$

governing the disappearance of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  ( $k_1$  values of 0.077 and 0.108  $\text{min.}^{-1}$ , respectively) definitely show that during the first two half-lives, the stoichiometry of the reaction deviates from that represented

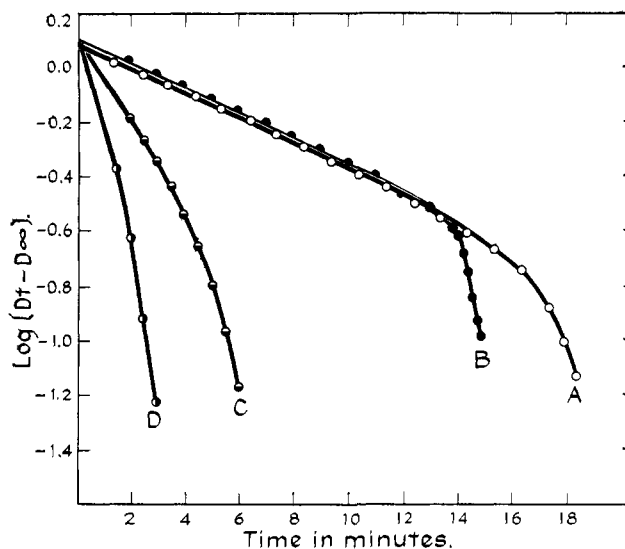


Fig. 1.—The reaction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with  $\text{H}_2\text{O}_2$ ;  $4.86 \times 10^{-4} M \text{Co}(\text{NH}_3)_5\text{I}^{++}$ ,  $0.935 M \text{H}^+$ ,  $0.38 M \text{H}_2\text{O}_2$ , 25°: O, no addition (curve A); ●,  $1.0 \times 10^{-3} M \text{I}_2$  added (curve B); ○,  $2.0 \times 10^{-3} M \text{IO}_3^-$  added (curve C); ●,  $2.0 \times 10^{-3} M \text{IO}_3^-$  and  $1.0 \times 10^{-3} M \text{I}_2$  added (curve D).

by eq. 1. A measure of iodine formation as the reaction proceeds was obtained from the expression (see footnote 10 for definition of the symbols)

$$A = \left[ \frac{D - C_T \epsilon_{\text{RI}}}{(\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3})} + \epsilon_{\text{RI}} - \epsilon_{\text{ROH}_2} \right] \frac{2}{\epsilon_{\text{I}_2}} \quad (4)$$

where  $\epsilon_{\text{I}_2}$ ,  $\epsilon_{\text{RI}}$ , and  $\epsilon_{\text{ROH}_2}$  are the extinction coefficients of  $\text{I}_2$ ,  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ , and  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$ , respectively,  $C_T$  is the initial concentration of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ , and  $A$  is the fraction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  reacted which appears as  $\text{I}_2$ .

The concentration of  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  present at the time  $D$  was measured with computed from the expression  $(\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}) = C_T(1 - e^{-k_1 t})$  where  $k_1$  was taken as  $0.108 \text{ min.}^{-1}$ . The results on the formation of  $\text{I}_2$  are summarized in Table III. The values of  $A$  listed in column 4 show that the fraction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  reacted which is transformed to  $\text{I}_2$  increases as the reaction proceeds.

TABLE III

FORMATION OF  $\text{I}_2$  IN THE REACTION OF  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  AND  $\text{H}_2\text{O}_2$  0.935  $M$   $\text{H}^+$ , 0.36  $M$   $\text{H}_2\text{O}_2$ , 25°,  $4.35 \times 10^{-4} M$   $\text{Co}(\text{NH}_3)_5\text{I}^{++}$

Time, min.	$D^a$	$(\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}), M \times 10^{10}{}^b$	$A^c$
0	1.180 <sup>d</sup>	0	..
1.5	1.240	0.65	0.88
2.0	1.258	0.84	.88
2.5	1.276	1.06	.87
3.0	1.295	1.19	.89
3.5	1.312	1.37	.89
4.0	1.332	1.53	.89
5.0	1.368	1.81	.90
6.0	1.402	2.07	.91
7.0	1.431	2.30	.92
8.0	1.464	2.52	.92
9.0	1.490	2.80	.92
10.0	1.515	2.91	.94
11.0	1.549	3.03	.95
12.0	1.559	3.16	.95
13.0	1.575	3.27	.95

<sup>a</sup> Measured optical density at 460  $m\mu$ . <sup>b</sup> Calculated from the expression  $(\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}) = 4.35 \times 10^{-4}(1 - e^{-0.108t})$ . <sup>c</sup> Fraction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  reacted that appears as  $\text{I}_2$ . <sup>d</sup> Calculated from the initial concentration of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ .

The last column of Table II lists the specific rate  $k_3$  of the rate function  $k_3(\text{Co}(\text{NH}_3)_5\text{I}^{++})(\text{H}_2\text{O}_2)(\text{H}^+)$ . The bulk of the experiments were performed at 0.935  $M$   $\text{H}^+$  and  $4.2$ – $5.2 \times 10^{-4} M$   $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ . Under these conditions, the first-order dependence upon  $(\text{H}_2\text{O}_2)$  is fairly well established (*cf.* expt. 1, 2, 4–9, 13). In two experiments (3, 10) performed at *ca.* one-tenth  $(\text{Co}(\text{NH}_3)_5\text{I}^{++})$ ,  $k_3$  is 20–25% smaller; in experiment 14 performed at 0.0748  $M$   $\text{H}^+$ ,  $k_3$  is 25% smaller. The smaller rate at lower ionic strength (expt. 11) is consistent with the expected ionic strength dependence for a reaction of the charge type +2, +1.

