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SEMI-MICRO CONVERSION OF ISOTOPICALLY ENRICHED WATER TO DIOXYGEN AND CARBON DIOXIDE

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SUMMARY

The quantitative conversion of heavy water on the decigram scale to dioxygen and carbon dioxide via the following sequence

$U + 2D_2O^{18} = UO_2^{18} + 2D_2$; $UO_2^{18} + 2BrF_3 = UF_6 + Br_2 + O_2^{18}$ and $C + O_2^{18} = CO_2^{18}$

is described in detail. The reasons for choosing this particular route are outlined.

Key Words : O^{18} enriched dioxygen, carbon dioxide, uranium dioxide, bromine trifluoride.

INTRODUCTION

Non-active O^{18} is the preferred oxygen isotope for tracer work because the active isotopes are too short lived. Water, enriched in non-active oxygen isotopes by distillation, is the primary source for other oxygen enriched compounds made for example by hydrolysis or isotopic exchange (1). Enriched oxygen containing gases are required for absorption, diffusion and kinetic studies or to assist in spectral assignments. Electrolysis of aqueous solutions is the usual method for generating oxygen which can then be converted to other gases. However, the method is slow and not amenable to quantitative semi-micro conversions (2,3). An alternative method for such a quantitative conversion to oxygen and carbon dioxide is described. This is a worthwhile operation because the expense of water increases rapidly with isotopic enrichment.

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EXPERIMENTAL

The uranium - water reaction : The apparatus shown in Fig. 1 was used to effect the oxidation

$$U + 2H_2O = UO_2 + 2H_2$$

Aliquots of about 0.1 g of enriched water were collected by vacuum transfer in ampoules. The content of each ampoule could be estimated to ± 10% from the depth of liquid in the stem so that the approximate amount of uranium needed (0.75 g /0.1 g H_2O) could be introduced into the silica reaction tube. The whole apparatus was evacuated, A closed and the ampoule neck snapped by rotating the A19 socket-handle.

After distilling the water onto the uranium, by cooling the silica tube in liquid nitrogen, the reaction vessel was separated and sealed at B. This vessel was placed in an oven at 180°C with the lower part of the silica tube heated at 550°C and the palladium thimble at 750°C with separate miniature tube furnaces. Completeness of reaction could be judged by passage of a Tesla coil discharge through the cold tube. Quantitative trials with ordinary water showed complete reaction within 4 hrs. When heavy water was used the heating period was extended to overnight (16 hrs) to allow for slower reaction and diffusion of deuterium. The tube was cut off at C and the contents transferred to the fluorination flask in the next stage. (The silica tube after cleaning with HNO_3 was rejoined for further runs).

Fluorination of uranium dioxide : The apparatus for converting the oxide to oxygen via

$$UO_2 + 2BrF_3 = UF_6 + Br_2 + O_2$$

is shown in Fig. 2. Apart from E and F the apparatus was of "Pyrex" glass. Only the B14 joints need to be lubricated with a fluorinated grease. The whole apparatus was initially dried by pumping. C was closed and the part to the right let down to atmospheric pressure. About 1-2 ml of bromine trifluoride were placed in G, frozen and replaced. The UO_2 had been placed in F. After re-evacuation, about 10 cm pressure of 'white spot' nitrogen

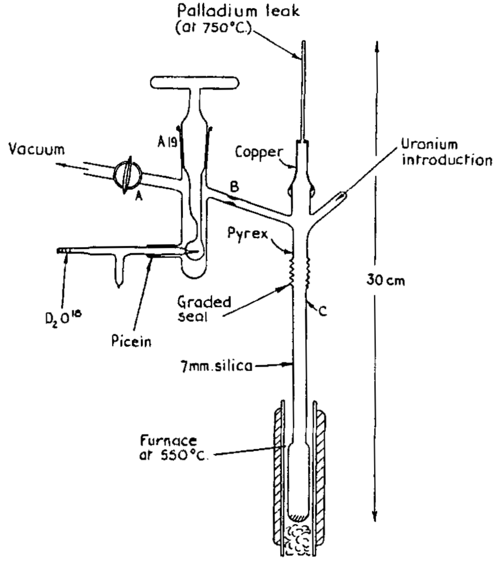

Figure 1: U to UO_2 conversion.

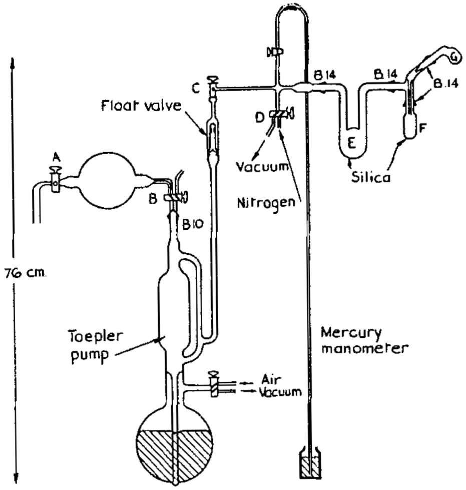

Figure 2: UO_2 to O_2 conversion.

