PERCHLORIC ACID AS A REDUCING AGENT: REACTION WITH Cr(VI)

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Abstract: Cr(VI) in low concentrations is reduced at room temperature by either concentrated perchloric acid or 1M perchloric acid to produce Cr^{3+}, $CrCl^{2+}$ and $CrCl_2^{+}$.

Haight, Richardson and Coburn [1] observed that Cr(VI) reacts to produce Cr(III) in concentrated aqueous solutions of perchloric acid. They attributed this to the reduction of Cr(VI) by water. Since it is not obvious that the activity of water in concentrated $HClO_4$ solutions should be greater than that in various dilute aqueous solutions, in which we have found essentially no reduction of Cr(VI) in many weeks of storage, we have examined the reduction of $^{51}Cr(VI)$ in $HClO_4$ solutions of different concentrations by means of a cation exchange chromatographic procedure [2].

When microgram quantities of $Na_2{}^{51}CrO_4$ are dissolved in concentrated (70-72%) $HClO_4$, there is a rapid reduction of the $^{51}Cr(VI)$ to several species of $^{51}Cr(III)$. Within a few minutes at room temperature, the reduction is essentially complete. Figure 1 shows the species distribution following 10 minutes of contact time.

A similar experiment with 1M $HClO_4$ shows the reaction to be much slower: 72% of the $^{51}Cr(VI)$ remains after one hour and 20% after five days. The product spectrum again shows several species of $^{51}Cr(III)$.

In more dilute solutions, the reduction becomes even slower: 20% of the $^{51}Cr(VI)$ is reduced in one day by 10^{-2}M $HClO_4$ and in three weeks by 10^{-4}M $HClO_4$.

The overall process whereby $^{51}Cr(VI)$ is reduced to $^{51}Cr(III)$ is undoubtedly a complex one, since three electrons must be transferred to the chromium atom and since the central chlorine atom of the perchlorate group attaches to at least some of the $^{51}Cr(III)$-labelled product species.

To explore the mechanism of this process, we are presently investigating the Cr(VI) concentration dependence and the $HClO_4$ concentration dependence of both the rate of Cr(VI) reduction and the product spectrum.

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References

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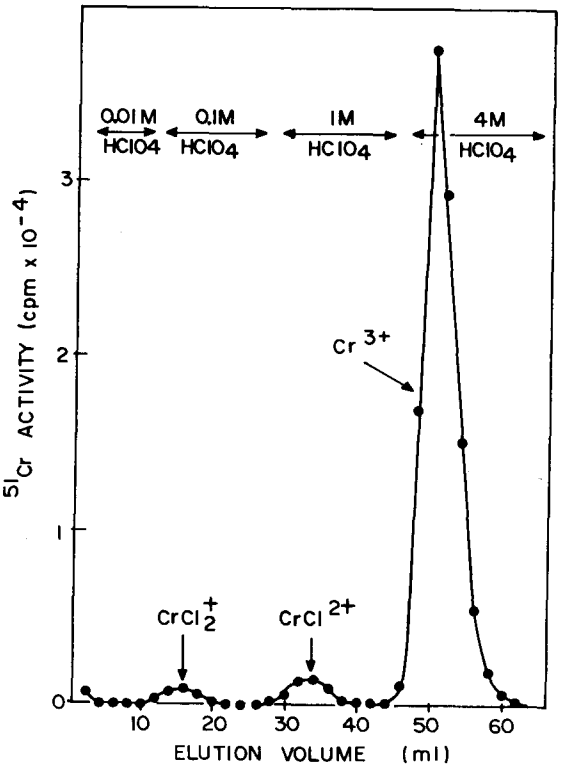

Figure 1: ^{51}Cr-labelled product distribution from reduction of $^{51}Cr(VI)$ in concentrated $HClO_4$