Included in Table II are the results obtained with  $\text{Cl}^-$  and  $\text{SO}_4^{-2}$  added. A comparison of the rate constants for expt. 15 and 16 shows that increasing  $(\text{Cl}^-)$  by a factor of ten does not appreciably change the value of the rate constant. However, the rate in the presence of  $\text{Cl}^-$  is approximately 20% lower than in the absence of  $\text{Cl}^-$ . An entirely similar set of results was obtained at 0.38  $M$   $\text{H}_2\text{O}_2$ . As shown by experiments 18–21, the rate constant is independent of  $(\text{Cl}^-)$  from 0.0124 to 0.124  $M$  and 20% lower than in the absence of  $\text{Cl}^-$ . Addition of  $\text{I}_2$  again does not change the initial rate of the reaction (*cf.* expt. 16, 17, and 22). The results with added  $\text{SO}_4^{-2}$  (expt. 24, 25) are consistent with a reaction proceeding by two parallel paths: one identical with that observed in the absence of  $\text{SO}_4^{-2}$ , and a new path with a rate law of the form  $k_4(\text{Co}(\text{NH}_3)_5\text{I}^{++})(\text{H}_2\text{O}_2)(\text{H}^+)(\text{SO}_4^{-2})$  where  $k_4 = 4.7 M^{-3} \text{ min.}^{-1}$ .

**Stoichiometry of the  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ – $\text{H}_2\text{O}_2$  Reaction in the Presence of  $\text{Cl}^-$ .**—Although the rate of the reaction between  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  and  $\text{H}_2\text{O}_2$  is not much affected by added  $\text{Cl}^-$ , the stoichiometry of the reaction is drastically altered. In the absence of added  $\text{Cl}^-$ ,  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  is quantitatively formed. As the  $\text{Cl}^-$  concentration is increased,  $\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$  becomes an increasingly important product. The results of the stoichiometric experiments are summarized in Table

TABLE IV

PRODUCT DISTRIBUTION IN THE REACTION OF  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  WITH  $\text{H}_2\text{O}_2$  IN THE PRESENCE OF  $\text{Cl}^-$ ;  $(\text{H}^+) = 0.935 M$ ,  $T = 25^\circ$

Expt.	$(\text{Co}(\text{NH}_3)_5\text{I}^{++}), M \times 10^4$	$(\text{H}_2\text{O}_2), M$	$(\text{Cl}^-), M$	$(\text{I}_2), M \times 10^4$	$F^a$	$R^b$
1	5.20	0.38	0.0125	..	65.0	1.9
2	9.77	.098	.025	..	74.4	2.9
3	9.77	.098	.050	..	81.8	
4	8.66	.196	.050	..	83.6	
5	8.99	.39	.050	..	81.3	
6	8.66	.98	.050	..	83.6	
7	8.21	.098	.075	..	81.2	
8	8.21	.098	.075	0.75	81.6	
9	5.10	.38	.075	..	82.5	
10	8.99	.39	.075	..	89.8	
11	8.74	.39	.075	..	87.1	
12	8.74	.39	.075	0.50	85.3	
13	8.74	.39	.075	1.0	86.3	
14	8.55	.098	.100	..	84.8	5.6
15	8.99	.39	.100	..	88.9 <sup>c</sup>	
16	8.45	.39	.100	..	88.6	
17	9.77	.098	.125	..	89.6	
18	4.96	.096	.125	0.50	86.2	
19	5.06	.097	.125	..	88.1	
20	5.00	.38	.125	0.50	90.4	
21	8.99	.39	.125	..	91.4	
22	8.21	.098	.150	..	89.1	8.2
23	8.21	.098	.150	0.75	89.0	
24	8.45	.39	.150	..	88.2	
25	8.45	.39	.150	..	91.4	
26	8.35	.39	.150	..	92.3	
27	8.35	.39	.150	0.75	90.8	
28	8.21	.098	.200	..	88.5	
29	8.21	.098	.200	0.75	90.0	9.0
30	8.35	.39	.200	..	87.7	
31	8.35	.39	.200	0.75	91.6	
32	8.45	.39	.200	..	91.6	
33	8.45	.39	.200	..	92.3	
34	9.90	.050 <sup>d</sup>	.050	..	93.8	
35	9.90	.050 <sup>d</sup>	.125	..	91.2	10.3
36	10.0	<sup>e</sup>	.050	..	82.0	4.6
37	10.0	<sup>e</sup>	.125	..	89.5	8.5
					84.9	5.6
					91.0	10.1

<sup>a</sup>  $F$  is the %  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  converted to  $\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$ . <sup>b</sup>  $R$  is the ratio  $(\text{Co}(\text{NH}_3)_5\text{Cl}^{++})/(\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3})$ . <sup>c</sup>  $(\text{H}^+)$  is 0.0935. <sup>d</sup> The oxidant is  $\text{S}_2\text{O}_8^{-2}$ . <sup>e</sup> The oxidant is  $\text{O}_3$ .

IV where  $F$  (column 7) is defined as the % of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  which is converted to  $\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$  and  $R$  (column 8) as the ratio  $(\text{Co}(\text{NH}_3)_5\text{Cl}^{++})/(\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3})$ . Although the scatter of the results is considerable, the following features appear to be well established: (1) At constant  $(\text{H}^+)$  and  $(\text{Cl}^-)$ ,  $F$  is independent of  $(\text{H}_2\text{O}_2)$  (*cf.* expt. 3–6, 8 and 10, 15 and 18 and 22, 23 and 25–27, 29 and 31); (2) at constant  $(\text{H}_2\text{O}_2)$  and  $(\text{Cl}^-)$ ,  $F$  is independent of acidity (*cf.* expt. 15, 16); (3) addition of iodine does not affect the value of  $F$  (*cf.* expt. 9–10, 12–14, 23–24, 27–28, 29–30, 31–32); (4) as shown in Fig. 2 where  $R$  has been plotted *vs.*  $(\text{Cl}^-)$ , the dependence of  $R$  upon  $(\text{Cl}^-)$

TABLE V

PRODUCT DISTRIBUTION IN THE REACTIONS OF  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  WITH VARIOUS OXIDANTS IN THE PRESENCE OF  $\text{SO}_4^{-2}$  ( $\mu = 0.94$ ,  $T = 25^\circ$ )

