above 300 mμ superimposed on the n-π* Cotton effect.

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OXIDATION OF CHROMIUM(II) BY IRON(III) IN THE PRESENCE OF CHLORIDE ION

Sir:

The oxidation of Cr^{2+} by Fe^{3+} in aqueous perchloric acid produces Fe^{2+} and $Cr(H_2O)_6^{3+}$, but in the presence of chloride ion the complex $Cr(H_2O)_5Cl^{2+}$ is produced along with $Cr(H_2O)_6^{3+}$ in proportions depending on the concentrations of Cl^- and H^+.[1] This reaction may proceed *via* the chloro complex of Fe(III) $FeCl^{2+} + Cr^{2+} \rightarrow Fe^{2+} + CrCl^{2+}$ in an inner sphere activated complex mechanism, similar to that observed in the oxidation of Cr^{2+} by $Co^{3+}(NH_3)_5X$.[1,2] Alternatively, Fe^{3+} may enter the activated complex without prior substitution by Cl^-, in a mechanism similar to that taking place in the oxidation of Cr^{2+} by $Co(NH_3)_6^{3+}$ in the presence of Cl^-.[3] It is difficult to distinguish between the two mechanisms at room temperature because the equilibrium $Fe^{3+} + Cl^- \rightleftarrows FeCl^{2+}$ is attained too rapidly. At −50° the formation of the $FeCl^{2+}$ complex proceeds quite slowly, therefore this temperature was chosen to distinguish between the two alternative paths.

The solvent used in this investigation was a eutectic aqueous solution of perchloric acid (5.27 *M*) having a melting point of −59.7°.[4] A Pyrex reaction vessel consisting of three compartments was used: two side compartments were connected through a common T-shaped mixing chamber to the main compartment. An inert atmosphere was maintained by a slow stream of CO_2 and the whole vessel was immersed in an ethanol bath, maintained at −50°. A chromous solution was placed in the main compartment, a ferric perchlorate solution in one of the side compartments and a hydrochloric acid solution in the other. By applying a pressure of CO_2 the ferric and the chloride solutions were driven through the common mixing chamber into the chromous solution, which they reached within 0.1 sec. after mixing. The concentrations of the reactants after mixing were: $[Fe^{3+}]$ 0.075 *M*, $[Cl^-]$ 0.075 *M*, $[Cr^{2+}]$ 0.031 *M*.

The oxidation reaction was "instantaneous" and produced a green solution. After warming to room temperature, this solution was separated chromatographically by absorption on a Dowex 50 (8%) cation exchange column and elution with 1 *M* perchloric acid. It consisted mainly of $CrCl^{2+}$ and a smaller amount of $Cr(H_2O)_6^{3+}$. The same reaction was carried out in the absence of chloride ion (which was replaced by the pure solvent) and was found to proceed quite slowly at −50°, thus demonstrating the marked catalytic activity of Cl^-. The only chromic species produced in this experiment was the hexaaquochromic ion, as expected.

The assumption that $FeCl^{2+}$ is not formed prior to the oxidation reaction was confirmed by another blank experiment in which Cr^{2+} was replaced by the pure solvent into which the ferric and chloride solutions were injected at −50° as above. After 60 seconds the yellow color of $FeCl^{2+}$ was not yet observed. A very faint color was first noted after three minutes, and even after one hour equilibrium concentration was not attained. These results are in accord with the kinetic data given by Connick and Coppel[5] for this reaction at room temperature. Using their values of the rate constants and activation enthalpies, we found that at the initial ferric and chloride concentrations used by us (0.075 molar) less than 0.4% of the total Fe^{3+} was converted to $FeCl^{2+}$ at −50° after 60 seconds.

The results of these experiments show that the chloride-catalyzed oxidation of Cr^{2+} by Fe^{3+} does not proceed *via* the $FeCl^{2+}$ complex at −50°, but they do not rule out this path at room temperature.

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[1] H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

[2] H. Taube, *ibid.*, **77**, 4481 (1955).

[3] H. Taube, *Chem. Soc. Spec. Publ.*, **13**, 57 (1959).

[4] L. H. Brickwedde, *J. Research Natl. Bur. Standards*, **42**, 309 (1949).

[5] R. E. Connick and C. P. Coppel, *J. Am. Chem. Soc.*, **81**, 6389 (1959).

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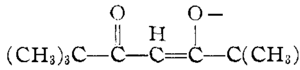
ABSORPTION INTENSITIES AND ELECTRONIC STRUCTURES OF TETRAHEDRAL COBALT(II) COMPLEXES

Sir:

We wish to report some observations which seem to us to be both novel and important in respect to the problem of the intensities of electronic absorption bands in transition metal complexes.

Using the ligand I, the enolate anion of dipivaloylmethane, hereafter abbreviated DPM, we have prepared the complexes $Co(DPM)_2$



$$(CH_3)_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{H}{C}{=}\overset{\overset{\displaystyle O-}{|}}{C}{-}C(CH_3)_3 \quad \text{I}$$

and $Zn(DPM)_2$. It has been shown previously that in $Ni(DPM)_2$ the size of the *t*-butyl groups prevents the trimerization which occurs in Ni(II) complexes with less hindered β-diketone enolates so that $Ni(DPM)_2$ is a planar, diamagnetic monomer.[1] $Co(DPM)_2$ has three unpaired electrons

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[1] F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961); J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **83**, 3775 (1961).