From the data in Fig. 8 the activation energy was calculated to be 6.0 ± 0.3 kcal./mole for (1) and 14.0 ± 0.5 kcal./mole for (2).

Different rate constants and activation energies for the different acids suggest at least two mechanisms for the oxidation of Pu(III) by nitrous acid. More complicated mechanisms may be involved but two possible mechanisms that are in accord with the results are

$$HNO_2 + H^+ \rightleftarrows NO^+ + H_2O;\ \text{rapid reversible} \quad (3)$$

$$NO^+ + Pu(III) \longrightarrow NO + Pu(IV);\ \text{rate controlling}$$

$$HNO_2 + HNO_3 \rightleftarrows N_2O_4 + H_2O;\ \text{rapid, reversible} \quad (4)$$

$$N_2O_4 + Pu(III) \longrightarrow NO_2^- + NO_2 + Pu(IV);\ \text{rate controlling}$$

In (3) the oxidation of Pu(III) by NO^+ is analogous to the mechanism proposed by Abel[4] for the oxidation of Fe(II) by HNO_2 in acid media. It is proposed that in solutions of nitric acid oxidation occurs through both mechanisms. Studies in HCl showed that (3) becomes important only at low concentration of the nitrate ion.

[4] E. Abel, *Monatsh.*, **80**, 379 (1949).

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The Oxidation of Captive Oxalate

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The oxidation of $(NH_3)_5CoC_2O_4^+$ by Ce(IV) takes place with almost perfect stoichiometry, one Ce(IV) being consumed for each mole of the Co(III) complex, and one Co^{++} being formed. Co^{+++} aq. and $S_2O_8^=$ with Ag^+ as catalyst behave similarly. However, H_2O_2 catalyzed by Mo(VI), and Cl_2 act to preserve the oxidation state of Co(III) and $(NH_3)_5CoOH_2^{+++}$ is formed. The difference in behavior of the two classes of oxidizing agents is ascribed to this: Ce(IV), Co(III) and some intermediate in the $S_2O_8^= + Ag^+$ system act by extracting one electron at a time, while the other two act in a manner which is equivalent to extracting two electrons simultaneously.

In many systems it has been observed that metal ions though present in small amounts may alter the kinetics and even the course of oxidation–reduction reaction. Usually the studies have been done with metal ions which are substitution-labile and the interpretation of the results is made difficult because the way the metal ion is combined in the various stages of the reaction in which it is active is not known. The experiments reported in this paper, on the reaction of oxidizing agents with a reducing agent bound to a substitution-inert metal ion center, are relevant to this subject. The reducing agent–metal ion complex we chose for study is $(NH_3)_5CoC_2O_4^+$, and the feature of particular interest was to learn whether and when the Co(III) takes part in the oxidation of the bound oxalate brought about by external oxidizing agents.

Materials.—The $(NH_3)_5CoC_2O_4H(ClO_4)_2$ was prepared by warming a solution of $(NH_3)_5CoH_2O(ClO_4)_3$ with a slight excess of oxalic acid. The solid which separated on cooling was recrystallized and submitted for analysis (analysis reported at 16.02% N and 16.35% Cl to be compared with the theoretical values of 16.21 and 16.41%, respectively). The solution containing Co^{+++} aq. was prepared by the method of Weiser.[1] The carbonato complex is prepared in saturated $NaHCO_3$ using H_2O_2 as oxidant on a cobaltous salt. The solution is added slowly to a cooled solution of $HClO_4$ aq.

All other reagents were standard C.P. or A.R. chemicals.

Results

Reaction with Ce(IV) Perchlorate.—In a typical experiment, a solution was used which was 0.025 *M* in $(NH_3)_5CoC_2O_4H(ClO_4)_2$, 0.047 *M* in Ce(IV) and 1 *M* in $HClO_4$. The progress of the reaction was followed by titrating Ce(IV) with Fe^{++} (the cobalti complex does not react rapidly with this reducing agent). The reaction of Ce(IV) with the cobalti complex is very much slower than it is with uncomplexed oxalate, and a period of *ca.* 20 hr. is required to ensure complete reaction at room temperature at the concentrations obtaining in our present experiments; for the uncomplexed oxalate, a few minutes would suffice.

