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AEC-NASA TECH BRIEF

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Synthesis of Perbromates

The problem:

To prepare perbromates. Past attempts to prepare perbromates—salts of heptavalent bromine—were generally unsuccessful. Early reports of such compounds cannot be confirmed.

The solution:

Successful synthesis of perbromates and isolation of the rubidium salt by a hot-atom process.

How it's done:

Perbromate was synthesized by a hot-atom process —the beta decay of radioactive Se^{83} incorporated into a selenate:

$$(Se^{83}O_4 \rightarrow Br^{83}O_4^- + B^-)$$

Enriched Se^{83} (90%) was irradiated with thermal neutrons, dissolved in nitric acid, and oxidized to selenate by ozone in alkaline solution. After decay of the 25-min Se^{83} activity sodium perchlorate and bromate were added, and rubidium perchlorate was precipitated at 0°C under conditions such that only 1% of the bromate was coprecipitated. Approximately 14% of the 2.4-hr Br^{83} activity was found in the precipitate. After treatment with iodide in 6$\underline{M}$ HCl, however, only about 1% of the Br^{83} activity coprecipitated with rubidium perchlorate.

These results indicated the formation of a relatively unreactive perbromate ion and led to the preparation of macro amounts of perbromates.

An electrolytic cell was set up having a platinium cathode immersed in 3 ml of 2.8$\underline{M}$ $HClO_4$ in a porous-porcelain cup. The anode was a rotating platinum microelectrode immersed in a slurry of Li_2CO_3 in 3 ml of 2.8 M $LiBrO_3$ tagged with 36-hr Br^{82} in a similar cup. The two cups were placed in a container of 2.8$\underline{M}$ $LiClO_4$, which in turn was immersed in a cooling bath at −15°C. The cell was run for about 1 A-hr at an anodic-current density of about 20 A/cm^2 Successive portions of Li_2CO_3 were added to the anolyte to maintain its neutrality, while the catholyte was periodically replaced for maintenance of its acidity.

At the end of the electrolysis, about 2% of the bromine activity coprecipitated with $RbClO_4$, but not with $Ba(BrO_3)_2$. When electrolysis was carried out at a similar density but in an unpartitioned cell with dichromate used to inhibit cathodic reduction, essentially all the bromide activity could be coprecipitated with $Ba(BrO_3)_2$. A technique was also developed for analysis for perbromate in the presence of bromate.

In connection with this study, perbromic acid was shown to be a stable compound, and its mass spectrum was determined; spectra from a heated sample persisted for 1 hr. The volatility of perbromic acid lies between those of perchloric acid and periodic acid.

Notes:

1. Inquiries concerning this innovation may be directed to:

Office of Industrial Cooperation
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439
Reference: B69-10647

Source: M. H. Studier and E. H. Appelman
Chemistry Division
(ARG-10459)

(continued overleaf)

Patent status:

Inquiries concerning rights for commercial use of this innovation may be made to:

Mr. George H. Lee, Chief
Chicago Patent Group
U.S. Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois 60439