Expt.	$(\text{Co}(\text{NH}_3)_5\text{I}^{++})$ $M \times 10^3$	Oxidant, $M$	$(\text{H}^+)$	$(\text{SO}_4^{-2})^a$	$F^b$	$f^c$	$R'_s$
1	1.57	$\text{H}_2\text{O}_2$ , 0.74	0.532	0.098	32.7	62.3	0.49
2	1.63	$\text{H}_2\text{O}_2$ , 0.74	.47	.035	14.7	37.2	.17
3	1.56	$\text{H}_2\text{O}_2$ , 0.74	.44	.016	7.8	21.1	.084
4	1.04	$\text{Ce}(\text{IV})$ , $7.65 \times 10^{-3}$	.507	.097	53.0 <sup>d</sup>		
5	1.09	$\text{Ce}(\text{IV})$ , $7.65 \times 10^{-3}$	.186	.060	56.0 <sup>d</sup>		
6 <sup>e</sup>	1.38	$\text{Ce}(\text{IV})$ , $3.06 \times 10^{-3}$	.60	.10	50.0 <sup>d</sup>		
7 <sup>e</sup>	1.38	$\text{Ce}(\text{IV})$ , $3.06 \times 10^{-3}$	.60	.10	58.0 <sup>d</sup>		
8	1.59	$\text{O}_3$ , bubbling	.507	.097	47		

<sup>a</sup> Calculated using 0.15 for the dissociation constant of  $\text{HSO}_4^-$ . <sup>b</sup>  $F$  is the % of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  converted to  $\text{Co}(\text{NH}_3)_5\text{SO}_4^+$ . <sup>c</sup>  $f$  is the fraction of the total reaction proceeding by the  $\text{SO}_4^{-2}$  path. <sup>d</sup> % of  $\text{Co}(\text{III})$  product present as  $\text{Co}(\text{NH}_3)_5\text{SO}_4^+$ . In experiments 4 and 5, 49% of the  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  ends up as  $\text{Co}(\text{II})$ ; see ref. 1. <sup>e</sup> These are experiments 3 and 4 of Table II, ref. 1. <sup>f</sup>  $R'_s = (\text{Co}(\text{NH}_3)_5\text{SO}_4^+)/(\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3})$ .

becomes less than first order as  $(\text{Cl}^-)$  increases. Included in Table IV are experiments in which  $\text{S}_2\text{O}_8^{-2}$  and  $\text{O}_3$  have replaced  $\text{H}_2\text{O}_2$  as the oxidizing agent. The values of  $F$  for these experiments are very close to the values obtained with  $\text{H}_2\text{O}_2$  (compare the values of  $F$  for expt. 35, 37, and 3-5, and for expt. 36, 38, and 18-22).

A similar study with  $\text{SO}_4^{-2}$  instead of  $\text{Cl}^-$  was performed and the results are summarized in Table V. As shown by the values of  $F$  listed in the last column of Table V, when  $\text{H}_2\text{O}_2$  is the oxidizing agent (expt. 1-3)  $F$  increases with increasing  $(\text{SO}_4^{-2})$ . In contrast, with  $\text{Ce}(\text{IV})$  as the oxidizing agent (expt. 4-7)  $F$  appears to be independent of  $(\text{SO}_4^{-2})$ . The single run with  $\text{O}_3$  yielded an  $F$ -value higher than that with  $\text{H}_2\text{O}_2$  at the same  $(\text{SO}_4^{-2})$  (expt. 8 and 1).

**Tracer Experiments.**—The results of  $\text{O}^{18}$  tracer experiments in the reactions of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  are summarized in Table VI.

TABLE VI

 $\text{O}^{18}$  TRACER EXPERIMENTS IN THE REACTIONS OF  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  WITH  $\text{H}_2\text{O}_2$  AND  $\text{O}_3^a$  $(\text{Co}(\text{NH}_3)_5\text{I}^{++}) = 2.0 \times 10^{-2} M$ ,  $(\text{H}^+) = 0.935 M$ ,  $25^\circ$ 

Oxidant	$N_8 \times 10^{3b}$	$N_{\text{H}_2\text{O}} \times 10^{3c,d}$	$F^e$
$\text{H}_2\text{O}$	9.00	6.82	31
$\text{O}_3$	9.30	8.90	5.5

<sup>a</sup> Oxidizing agents of normal isotopic composition, with mole fraction of  $\text{O}^{18} = 2.00 \times 10^{-3}$ . <sup>b</sup> Mole fraction of  $\text{H}_2\text{O}^{18}$  in the solvent. <sup>c</sup> Mole fraction of  $\text{H}_2\text{O}^{18}$  in the  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  product. <sup>d</sup> Corrected for the  $[\text{Co}(\text{NH}_3)_5\text{OH}_2](\text{ClO}_4)_3$  present in the  $[\text{Co}(\text{NH}_3)_5\text{I}](\text{ClO}_4)_2$  preparation. <sup>e</sup>  $F$  is the % of O in  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  product derived from the oxidizing agent.

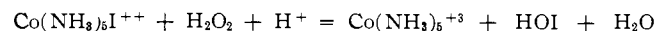
### Discussion

Of the reactions described in this paper, those involving  $\text{H}_2\text{O}_2$  as oxidizing agent have been studied most thoroughly. They are the most amenable to experimental tests of mechanism and it is only for them that we are able to reach definite conclusions about the nature of the oxidative substitution reactions which we have encountered. Since those conclusions form the basis for the discussion of results for the other systems as well, the results obtained with  $\text{H}_2\text{O}_2$  as oxidizing agent will be discussed first, but the discussion at this juncture will be limited to those features which provide the basis for our conclusions about the mechanism of the oxidative substitution at  $\text{Co}(\text{III})$  and  $\text{Cr}(\text{III})$ .

The features of the reaction which are significant for the present purposes are these. 1. The reaction is first order in  $(\text{H}^+)$ ,  $(\text{H}_2\text{O}_2)$ , and  $(\text{Co}(\text{NH}_3)_5\text{I}^{++})$ . 2. Although  $\text{Cl}^-$  can be incorporated into the products, the rate of reaction is independent of  $(\text{Cl}^-)$  (the slight decrease in rate occasioned by the first addition of  $\text{Cl}^-$  will be discussed later). 3. Sulfate ion does increase

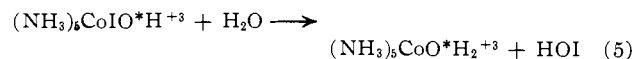
the rate, contributing an additional reaction path. The efficiency of formation of  $\text{Co}(\text{NH}_3)_5\text{SO}_4^+$  is the same for both kinetic paths. 4. Substantial transfer of peroxide oxygen to the aquo product takes place.

