A New Intermediate in the Reduction of Chromic Acid by Hydrogen Peroxide

Sir:

We wish to report the isolation of a new intermediate formed during the reduction of chromic acid by hydrogen peroxide. When conducted in perchloric acid, the final products of this reaction are oxygen and the hexaaquochromium(III) ion. During the preparation of chromium(III) perchlorate by this method, we observed that the deep blue perchromate formed upon mixing the reagents is not the only intermediate formed during the reaction. After its disappearance the solution turns green; the green color may persist for hours (at room temperature) and finally change to the grayish-blue color of the hexaaquo ion.

Ion-exchange chromatography was used to isolate the green intermediate. It turned out to be a highly charged cation which formed a green ring above the gray ring of the hexaaquo ion, and was eluted by perchloric acid at a much slower rate than the latter. The highest yields were obtained when the reaction was carried out in strong acid (2 to 4 *M* perchloric acid).

In order to minimize decomposition of the complex, all operations were carried out at −4°. An excess of chromic acid was used, so as to avoid free peroxide which tends to form bubbles on the ion-exchange column (cooled by circulating brine). A cation-exchange resin of low cross-linking was used (Dowex 50X2 100–200 mesh). The hexaaquo ion was easily eluted with 2 *M* perchloric acid, which also served to rinse the column (lower acid concentration was avoided in order to prevent freezing). The green band of the complex was eluted with 4 *M* acid. The chromium content of the solution was determined spectrophotometrically after oxidation with alkaline hydrogen peroxide at 372 mμ.[1] The absorption spectra of the complex has two maxima in the visible region, at 434 mμ (ϵ 381) and at 625 mμ (ϵ 414), and two in the ultraviolet region, at 230 and 268 mμ.

The band at 625 mμ was used to follow the decomposition of the complex. The rate of decomposition depends only slightly on acidity in the range investigated: at 26.5° the first-order rate constants are 1.23×10^{-4}, 1.24×10^{-4}, 1.45×10^{-4}, and 1.58×10^{-4} sec^{-1} at 4, 1, 0.4, and 0.2 *M* acid, respectively. The rate constant was measured at four different temperatures (in 4 *M* acid) and found to be 4.4×10^{-4}, 2.5×10^{-4}, 1.24×10^{-4}, and 0.34×10^{-4} sec^{-1} at 36.5, 31.5, 26.5, and 16.5°, respectively. The rate constant at −4° was estimated to be 1.43×10^{-6} sec^{-1} ($t_{1/2}$ = 134 hr); *i.e.*, decomposition of the complex during its preparation and analytical determination is negligible.

The green complex is a strong oxidizing agent; iodide is oxidized to iodine, ferrous to ferric ion, etc. The number of oxidizing equivalents per chromium atom was determined by two independent analytical methods: (a) iodometrically, by addition of KI and titrating the liberated iodine with thiosulfate (the result of eight titrations was 1.48 ± 0.04 equiv per chromium atom); and (b) spectrophotometrically, by addition of excess NaOH and measuring the chromate formed by self-oxidation at 372 mμ (the result of 12 determinations was that 50.6 ± 2.6% of the total chromium was oxidized; *i.e.*, there are 1.518 oxidizing equiv per chromium atom).

The decomposition products of the complex ion are the hexaaquochromic ion and chromic acid. The high charge of the complex (revealed by its strong affinity to the ion-exchange resin) supports a polynuclear structure. A structure that accounts for the properties described here is

$$[(H_2O)_5Cr{-}O{-}O{-}Cr(H_2O)_5]^{5+}$$

which is similar to the well-known cobalt ammine

$$[(NH_3)_5Co{-}O{-}O{-}Co(NH_3)_5]^{5+}$$

Other structures are not excluded and further work is required to establish the correct structure.

Michael Ardon, Benjamin Bleicher
Department of Inorganic and Analytical Chemistry
The Hebrew University, Jerusalem, Israel

Received December 3, 1965

---

(1) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

The Chemistry of Alane. XI.[1] A New Complex Lithium Aluminum Hydride, Li_3AlH_6[2]

Sir:

Although many alane derivatives are known, until now the metal aluminum hydrides, such as $LiAlH_4$, and quaternary ammonium aluminohydrides, R_4NAlH_4,[3] have been the only compounds containing only one group III-B element, in which more than three hydrogens were bonded to one aluminum. We now wish to report the first synthesis of a complex lithium aluminum hydride with a hydrogen-to-aluminum ratio greater than 4, lithium hexahydroalanate, Li_3AlH_6.

A solution of 0.10 mole of *n*-butyllithium in 60 ml of hexane was added to a solution of 0.20 mole of lithium tetrahydroalanate ($LiAlH_4$) in 150 ml of diethyl ether. A white precipitate formed immediately on addition of the reagents and the mixture was stirred for 30 min at room temperature. The white, microcrystalline solid (2.30 g) was isolated by filtration, washed thoroughly with anhydrous *n*-hexane and anhydrous diethyl ether, and dried *in vacuo* at room temperature. *Anal.* Calcd for Li_3AlH_6: Li, 38.66; Al, 50.11; H, 11.23; Li:Al:H, 3:1:6. Found: Li, 37.68; Al, 50.29; H, 11.12; C, 0.46; Cl, 0.75; Li:Al:H, 2.9:1:5.9.

That the new hydride was not a mixture of LiH and $LiAlH_4$ was demonstrated by its density which was greater than that of either LiH or $LiAlH_4$ (1.13 g/cc *vs.* 0.915 g/cc for $LiAlH_4$ and 0.775 g/cc for LiH); by thermal and hydrolytic stabilities better than those of LiH and $LiAlH_4$; by a chemical reactivity considerably lower than that of LiH or $LiAlH_4$; and by a unique powder X-ray diffraction pattern. The infrared spectrum of Li_3AlH_6 (KBr pellet) showed only a broad absorption centered at 1720 cm^{-1}.

Lithium hexahydroalanate decomposes without melting or subliming above 210° and, so far, no solvent has been found for it. It decomposes in air without ignition

---

(1) Paper X: R. Ehrlich and A. R. Young, II, *J. Inorg. Nucl. Chem.*, in press.

(2) This work was sponsored by ARPA under Order No. 24-62 and was monitored by the Air Force Systems Command, Research and Technology Division, Rocket Propulsion Laboratory, Edwards Air Force Base, Calif., under Contract AFO4(611)-7046.

(3) R. Ehrlich, A. R. Young, II, and D. D. Perry, *Inorg. Chem.*, **4**, 758 (1965).