# On an X-Ray and Electron Microscope Study of Precipitates Formed by the Hydrolysis of Iron(III) in 0.5 M NaCl Ionic Medium

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Several investigators [2-6] have studied precipitates from the hydrolysis of iron(III) in chloride solutions by X-ray and electron microscopy. These precipitates, named β-FeOOH, were found to be crystalline, having a tetragonal lattice with the following cell dimensions.[2]

$$a = b = 10.48 \pm 0.01 \text{ Å}$$
$$c = 3.023 \pm 0.005 \text{ Å}$$

Mackay [3] has suggested that β-FeOOH has essentially a hollandite (α-$MnO_2$) structure.

X-Ray and electron microscope studies have been made in order to correlate the solubility measurements with particle size on a series of precipitates obtained by Biedermann and Chow as described in a recent article.[1] Most of the mother liquid was removed by centrifugation, leaving thixotropic gels, which exhibited optical extinction under the polarizing microscope, indicating crystallinity. X-Ray powder photographs were taken of the moist precipitates in a Hägg-Guinier focusing camera, built in a fixed arrangement for Cu$K\alpha$ radiation. This had the disadvantage that the films were blackened by Fe fluorescence radiation which made estimation of the line breadth somewhat uncertain.

Precipitates from solutions with total iron concentration 0.025 M and 0.010 M and a low degree of hydrolysis gave sharp diffraction patterns which could be explained by a tetragonal unit cell with

$$a = b = 10.47 \pm 0.01 \text{ Å}$$
$$c = 3.020 \pm 0.004 \text{ Å}$$

This cell agrees, within the accuracy of the measurement, with the unit cell of β-FeOOH given above. No shift of the lines could be detected from samples with increasing degree of hydrolysis. Admittedly, the comparison was difficult for some samples with more broadened lines. On these photograms the reflections from the prismatic planes (*hk*0) and the steep pyramidal plane (541) were also more broadened than those from the flat pyramids and the basal plane (001). This agrees with the shape of the crystals (needles along the *c*-axis) deduced by Mackay [3] from single crystal electron diffraction studies.

Electron diffraction patterns (Trüb, Täuber & Co. KD3) were also obtained from the precipitates. The positions of the diffraction rings ($NH_4Cl$ as internal standard) agreed with the cell dimensions above and again the prismatic reflections were slightly broadened.

The electron micrographs (Philips EM 100) indicated a particle size of 100—300 nm. Fig. 1 shows an electron micrograph representative of one of the more wellcrystallized samples. Preparations that have been aged in the mother liquid at 25°C up to one year do not show any detectable change in crystallite size, which also has been found by Watson *et al.*[4]

The effect of temperature was also studied by heating some of the precipitates in sealed bombs at 50—75°C for a few months. Electron micrographs showed that this treatment made the particle size increase to about 600—800 nm. In accordance with Watson *et al.*[5] the best developed of these crystallites seem to show a substructure, indicating that they are possibly


*Fig. 1.* Electron micrograph of precipitate from slightly hydrolyzed 10 mM Fe(III) in 0.5 M NaCl solution.

built up of bundles of smaller particles. The X-ray powder diffraction lines are sharpened but otherwise the pattern remains the same. A very small fraction had transformed to $\alpha$-$Fe_2O_3$.

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## Cyclic 2-Aminoethylborane (1,2-Azaboretidine), a Product from the Reaction between Aziridine and Sodium Borohydride

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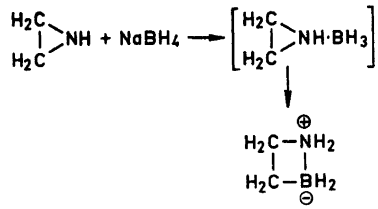
Addition compounds of the structure $RNH_2 \cdot BH_3$ or $R_2NH \cdot BH_3$ are strongly reducing and are thus of interest as potential radical scavengers and radioprotective agents. They are easily formed by reaction of alkylamine salts with borohydride. When aziridine was reacted with sodium borohydride in moist tetrahydrofuran, however, another type of substance was obtained.

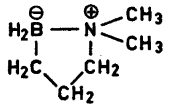
Elemental analysis showed the substance to have the composition $C_2H_8BN$. NMR spectra in $CDCl_3$ showed two methylene group signals at $\tau$ = 7.6 and 8.1 ppm, respectively (relative TMS as external reference). This excludes the substance from being the addition compound between aziridine and borane, which would be expected to give only one methylene signal. Thus evidence had been obtained for the following reaction



IR spectra in chloroform and KCl showed strong absorption at 1168 $cm^{-1}$ ($BH_2$ scissoring [2]) and at 2330 $cm^{-1}$ (BH stretching [2]). Furthermore $CH_2$-absorption at 3020 $cm^{-1}$ indicated the cyclic nature of the isolated compound. Absorption at 1440 $cm^{-1}$ suggested the presence of $-CH_2-N^+$.[3] The absorption at about 1630 $cm^{-1}$ is very weak thus confirming the presence of a secondary amine.

Further investigations of this and similar compounds will be published in a forthcoming paper.

Adams and Poholsky [4] have shown that N,N-dimethylallylamine and trimethylamine borane react in toluene to give a five membered ring, similar in structure to the one isolated during this work, namely 1,1-dimethyl-1,2-azaborolidine:



This compound apparently exists as the monomer.[4]

Experiments later revealed that 1,2-azaboretidine is obtained in the absence of water when acetic acid is used to decompose the sodium borohydride. This method appears to be the best one for preparations on a larger scale.

The compound is relatively toxic, having an $LD_{50}$ of 40 mg/kg in mice. It lacks radioprotective properties when tested in mice.

*Experimental. 1) Synthesis in the presence of water.* 0.8 g (20 mmole) of $NaBH_4$, 3 ml of water, 5 ml of tetrahydrofuran and 0.5 ml (10 mmole) of aziridine were refluxed for 40 min, whereafter the reaction mixture was extracted with about 50 ml of ether. The ether phase was separated, dried over sodium sulfate