The fact that at high enough  $(\text{Cl}^-)$  the product is almost entirely  $\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$  proves that a 4-center reaction, that is, a reaction in which at  $\text{Co}-\text{OH}$  bond is made simultaneously with an  $\text{I}-\text{OH}$  bond, is not in question (it should perhaps be stressed that the direct reaction of  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  with  $\text{Cl}^-$  is much too slow to account for the observations and that in fact the equilibrium is unfavorable to the formation of the chloro complex). The chemistry and the kinetic behavior observed when  $\text{Cl}^-$  is present show that an intermediate (or intermediates) are formed by the reaction of  $\text{H}_2\text{O}_2$  with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ . This intermediate, however, cannot be the species  $\text{Co}(\text{NH}_3)_5^{+3}$  which conceivably could be generated by the reaction



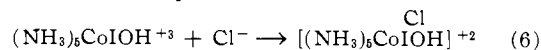
The selectivity for the formation of  $\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$  seems much too great to be accounted for on this basis— $\text{Co}(\text{NH}_3)_5^{+3}$  can reasonably be expected to be very reactive. The fact that oxygen transfer from  $\text{H}_2\text{O}_2$  to  $\text{Co}(\text{III})$  takes place in any event argues against  $\text{Co}(\text{NH}_3)_5^{+3}$  as the intermediate in question. We suggest that the intermediate formed by the reaction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with  $\text{H}_2\text{O}_2$  is  $[\text{Co}(\text{NH}_3)_5\text{IOH}]^{+3}$ . The observations cited are accounted for by ascribing to this intermediate the reasonable competitive reactions given below.

#### (a) Rearrangement



thus explaining the transfer of oxygen from  $\text{H}_2\text{O}_2$  to  $\text{Co}(\text{III})$ . Transfer is not complete and it is not expected to be complete because, as will be shown later, at least 50% of the aquo product formed arises from the reaction of  $(\text{NH}_3)_5\text{CoI}^{++}$  with other oxidizing agents which are formed in the system. Taking account of this circumstance, the results show that transfer from  $\text{H}_2\text{O}_2$  to  $\text{Co}(\text{III})$  takes place in at least 62% of the  $\text{H}_2\text{O}_2-(\text{NH}_3)_5\text{CoI}^{++}$  reaction events. Exchange of the intermediate with solvent may account in part for the defect from 100%, but we cannot conclude that such exchange does in fact occur to a significant extent.

#### (b) Substitution by $\text{Cl}^-$ on $\text{I}^+$



The experimental results on atom exchanges for hypohalous species<sup>11</sup> as well as a number of correlations

(11) M. Anbar and H. Taube, *J. Am. Chem. Soc.*, **80**, 1073 (1958); M. Anbar, S. Guttman, and R. Rein, *ibid.*, **81**, 1816 (1959).

made by Edwards<sup>12a</sup> are in accord with the high reactivity which the intermediate shows to  $\text{Cl}^-$ . It should be pointed out that the experimental results do not require that  $\text{OH}^-$  is replaced by  $\text{Cl}^-$ . In fact, in view of the observation that the reactivity to  $\text{Cl}^-$  is independent of  $(\text{H}^+)$  it seems likely that rearrange-

ment of  $\text{Co}(\text{NH}_3)_5\text{IOH}^{++}$  takes place without replacement of  $\text{OH}^-$ .

When  $\text{SO}_4^{-2}$  is present, an additional path enters, which is described by the rate equation

$$\text{rate in } M \text{ min.}^{-1} = 0.70(\text{Co}(\text{NH}_3)_5\text{I}^{++})(\text{H}_2\text{O}_2)(\text{HSO}_4^-) \quad (7)$$

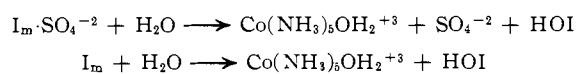
[note that  $0.70(\text{HSO}_4^-) = 4.7(\text{H}^+)(\text{SO}_4^{-2})$ ]. Because the coefficient multiplying the rate function of eq. 7 is greater than that which multiplies  $(\text{Co}(\text{NH}_3)_5\text{I}^{++})(\text{H}_2\text{O}_2)(\text{H}^+)$ , it is unlikely that  $\text{HSO}_4^-$  is acting merely as an acid and we conclude that  $(\text{SO}_4^{-2})$  assists in the reaction. Some interesting conclusions can be drawn from the correlation of product formation with the kinetic data. Comparison of  $f$  with  $F$  (Table V) shows that not all of the reaction flowing by the  $\text{SO}_4^{-2}$  path forms  $\text{Co}(\text{NH}_3)_5\text{SO}_4^+$ . The fact that the product ratio

$$R_s = (\text{Co}(\text{NH}_3)_5\text{SO}_4^+)/(\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3})$$

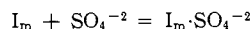
is linear in  $(\text{SO}_4^{-2})$  [ $R_s/(\text{SO}_4^{-2}) = 5.0, 4.9, \text{ and } 5.3$  at  $(\text{SO}_4^{-2}) = 0.98, 0.35, \text{ and } 0.016 M$ ] may be of special significance. Since the fraction of the reaction flowing by the sulfato path changes quite markedly over the range in  $(\text{SO}_4^{-2})$  covered, the constancy of  $R_s/(\text{SO}_4^{-2})$  implies that the efficiency of formation of the sulfato complex is the same for both paths. This is the result expected if the same intermediate is formed by the two paths, and if the intermediate lives long enough to come to equilibrium with respect to the ionic atmosphere. The product ratio  $R_s$  can be shown to be related to the concentration of  $\text{SO}_4^{-2}$  by an equation of the form

