react with small base molecules in preference to larger ones which are electronically stronger donors.

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The Methylpentaaquochromium(III) Ion

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Kochi[1] assumed the existence of a methylpentaaquochromium(III) ion in order to account for the formation of methane by the reaction between *tert*-butyl peroxide and chromium(II). The main product of this reaction is *tert*-butyl alcohol formed by

$$tert\text{-}C_4H_9OOH + Cr^{2+} \longrightarrow tert\text{-}C_4H_9O\cdot + Cr^{3+} + OH^- \tag{1}$$

$$tert\text{-}C_4H_9O\cdot + Cr^{2+} + H_2O \longrightarrow tert\text{-}C_4H_9OH + Cr^{3+} + OH^- \tag{2}$$

The detection of acetone and methane gas among the reaction products (in nearly equivalent amounts and a maximum yield of 16%) was explained by the competing reaction path

$$C_4H_9O\cdot + Cr^{2+} \longrightarrow \text{acetone} + Cr(H_2O)_5CH_3^{2+} \tag{3}$$

$$Cr(H_2O)_5CH_3^{2+} + H_2O \longrightarrow Cr(H_2O)_6^{3+} + CH_4 + OH^- \tag{4}$$

The fact that no methylo complex was found led to the conclusion that it is a transient, unstable ion, in contrast to its stable halogen-substituted derivatives.[2]

After the work described in the present paper was concluded, Schmidt, Swinehart, and Taube[3] reported the discovery of the methylpentaaquochromium(III) and gave the rate law of its aquation: $-d \ln [CrL^{2+}]/dt = k_2[H^+]$; $10^3k_2 = 5.2 \pm 0.2\ M^{-1}\ sec^{-1}$ at 298°K.

Our results confirm these findings and contain data of the absorption spectrum and the $Cr:CH_4$ ratio of this complex, which was observed during a reinvestigation of the reaction between *tert*-C_4H_9OOH and Cr(II) in this laboratory. The methylpentaaquochromium(III) ion was found to be a relatively stable complex with a half-life of several hours at 0°. Its low yield prevents visual detection because its red color is masked by the gray-blue color of the hexaaquo ion which is present in large excess in the solution.

Ion-exchange chromatography enabled us to separate the methylo complex from the reaction mixture by the following procedure. A 20-ml amount of 0.65 *M* $CrClO_4$ in 0.65 *M* $HClO_4$ was added under nitrogen to 170 ml of an ice-cooled stirred solution containing 6.5 m*M* *tert*-C_4H_9OOH and 7.5 m*M* $HClO_4$. The color change from sky blue Cr(II) to gray-blue Cr(III) follows without delay. Air was introduced in order to oxidize the excess of Cr(II) and the solution was passed through an ice-cooled Dowex 50-X2 cation-exchange column. A narrow purple band was observed, just ahead of the blue hexaaquo band and was eluted by the reaction mixture together with some hexaaquo ion. The resulting mixed solution was absorbed on a second ice-cooled Dowex 50-X2 column and the brown-red methyl complex band was eluted with 0.35 *M* $HClO_4$. This ion-exchange behavior is typical for a 2+ ion. Hexaaquochromium(III) was eluted with $HClO_4$ (4 *M*), and some green chromium(III) dimer[4] was left on the column.

The red fraction was collected into a 50-cm^3 gas bulb submerged in a salt–ice bath and the bulb was sealed. The sample thus collected was allowed to decompose at room temperature overnight. After 0.5 hr of exposure to room temperature the purple color turned to gray-blue and the sample was replete with bubbles.

The evolved gas was identified as methane by gas chromatography on an activated charcoal column heated to 80° using helium as the carrier gas. The quantity of methane in the bulb was measured by injection of a fraction of the gas from the gas bulb and measurement of the peak area. Calibration was done by injection of the same fraction of known quantities of methane introduced into the same glass bulb containing the decomposed sample solution in order to duplicate solubility losses. A calibration curve with six different known quantities of methane was prepared for each sample of complex analyzed. The chromium content of the solution was determined spectrophotometrically as CrO_4^{2-} at 372 mμ.[5] The ratio of chromium to CH_4 was 1.01 ± 0.05 (average of eight samples).

The absorption spectrum of the complex was measured at ~2° with a Cary 14 spectrophotometer in the visible and near-uv region. Peaks were observed at 258 mμ (ε 2160), 392 mμ (ε 196), and 550 mμ (ε 9.6). The spectrum is similar to those of the halogen-substituted complexes reported by Johnson, *et al.*[2]

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