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

Kenneth E. Collins, Cielita Archundia* and
Carol H. Collins
Instituto de Quimica da UNICAMP, C.P. 6154,
13100 Campinas, SP, Brazil
(Received on 26/06/83)

Abstract: Cr(VI) in low concentrations is
reduced at room temperature by either con-
centrated perchloric acid or 1M perchloric
acid to produce Cr\(^{3+}\), CrCl\(_2^{2+}\) 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 exam-
ined the reduction of \(^{51}\)Cr(VI) in HClO\(_4\)
solutions of different concentrations by
means of a cation exchange chromato-
graphic 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 dis-
tribution 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 reduc-
tion 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 perchlo-
rate group attaches to at least some of
the \(^{51}\)Cr(III)-labelled product species.

To explore the mechanism of this pro-
cess, 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.

Acknowledgement: The authors wish to thank
CNPq and Dow Química S.A. for support of
this work.

* Visiting scientist on sabbatical leave
from the Centro de Estudios Nucleares,
UNAM, México.

References
1. G.P. Haight, D.C. Richardson and N.H.
2. C.H. Collins, K.E. Collins and R.E.
Ackerhalt, J. Radioanal. Chem. 8,
263 (1971).

Figure 1: \(^{51}\)Cr-labelled product distribu-
tion from reduction of
\(^{51}\)Cr(VI) in concentrated HClO\(_4\)