$$R_s = a(\text{SO}_4^{-2})/(1 + bK(\text{SO}_4^{-2}))$$

The term 1 compared to  $bK(\text{SO}_4^{-2})$  represents the relative rate at which  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  is formed from the intermediate,  $\text{I}_m$ , and from the outer-sphere sulfate complex,  $\text{I}_m \cdot \text{SO}_4^{-2}$ ;  $b$  represents the specific rate ratio for the two reactions



and  $K$  represents the equilibrium quotient for the reaction



$R_s$  is observed to be linear in  $(\text{SO}_4^{-2})$ ; we can therefore conclude that  $bK(\text{SO}_4^{-2})$  is small compared to 1. The value of  $K$  is the item of immediate interest because its magnitude would give a clue to the charge on the intermediate (*i.e.*, is the intermediate  $\text{Co}(\text{NH}_3)_5\text{IOH}^{+3}$  or  $\text{Co}(\text{NH}_3)_5\text{IO}^{++}$ ?), but any conclusion as to the magnitude of  $K$  would depend on an assumption about the magnitude of  $b$ .<sup>12b</sup>

In the present context, the results obtained with  $\text{Ce(IV)}$  as oxidizing agent (*cf.* Table V) are interesting in showing that this reaction does not form the same intermediate as does the reaction when  $\text{H}_2\text{O}_2$  acts. It is worthy of note in addition that the results on product formation in this particular system are consistent with the formation of an outer-sphere sulfate complex, possibly  $\text{Co}(\text{NH}_3)_5^{+3} \cdot \text{SO}_4^{-2}$ , which reacts in part to form aquo ion and in part collapses to the inner-sphere form.

(12) (a) J. O. Edwards, *Chem. Rev.*, **50**, 455 (1952); *J. Am. Chem. Soc.*, **76**, 1540 (1954); (b) F. A. Posey and H. Taube, *ibid.*, **78**, 15 (1956).

At the same concentration of  $\text{SO}_4^{-2}$ , the yield of the sulfato complex is higher when  $\text{O}_3$  acts as the oxidizing than when  $\text{H}_2\text{O}_2$  acts. We must conclude therefore that a different intermediate is formed at least in part when  $\text{O}_3$  rather than  $\text{H}_2\text{O}_2$  reacts. This conclusion is suggested also because the efficiency of oxygen transfer in the two cases is different. It is possible, though not proved, that the reaction of  $\text{O}_3$  does in fact form the  $\text{H}_2\text{O}_2$  intermediate in the first stage, as seems reasonable, but the intermediate then reacts quite rapidly with  $\text{O}_3$ .

Although it is by no means proved that the other reactions proceed by the rearrangement mechanism outlined for  $\text{H}_2\text{O}_2$ , it does seem reasonable that the reactions are in fact similar. The rearrangement mechanism does give a means of understanding the other results on product formation, and they will be considered in relation to this kind of mechanism. In the following some conclusions are drawn from the data of Table I, assuming that in each case the rearrangement mechanism obtains.

The results with  $\text{HSO}_5^-$  and  $\text{CH}_3\text{CO}_3\text{H}$  merit little additional comment; in their present incomplete form they are compatible with the formation of  $\text{Co}(\text{NH}_3)_5\text{IOH}^{+3}$  as the intermediate or with the formation of  $\text{Co}(\text{NH}_3)_5\text{ISO}_4^{++}$  and  $\text{Co}(\text{NH}_3)_5\text{IOAc}^{+3}$ , respectively, but with the stipulation that in the latter case they hydrolyze before rearrangement. This stipulation is necessary also when the reaction of  $\text{S}_2\text{O}_8^{-2}$  is considered because no formation of the sulfato complex takes place in this system. The excellent agreement of the results for  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{-2}$  on product competition when  $\text{Cl}^-$  is present suggests that the intermediates for the two systems are in fact the same. It should also be mentioned that a 4-center activated complex is eliminated by the  $\text{S}_2\text{O}_8^{-2}$  results as a reaction path in that system.

The reactions,  $\text{Co}(\text{NH}_3)_5\text{I}^{++} + \text{Cl}_2$  or  $\text{Br}_2$ , and  $\text{Co}(\text{NH}_3)_5\text{Br}^{++} + \text{Cl}_2$ , are remarkable in the high yield of halide-containing product which they feature (*cf.* Table I). This results leads to the conclusion that  $\text{Co}(\text{NH}_3)_5\text{ICl}^{+3}$ ,  $\text{Co}(\text{NH}_3)_5\text{IBr}^{+3}$ , and  $\text{Co}(\text{NH}_3)_5\text{BrCl}^{+3}$  rearrange much more rapidly than they hydrolyze. Thus we conclude further that when  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  reacts with  $\text{ICl}$ ,  $\text{Co}(\text{NH}_3)_5\text{ICl}^{+3}$  is not formed. The reaction may proceed to form  $\text{Co}(\text{NH}_3)_5\text{I}_2^{+3}$ , which then hydrolyzes and rearranges, or  $\text{ICl}$  may hydrolyze rapidly enough so that  $\text{HOI}$  rather than  $\text{ICl}$  is the species which attacks the iodo complex.

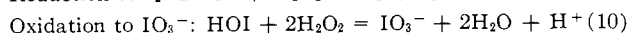
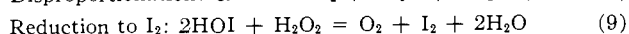
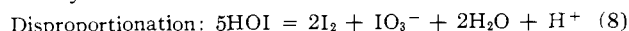
Comparison of the result obtained for the reaction of  $\text{Co}(\text{NH}_3)_5\text{Br}^{++}$  with  $\text{Cl}_2$ , which yields only the chloro complex, with that for the reaction with  $\text{HOCl}$ , which yields only the aquo ion, leads to the interesting conclusion that attack by the bromo complex in  $\text{HOCl}$  is at O rather than at Cl. No conclusion can, however, be drawn on the point of attack in  $\text{HOBr}$  by the bromo complex; if it is at oxygen the experimental result is explained directly; if at Br, we need only add the proviso that hydrolysis to  $\text{Co}(\text{NH}_3)_5\text{BrOH}^{++} + \text{Br}^-$  be possible. Nor can a conclusion on the point of attack in  $\text{HOBr}$  by  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  be drawn from the results obtained for this reaction, since  $\text{HOBr}$  is known to form  $\text{Co}(\text{NH}_3)_5\text{OH}^{+3}$  from the bromo complex. Finally, we wish to draw attention to the results obtained with  $\text{Cr}(\text{NH}_3)_5\text{Br}^{++}$  in comparison to those for  $\text{Co}(\text{NH}_3)_5\text{Br}^{++}$ . We conclude that for the former reactant,  $\text{HOCl}$  forms the aquo complex and  $\text{Cl}_2$  the chloro complex just as in the  $\text{Co(III)}$  case, but the quantitative difference between the systems is remarkable:  $\text{Cr}(\text{NH}_3)_5\text{Br}^{++}$  shows a very much higher reactivity for  $\text{HOCl}$  compared to  $\text{Cl}_2$  than is the case with the  $\text{Co(III)}$  complex. The large difference is astonishing in view of the fact that the polarizing capacity of  $\text{Cr}(\text{NH}_3)_5^{+3}$  is much like that of  $\text{Co(N-}$