There is apparently a slow loss of Ce(IV) even after the oxalato complex has disappeared; this loss is perhaps attributable to the oxidation of water by Ce(IV), catalyzed by Co^{++}. The effect is much reduced at 10°, and at this temperature clear-cut results on the stoichiometry are obtained. After 73 hr., the oxalato complex has disappeared and the ratio of Ce(IV) consumed to total oxalato complex is 1.01, after 146 hr. the ratio is 1.02 and after 250 hr., 1.04. Correcting for the continued slow loss of Ce(IV), the conclusion follows that the reaction of Ce(IV) with the oxalato complex takes place with almost perfect stoichiometry, *one* Ce(IV) being required for each oxalate. The cobalt product is not $(NH_3)_5CoOH_2^{+++}$ as would be expected if the cobalt oxidation state were preserved, but Co^{++}. The net change can be represented by the equation

$$(NH_3)_5CoC_2O_4H^{++} + Ce(IV) + 4H^+ = Co^{++} + Ce^{+++} + 2CO_2 + 5NH_4^+$$

Reaction with Co^{+++}.—The observations with Co^{+++} aq. as oxidizing agent are complicated by the reaction of Co^{+++} aq. to liberate O_2 from water but the intrinsic stoichiometry in the reaction of interest can nevertheless be fairly well established. In an experiment with $(NH_3)_5CoC_2O_4H(ClO_4)_2$ at 0.0021 *M*, Co^{+++} initially at 0.0041 *M* and $HClO_4$ at 2 *M*, at 10° and in the dark, after 144 hr. the total amount of Co^{+++} aq. consumed (as determined by titration) compared to the initial amount of the oxalato complex was 1.28. After this time, the extinctions of the solution at λ's = 4020 and 6020 Å. could be accounted for quantitatively by the residual Co^{+++} shown by titration and the Co^{++} resulting from the reduction of Co^{+++} and the Co(III) complex. If $(NH_3)_5Co(OH_2)^{+++}$ or $(NH_3)_5CoC_2O_4H^{++}$ were present, it would contribute appreciably to the extinction at 4020 Å.; at most 5% of an ammino complex remains. We conclude that in this reaction also, the oxidation of the bound oxalate by the external oxidizing agent brings about the reduction of Co(III) in the complex. The consumption of Co^{+++} aq. in excess of that prescribed by this stoichiometry is attributable to the spontaneous oxidation of H_2O by Co^{+++} aq., rather than to the $2e^-$ oxidation of the oxalato complex by the Co^{+++} aq.

The Ag^+ Catalyzed Reaction with $S_2O_8^=$.—The reaction of $S_2O_8^=$ with $(NH_3)_5CoC_2O_4^+$ is very slow, but when Ag^+ is present ($\sim$ 0.1 *M* $AgClO_4$ was used), reaction takes place immediately and Co^{++} is formed. A blank experiment with $(NH_3)_5CoOH_2^{+++}$ in place of the oxalato complex shows that the aquo ion survives this treatment. We can conclude

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[1] D. W. Weiser, Ph.D. Dissertation, University of Chicago, 1956.

therefore that the aquopentammine complex is not an intermediate in the Ag^+ catalyzed reaction of $(NH_3)_5CoC_2O_4^+$ with $S_2O_8^=$.

The Mo(VI) Catalyzed Reaction with H_2O_2.—The direct reaction of $(NH_3)_5CoC_2O_4^+$ with H_2O_2 is too slow for convenient study even when H_2O_2 is at 9 *M*. However, when ammonium molybdate is added reaction does take place in a reasonable time. When H_2O_2 is 9 *M*, $HClO_4$ is 1 *M*, the catalyst is 10^{-4} *M*, and $(NH_3)_5CoC_2O_4^+$ is initially at 5×10^{-4} *M*, 85% of the oxalato complex is converted to $(NH_3)_5CoOH_2^{+++}$ in 103 hr. at room temperature, and after 250 hr., substantially all of it is converted. Analysis of the solutions was performed spectrophotometrically, using four different wave lengths. The analyses are accurate enough to show that at most 5% of the Co(III) appears as Co^{++}.

