REPORT ON RESEARCH PROJECT THE REACTION OF SAMARIUM (II) AND YTTERBIUM (II) SOLUTIONS WITH MOLECULAR OXYGEN

二價釤與二價鐿溶液與氧分子之反應

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The immediate object of this research is to prepare samarium(II) chloride and ytterbium(II) chloride. Solutions of these rare earth salts are then to be compared with chromium(II) solutions with respect to their rates of reaction with molecular oxygen.

Chromium(II) solutions are unique in that they react with molecular oxygen with great rapidity, much more rapidly than any other aqueous solutions which have been investigated. Previous work by H.W. Stone, Jour. Am. Chem. Soc., 58, 2581 (1936) show that chromous solutions are twentyfive times more rapid in reacting with oxygen than such well known oxygen absorbing reagents as potassium pyrogallate, cuprous ammonium chloride or sodium hyposulfite containing β -anthraquinone sulfate.

Consideration of the molal oxidation-reduction values suggested a number of powerful reducing agents which are similar to chromium (II) in several respects and hence might be expected to react at a very rapid rate. The possibilities noted include:

$$Yb^{++} = Yb^{+++} + le$$
 $E^{\circ} = 1.15V$
 $Sm^{++} = Sm^{+++} + le$ $E^{\circ} = ca. 0.8V$
 $Eu^{++} = Eu^{+++} + le$ $E^{\circ} = 0.43V$
 $Cr^{++} = Cr^{+++} + le$ $E^{\circ} = 0.40V$
 $V^{++} = V^{+++} + le$ $E^{\circ} = 0.255V$

Each of the couples listed, like chromium (II), is a powerful reducing agent which on reacting with oxygen loses a single electron and changes from the dipositive to the tripositive state. It seemed probable that any of these might well react with oxygen as rapidly as chromium(II).

With this in mind the rates of reaction of europium(II) and vanadium(II) with oxygen were compared with the chromium(II)-oxpgen reaction. It was found that though both of these divalent ions reacted with oxpgen the rates were much slower than that of the chromium(II) solutions. This work was reported reported in a paper by H. W. Stone at the National Meeting of the American Chemical Society at Atlantic City N. J. last September.

It is believed that the explanation for the unusually fast chromium(II)-oxygen reaction lies in the fact that when oxidized by oxygen, chromium forms a stable dinuclear oxygen or hydroxy bridge complex, while none of the slower acting reductants which have been studied are known to form such complexes.

$$\left[(\mathrm{H_2O})_5\mathrm{Cr-O-Cr}(\mathrm{H_2O})_5 \right]^{+4} \qquad \text{or} \qquad \left[(\mathrm{H_2O})_5\mathrm{Cr} \right]^{+4} \\ \mathrm{OH} \qquad \qquad \mathrm{OH} \qquad \mathrm{OH}$$

Samarium (II) and ytterbium(II) salts are similar to chromium(II) in many respects and might be expected to react rapidly with molecular oxygen while they have no strong tendencies to form stable complex coordination compounds similar to chromium. For these reasons it should be interesting to discover whether they will react rapidly with the oxygen as does the chromium(II) or will react much more slowly as the other reducing solutions which have been investigated.

The preparation of these divalent rare earths is proving to be unusually demanding both as to equipment and skill on the part of the workers. Their tendency to react with the water solvent itself presents additional complications but never-the-less it is believed that the interesting comparison with the chromium(II) is possible.