$\text{H}_3)_5^{+3,13}$  and suggests participation by d-electrons in the reactions.

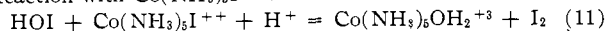
Although we are unable to offer a complete interpretation of the kinetic observations made on the  $\text{Co}(\text{NH}_3)_5\text{I}^{++} + \text{H}_2\text{O}_2$  reaction over the entire course, additional comments seem called for, particularly since some of the general conclusions we have drawn depend in part on these additional considerations. In the foregoing we have not considered the possibility that  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  arises from a process other than the direct reaction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with  $\text{H}_2\text{O}_2$ , but it follows at once from the fact that  $\text{I}_2$  is the principal iodine-containing product over the major portion of the reaction that only about one-half or less of the aquo ion is formed by the direct reaction; that is  $\text{HOI}$ , or some product derived from it by oxidation or disproportionation, is reduced efficiently by  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ . In the limit, if no iodine-containing product other than  $\text{I}_2$  were formed, at most 50% of the aquo product could be formed by the direct reaction.

It appears that at least half of the aquo ion is produced in the direct reaction. This follows because: (1) the reaction obeys fairly good pseudo-first-order kinetics over two half-lives; (2) addition of  $\text{I}_2$  in amounts equivalent to the  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  does not affect the rate of reaction during the first two half-lives (although the rapid disappearance of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  is brought about at earlier times); (3) addition of  $\text{IO}_3^-$  in amounts equivalent to 5% of the iodo complex does not affect the rate of reaction (it must be realized that reaction of  $\text{IO}_3^-$  with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  to form  $\text{I}_2$  and  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  involves the disappearance of  $5\text{Co}(\text{NH}_3)_5\text{I}^{+3}$  per  $\text{IO}_3^-$ ); (4) the formation of  $\text{I}_2$  approaches within 12% that expected for reaction 1, even during the initial stages of the reaction. Some of these points will be further elaborated in the following discussion.

By analogy with the corresponding acid-catalyzed oxidation of  $\text{I}^-$  by  $\text{H}_2\text{O}_2$ ,<sup>8</sup> it may be reasonably assumed that  $\text{HOI}$  is formed in the reaction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with  $\text{H}_2\text{O}_2$ , and the question arises as to the fate of  $\text{HOI}$ . In principle,  $\text{HOI}$  can undergo 4 reactions in this system



Reaction with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ :



The results presented in Table III, which show that formation of  $\text{I}_2$  is in fact observed, rule out reaction 10 as the only reaction occurring. To be sure, it might be argued that the oxidation of  $\text{HOI}$  involves some intermediate oxidation state (perhaps  $\text{HIO}_2$ ) which rapidly reacts with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ . This scheme would require a strong autocatalytic behavior even during the initial stages of the reaction, in contradiction with the experimental observations. It might be argued that indeed  $\text{HOI}$  is oxidized to  $\text{IO}_3^-$ , but that  $\text{IO}_3^-$  rapidly reacts with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  to form  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  and  $\text{I}_2$ . This possibility may be ruled out on the following grounds: first, addition of small amounts of  $\text{IO}_3^-$  does not increase the rate of disappearance of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ ; second, a rapid reaction between  $\text{IO}_3^-$  and  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  requires the presence of  $\text{I}_2$ .<sup>14</sup> Reaction 9

(13) The  $\text{pK}$  values for  $\text{Cr}(\text{NH}_3)_5\text{OH}_2^{+3}$  and  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  are 5.2 and 5.7.

(14) Experiments not reported here show that the  $\text{Co}(\text{NH}_3)_5\text{I}^{++}-\text{IO}_3^-$  reaction in  $1\text{ M H}^+$  and in the absence of  $\text{H}_2\text{O}_2$  follows a strongly autocatalytic course, presumably because  $\text{I}_2$  is formed as reaction proceeds. No attempts have yet been made to correlate the  $\text{IO}_3^-$ - $\text{I}_2$  catalyzed aquation of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with the rate of  $\text{I}$  exchange between  $\text{IO}_3^-$  and  $\text{I}_2$  (O. E. Meyers and J. W. Kennedy, *J. Am. Chem. Soc.*, **72**, 897 (1950)).