The Reaction with Cl_2.—The reaction of the oxalato complex with chlorine shows some interesting behavior. At high acid it is very slow; at higher alkalinity decomposition of the Co(III) complex to a black oxide takes place. The best results were obtained in a solution prepared by passing Cl_2 into 0.2 *M* $NaHCO_3$ until a *p*H of 6–7 is reached, the oxalato complex then being added. In 12 hr., as much as 80% of the complex is converted to the aquo ion, with little or no Co^{++} being formed. The analysis was made spectrophotometrically after the solution was acidified and air was drawn through to remove chlorine. But among the mysteries that remain are these: complete conversion apparently is not achieved even after a considerably longer time, the rate in a phosphate buffer at similar *p*H's is very much less than in the bicarbonate buffer and it is also much less in a mixture made up to exploit the buffer capacity of the combination $HClO-ClO^-$. A thorough kinetic study is necessary to understand these observations.

Discussion

The results show quite clearly that one-electron oxidizing agents bring about the reduction of Co(III) by the oxalate. Presumably the state $C_2O_4^-$ generated by the attack of Ce(IV) is a powerful enough reducing agent to reduce Co(III) to Co(II). Efforts to find evidence for the intermediate $(NH_3)_5CoC_2O_4^{++}$ proved unsuccessful. Its lifetime is so short that it doesn't persist long enough to react with a second Ce(IV), a reaction which would produce $(NH_3)_5CoOH_2^{+++} + 2CO_2$. The amount of the aquo ion formed even when the concentration of Ce(IV) is several times greater than that used in the experiment on stoichiometry is very small. Nor is Co(III) preserved when the reaction with Ce(IV) takes place in the presence of Br_2 (saturated solution).

The difference between Ce(IV) and Co^{+++} on the one hand and H_2O_2 (Mo(VI) present) or Cl_2 on the other is the difference between one-electron and two-electron oxidizing agents. Presumably the latter two reagents withdraw two electrons simultaneously so that there is no opportunity for the Co(III) to take part in the oxidation–reduction process.

The experiment with $Ag^+ + S_2O_8^=$ as the oxidizing mixture shows that a one-electron oxidizing agent is generated in the solution. It does not imply however that Ag(III) is not formed by the action of $S_2O_8^=$ on Ag^+, but it does imply that Ag(III), if formed, reacts by one-electron steps, or that it is rapidly brought to Ag^{++} by Ag^+, for example.

The involvement of the Co(III) center in the reaction of the oxalato complexes with one electron oxidizing agents is interesting. It hardly can be argued however that Co(III) assists in the oxidation process, because the rate of reaction is much slower than with free oxalate. But with a more reactive oxidizing center than the pentamminecobaltic residue, the rates might well be much larger. A point of considerable interest which is not settled by the rate comparison is whether the reduction of the Co(III) center takes place in the activated complex, or whether an intermediate such as $(NH_3)_5CoC_2O_4^{++}$, of finite life, is formed. Even though the reduction of Co(III) takes place in the activated complex, the rate may be slow simply because of the polarization of the oxalate by the positive charge of the cation. A possible test, diagnostic of the point at issue, would be to determine the oxygen isotope fractionation in the reaction of the oxalato complex with Ce(IV). If the reduction takes place in the activated complex, stretching of the Co–O bond should be required, as it is in the reduction of $(NH_3)_5CoOH_2^{+++}$ by Cr^{++}.[2]

Oxygen tracer experiments with the $(NH_3)_5CoC_2O_4^+-H_2O_2$ system obviously would be of interest. It is conceivable that an oxidation process of the type involved in the reaction can be used to generate the intermediate $(NH_3)_5Co^{+++}$ which is of such interest for substitution reactions of complex ions.

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[2] R. K. Murmann, F. A. Posey and H. Taube, THIS JOURNAL, **79**, 262 (1957).

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