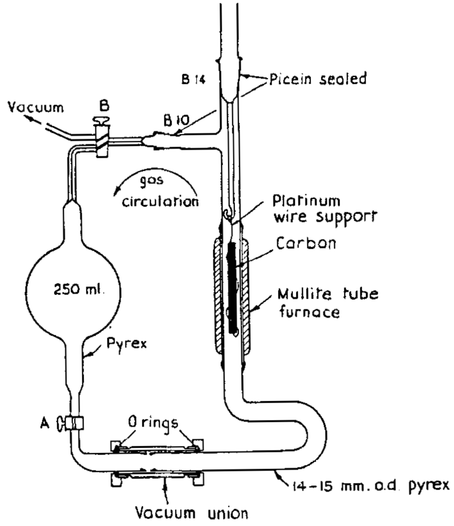

Figure 3: O_2 to CO_2 conversion.

was introduced via D. (If pure oxygen was required a carbon dioxide gas pressure could be substituted for nitrogen). The contents of G were unfrozen and added in one portion to F. Trap E was then cooled and, as F warmed to ambient temperature, oxygen was evolved in a mild reaction. To complete the reaction the liquid in F was gently refluxed for a minute until the yellow colour of the original solvent was restored. UF_6 and Br_2 collected in E. The permanent gases in the system were then transferred to bulb AB using the Toepler pump. (About 8 strokes sufficed with the volumes used).

Conversion of oxygen to carbon dioxide : Flask AB was removed after bringing the Toepler volume to atmospheric pressure. It was then fitted into the apparatus shown in Fig. 3. Spectroscopic-grade carbon was used. The B10 "piceined " join was made first and the circuit completed by sliding the metal union over the abutting glass ends. The furnace portion was evacuated via B which was then reversed and A opened to allow gas circulation over the carbon. Trial runs established that the volume of oxygen from 0.1 g of water were quantitatively converted to CO_2 in 4-5 hrs at 550°C. Again an overnight heating was employed to ensure complete isotopic oxygen conversion. The whole apparatus could be attached to a vacuum system for condensing and measuring out the CO_2 as required.

An example of the complete process is as follows :

An evacuated glass ampoule containing heavy water weighed 6.7167 g after transferring the sample onto 0.6974 g of uranium flake, the ampoule filled with air weighed 6.6076 g. The product weighed 0.7906 g of which 0.7874 g were transferred to the silica flask. Finally 61.0 ml of CO_2 at N.T.P. were collected.

The composition of the heavy water was certified as D_2O with 0.238% O^{17} and 30.75% O^{18} which is equivalent to a composition $D_2O^{16.62}$ containing 80.5% by weight of oxygen.

Assuming the increased weight of the uranium residue (93.2 mg) is all $O^{16.62}$ then the weight of carbon dioxide expected was $\frac{0.7874}{0.7906} \times 93.2 \times \frac{45.24}{33.24} = 126$ mg.

compared with the weight collected $\frac{61.0}{22,410}$ x 45.24 x 1.007 = 124 mg.

(The factor 1.007 allows for gas imperfection).

The weight increase expected for the uranium from the weight of water used was $[(6.7167 - 6.6076) + 0.0040]$ 0.805 = 91 mg.

(The small correction is the weight of the air volume in the opened ampoule).

The overall conversion of water to carbon dioxide was better than 98%.

DISCUSSION

With high isotope mass ratios, as for O^{18}/O^{16}, kinetic isotope effects are expected and the isotopic ratio in the product could alter with the stage of reaction. The quantitative conversions described avoid this effect. Again when there is more than one oxygen containing product they may contain different isotopic ratios. For example in the reaction

$$6\,CaCO_3 + 4BrF_3 = 6\,CaF_2 + 2\,Br_2 + 6\,CO_2 + 3O_2$$

the O^{18}/O^{16} ratio in the dioxygen was 30% less than in the carbon dioxide (4). Our single oxygen-product reactions avoid this difficulty.

Finally, another possible source of isotopic dilution is by an exchange reaction with the silica reaction vessel. However, it has been shown that silica vessels do not exchange with O_2^{18}, CO^{18} or CO_2^{18} at temperatures as high as 630°C for periods of up to thirteen hours (5). These limits were not exceeded in our experiments. However, if carbon monoxide were made from the reactions $C + H_2O = CO + H_2$ or $C + CO_2 = 2CO$ the high temperatures required would lead to some isotopic exchange.

Oxygen in many oxides can be displaced quantitatively with halogen fluorides and their derivatives (6). However, the direct reaction with water is violent and would also yield hydrogen fluoride necessitating the use of an all metal or fluorinated polymer apparatus. For simplicity the water needs conversion to another oxide which reacts mildly and quantitatively with the halogen fluoride. The reaction of water with uranium is suitable because it follows a linear oxidation law and is rapid even at 300°C. The possible non-stoichiometry of UO_2 is unimportant since uranium metal and all the oxides dissolve rapidly in bromine trifluoride with oxygen displacement. Bromine trifluoride is the most convenient halogen fluoride for small scale use. The uranium hexafluoride formed is readily separated.

Direct conversion of uranium dioxide to carbon dioxide with carbon tetrachloride was rejected because the maximum yield reported at 500°C was only 60% and other oxygen species also form (7).

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