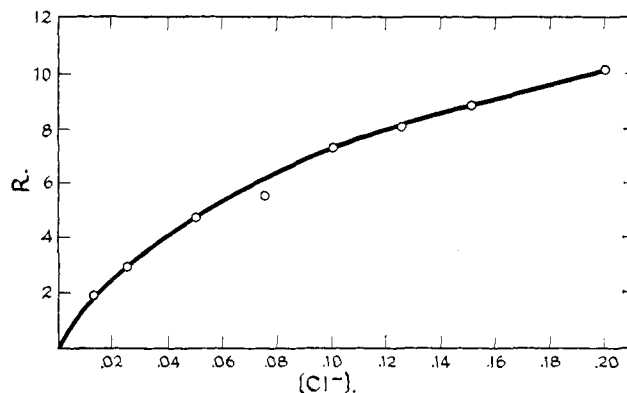


Fig. 2.—Ratio of  $(\text{Co}(\text{NH}_3)_5\text{Cl}^{++})$  to  $(\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3})$  formed by reaction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with  $\text{H}_2\text{O}_2$  in the presence of  $\text{Cl}^-$ .

cannot be ruled out at the concentrations used in the kinetic experiments. However, it must be noted that at  $0.935\text{ M HClO}_4$ ,  $0.036\text{ M H}_2\text{O}_2$ , and  $0.010\text{ M Co}(\text{NH}_3)_5\text{I}^{++}$ , the oxidizing titer of the solution remains constant, showing that under these conditions, reaction 9 occurs, if at all, to a negligible extent. The fraction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  disappearing which results in the formation of  $\text{I}_2$  would be expected to be 0.80, 1.0, 0, and 1.0 for reactions 8, 9, 10, and 11, respectively, to be compared with the experimental values ranging from 0.87 to 0.95. It must be concluded, therefore, that there are at least two paths for the disappearance of  $\text{HOI}$ , one leading to  $\text{IO}_3^-$  and the other(s) to  $\text{I}_2$ . In view of the arguments presented above, formation of  $\text{IO}_3^-$  by reaction 10 can be ruled out in the present system, and it is noteworthy that arguments against the participation of reaction 10 in the oxidation of  $\text{I}_2$  by  $\text{H}_2\text{O}_2$  have also been presented elsewhere.<sup>15</sup> We conclude, therefore, that  $\text{IO}_3^-$  formation occurs by reaction 8, with reaction 11 (and under some conditions perhaps reaction 9) accounting for the formation of  $\text{I}_2$ . Neglecting reaction 9 and using an average value of 0.92 for the fraction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  disappearing which results in the formation of  $\text{I}_2$ , we calculate that 43% of the  $\text{HOI}$  reacts with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ , with the rest undergoing disproportionation. It must be noted that the 43% value is an upper limit because reaction 9 has been neglected. Since the kinetic experiments obey fairly good pseudo-first-order behavior during the first two half-lives, it is concluded that at least 53% of the total  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  disappears by direct reaction with  $\text{H}_2\text{O}_2$ . Of the remaining  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ , some perhaps disappears by reaction with  $\text{HOI}$  and by rapid reaction with the intermediates generated in the  $\text{I}_2-\text{IO}_3^--\text{H}_2\text{O}_2$  system. The last conclusion follows from the observed effects of  $\text{I}_2$  and  $\text{IO}_3^-$  on the rate and also from the autocatalytic nature of the reaction in the later stages. In this connection it is important to note that the ratio of  $\text{I}_2$  formed to  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  reacted increases as the reaction proceeds, showing that although  $\text{IO}_3^-$  is formed from the beginning of the reaction, at later stages its rate of disappearance exceeds its rate of formation. All of these observations prove that  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  is an efficient scavenger for the intermediates generated in the  $\text{I}_2-\text{H}_2\text{O}_2-\text{IO}_3^-$  system, but in view of the complicated nature of this system it is not profitable to speculate about the nature of the intermediates involved. However, it is noteworthy that two effects observed in the  $\text{H}_2\text{O}_2-\text{I}_2-\text{IO}_3^-$  system have also been observed in the present investigation, namely the presence of in-

(15) W. C. Bray and H. A. Liebafsky, *ibid.*, **53**, 38 (1931); H. A. Liebafsky, *ibid.*, **53**, 2074 (1931).



duction periods and the elimination of such induction periods by addition of  $\text{IO}_3^-$ .

The conclusion that only approximately one-half of the  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  disappears by direct reaction with  $\text{H}_2\text{O}_2$  and that the balance reacts with  $\text{HOI}$  or some other intermediate oxidation state of iodine may explain the variation of  $R$  with  $(\text{Cl}^-)$  shown in Fig. 2. If a single intermediate reacts with  $\text{Cl}^-$ , then  $R$  must be linear in  $(\text{Cl}^-)$ ; but if intermediates of different reactivity and leading only to the same products are present, the form of the variation of  $R$  with  $(\text{Cl}^-)$  will be qualitatively at least like that shown in Fig. 2.

The absence of  $\text{Co}(\text{II})$  in all the reactions described contrasts with the formation of  $\text{Co}(\text{II})$  in the reactions of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  and  $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$  with "one-electron" oxidizing agents, but conforms to the results obtained in the reaction of  $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$  with "two-electron" oxidizing agents.<sup>16</sup> The absence of  $\text{Co}(\text{II})$  further shows that  $\text{I}$  and  $\text{OH}$  are not formed in the  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , and  $\text{S}_2\text{O}_8^{--2}$  systems since these radicals have

(16) P. Saffir and H. Taube, *J. Am. Chem. Soc.*, **82**, 13 (1960).

been shown to react rapidly with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  to yield  $\text{Co}(\text{II})$ .<sup>2</sup>

The most novel aspect of the present investigation is the extraordinary efficiency of the transfer of halide ions to the coordination sphere of  $\text{Co}(\text{III})$ , in particular for the reactions of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  and  $\text{Co}(\text{NH}_3)_5\text{Br}^{++}$  with  $\text{Cl}_2$ . These reactions do not appear to have a precedent in the organic systems where apparently the nonfree-radical chlorination of organic iodides proceeds by a nucleophilic displacement of a complex  $\text{>ClCl}_2$  by  $\text{Cl}_2$ .<sup>17</sup>

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(17) R. M. Keefer and L. J. Andrews, *ibid.*, **75**, 543 (1953); **76**, 253 (1954); E. J. Corey and W. J. Wechter, *ibid.*, **76**, 6040 (1954); F. M. Beringer and H. S. Schultz, *ibid.*, **77**, 5533 (1955).

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## Alkyl- and Acylcobalt Carbonyls Containing Olefinic Unsaturation. II. Cyclization of 5-Hexenoylcobalt Tetracarbonyl and Nonterminal Olefin Complexes

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Alkenoylcobalt tetracarbonyls,  $\text{RCH}=\text{CH}(\text{CH}_2)_n\text{COC}(\text{CO})_4$ , decompose thermally into a variety of products depending upon the value of  $n$  and upon the *trans*-substituent  $R$ . When  $n = 0$  or 2 and  $R = \text{H}$  or  $\text{CH}_3$ , relatively stable cyclic  $\pi$ -alkenoylcobalt tricarbonyls are formed. When  $n = 1$  and  $R = \text{H}$  or  $\text{CH}_3$ , decomposition leads mainly to  $\pi$ -allylcobalt tricarbonyl derivatives. If  $n = 3$  and  $R = \text{H}$  or  $\text{CH}_3$ , mixtures of saturated and unsaturated cyclic ketones are formed along with cobalt hydrocarbonyl or octacarbonyl. Unsaturated alkoxyacylcobalt tetracarbonyls behave similarly. Mechanisms are proposed to explain these and two related reactions from the literature.

### Introduction

The interactions of transition metal compounds with olefins are of considerable interest because these interactions are responsible for many catalytic reactions such as hydroformylation, catalytic hydrogenation, and the Ziegler olefin polymerization. In this and the previous paper of this series,<sup>1</sup> the reactions of olefins with acylcobalt tetracarbonyls have been investigated by determining structures and thermal decomposition products of a series of alkenoylcobalt tetracarbonyl complexes. These complexes undergo various reactions depending upon the structure of the unsaturated acyl group.

### Experimental

**5-Hexenoyl Chloride.**—3-Butenyl *p*-toluenesulfonate was prepared at  $-20^\circ$  by adding 90 g. of *p*-toluenesulfonyl chloride slowly to a solution of 28 g. of 3-butene-1-ol in 200 ml. of pyridine. After the addition, the solution was kept at  $0^\circ$  for 30 min. and then diluted with ice and cold water. The product was extracted with several portions of ether. The extracts were then washed with water, cold dilute hydrochloric acid, and finally with aqueous sodium bicarbonate. After being dried, the solvent was evaporated at room temperature under vacuum and the product was recrystallized twice from ether-pentane at  $-80^\circ$ . The entire product, m.p.  $7.5$ – $9.5^\circ$  and  $n_D^{20}$  1.5150, was then rinsed with a little dry methanol into a solution of 53 g. of dimethyl malonate in 400 ml. of dry methanol in which 9.7 g. of sodium had been previously dissolved. The reaction mixture was refluxed for about 4 hr. About half of the methanol was removed by distillation. Water was added to the residue and the product was extracted with ether and distilled, b.p.  $76$ – $87^\circ$  (5.5 mm.). There was thus obtained 13.5 g. of dimethyl 3-butenylmalonate. About 10 g. of higher boiling material, b.p.  $160$ – $180^\circ$  (5.5 mm.), was also obtained; it was probably the dibutenyl derivative. The monobutenyl ester was hydrolyzed by adding it to a solution of 30 g.

potassium hydroxide in 30 ml. of water and 30 ml. of methanol. After 1 hr. at room temperature, the solution was acidified with cold, concentrated hydrochloric acid, diluted with water, and extracted several times with ether. Evaporation of the ether and recrystallization from benzene gave 8.2 g. of 3-butenylmalonic acid, m.p.  $90$ – $91^\circ$ . *Anal.* Calcd. for  $\text{C}_7\text{H}_{10}\text{O}_4$ : C, 53.14; H, 6.37. Found: C, 53.18; H, 6.66.

5-Hexenoic acid was obtained by distilling the malonic acid at  $130^\circ$  at 20 mm. Redistillation gave 5.4 g. of pure acid, b.p.  $108.5$ – $109^\circ$  (21 mm.).

The 5-hexenoyl chloride was prepared by refluxing the 5-hexenoic acid with 10 ml. of thionyl chloride for 1 hr. and distilling. There was obtained 4.85 g. of colorless liquid, b.p.  $53$ – $54^\circ$  (21.5 mm.).

**5-Hexenoylcobalt Tricarbonyl Triphenylphosphine.**—In a gasometric apparatus<sup>1</sup> at  $0^\circ$ , which had been filled and flushed with ether-saturated carbon monoxide, were placed 30 ml. of 0.07 *M* sodium cobalt carbonyl in ether solution and 3.0 ml. of 1.0 *M* 5-hexenoyl chloride in ether. After 2 hr. at  $0^\circ$  there was no change in the gas volume but the infrared spectrum of the solution showed that all of the sodium cobalt carbonyl had reacted. (The characteristic  $5.3\ \mu$  band of cobalt carbonyl anion had disappeared.) The addition of 3.5 ml. of 1.0 *M* triphenylphosphine in ether resulted in the evolution of 1.54 mmoles of carbon monoxide. Evaporation of the solution below room temperature and several recrystallizations of the product from ether-pentane at  $-80^\circ$  gave yellow-brown prisms of the phosphine complex, m.p.  $90.5$ – $93^\circ$  dec. *Anal.* Calcd. for  $\text{C}_{27}\text{H}_{34}\text{O}_4\text{PCo}$ : C, 64.54; H, 4.82. Found: C, 64.70; H, 4.96. The infrared spectrum of the complex had bands in carbon tetrachloride at  $3.23$  (w),  $3.40$  (w),  $4.88$  (s),  $5.08$  (vs),  $5.96$  (vs),  $6.78$  (m),  $6.99$  (s),  $7.15$  (w),  $7.69$  (w),  $8.43$  (w),  $9.12$  (s),  $9.33$  (w),  $9.52$  (w),  $9.72$  (m),  $10.00$  (m),  $10.08$  (m),  $10.90$  (m),  $11.34$  (w) and in carbon disulfide at  $13.40$  (m),  $14.14$  (m), and  $14.42$  (s)  $\mu$ .

**Cyclization of 5-Hexenoylcobalt Tetracarbonyl.**—5-Hexenoylcobalt tetracarbonyl was prepared at  $0^\circ$  as described in the preceding experiment except that 1.0 ml. of dicyclohexylethylamine was added. The reaction mixture was then warmed to  $25^\circ$ . About 34 ml. of gas was evolved over a period of several hours. The infrared spectrum of the solution showed the bands of cobalt carbonyl and a new carbonyl band at  $5.73\ \mu$ . The bands of the

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