also, the relative constancy of carbon dioxide consumed over catalysts containing intermediate amounts of copper suggests the operation here of compensating electronic effects. Beyond about 50% alloyed copper the methanation reaction has disappeared and the carbon dioxide consumed soon falls slightly. In this region the alloy lattice parameter continues its nearly linear rise while the already small magnetic susceptibility of the alloys decreases only very slowly and it appears that the geometric factor may well be predominant here.

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[Contribution from the Chemistry Division, Oak Ridge National Laboratory]

Primary Cobalt-60 Radiolysis Yields in Heavy Water[1]

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The cobalt-60 γ-ray decomposition of several heavy water solutions, 0.4 M in sulfuric acid, has been studied and the initial yields of D, OD, D_2 and D_2O_2 determined. The reactions investigated were the formation of D_2 in a degassed dilute bromide solution, the formation of D_2O_2 in air-saturated solution and the oxidation of ferrous ion in air-saturated solution. The yields for D, OD, D_2 and D_2O_2 were evaluated to be 3.99, 3.14, 0.38 and 0.81 in heavy water solution and the H, OH, H_2 and H_2O_2 yields in light water were 3.68, 2.96, 0.45 and 0.81. All yields are relative to the light water ferrous dosimeter value of 15.6 molecules oxidized for each 100 e.v. of energy absorbed.

Introduction

Heavy water, like light water, may be considered to decompose when subjected to ionizing radiations into the molecular products D_2O_2 and D_2 and the free radicals D and OD described by equation 1

$$-G_{D_2O} = G_{D_2O_2} + G_{D_2} + {}^1/_2(G_D + G_{OD}) \qquad (1)$$

In this paper the 100 e.v. yields of the primary heavy water radiolysis products will be denoted by G_{D_2}, $G_{D_2O_2}$, G_D and G_{OD}, and the yields of measured products will be denoted by G(product).

The 0.4 M sulfuric acid systems studied to determine the molecular and free radical yields were: (1) D_2 production in a degassed dilute KBr solution; (2) D_2O_2 production in an aerated solution; and (3) oxidation of ferrous ions in an air-saturated solution. The radiolysis mechanisms proposed for light water were used to calculate the heavy water yields.

Experimental

The γ-radiation was provided by either a 150 or a 1100 curie cobalt-60 source.[2] These annularly loaded cylindrical sources provided homogeneous irradiations of centrally placed samples. The rate of energy absorption was determined by the rate of ferrous oxidation in an aerated 0.4 M H_2SO_4 solution assuming 15.60 ferrous ions oxidized per 100 e.v. of absorbed energy.[3] Energy transfer from Co-60 γ-rays to the medium through which they pass is dependent upon the electron density of the medium. Since the molar volumes of light and heavy water are essentially the same, it was assumed that on a volume basis the rate of energy absorption was the same in light and heavy water.

All of the chemicals used were Baker and Adamson reagent grade except the reagent grade ceric acid sulfate which was obtained from the G. Frederick Smith Chemical Company. The heavy water was purified by distillation from an acid permanganate solution, from a basic permanganate solution and in an all-silica system. Storage was in a silica vessel. To minimize contamination with light water, the acid permanganate solution was prepared by treating SO_3 with D_2O and then adding potassium permanganate. The basic permanganate solution was prepared by dissolving Na_2O_2 in the distillate from the acid permanganate distillation and refluxing the solution until the D_2O_2 formed was thermally decomposed; potassium permanganate was then added. The purified heavy water was analyzed to be 99.74 mole % deuterium oxide. Further purification of selected 0.4 M sulfuric acid heavy water solutions was effected by irradiating with cobalt-60 γ-rays and then photolyzing with a mercury lamp to destroy the D_2O_2 formed.[4]

The solutions used for the hydrogen determinations were degassed and then irradiated in the 1100 curie source. The S.T.P. volumes of hydrogen were determined by ignition with oxygen on a platinum filament in a semi-micro Saunders-Taylor type apparatus.[5]

Hydrogen peroxide concentrations were obtained by reaction of aliquots of the irradiated solution with a known amount of ceric ion. The initial and residual ceric ion concentrations were determined on a Model 11 MS Cary Recording Spectrophotometer at 3200 Å. using a molar extinction coefficient of 5580[3] at 25°. The ceric ion molar extinction coefficients in light and heavy water were the same. Ferrous solutions were irradiated in non-coloring silica spectrophotometer cells and the amount of oxidation determined by measuring directly the ferric absorption at 3050 Å. The ferric ion molar extinction coefficient at 3050 Å. and 25°, relative to the ceric molar extinction coefficient of 5580, was found to be 2358 in light water and 2195 in heavy water.

Results and Discussion

It is assumed in this paper that the mechanisms postulated for light water are also valid for heavy water and that the only difference between light and heavy water radiolysis is the difference in free radical and molecular yields.

Hydrogen Yields in Degassed Dilute KBr Solutions.—The production of hydrogen in a dilute degassed KBr solution is assumed to be equal to the primary molecular hydrogen yield

$$G(H_2)_{Br^-} = G_{H_2} \qquad (2)$$

The average $G(D_2)$ for three 10^{-4} M KBr, 0.4 M D_2SO_4 samples irradiated 45, 60 and 75 minutes at a dose rate of 7.88×10^{20} e.v., l.$^{-1}$, min.$^{-1}$ was 0.38 with a standard deviation of ± 0.01. The $G(H_2)$ was determined for five similar light water samples and found to average 0.45 with a standard deviation of ± 0.01.

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(1) Presented at the Fifth Annual Meeting of the Radiation Research Society, Rochester, New York, May 13–15, 1957. This paper is based upon work performed at Oak Ridge National Laboratory which is operated by Union Carbide Nuclear Company for the Atomic Energy Commission.

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Hydrogen Peroxide Yields in Air-saturated Solutions.—Hydrogen peroxide is produced with a greater yield in an air-saturated sulfuric acid solution than in a deaerated solution.[6] The net H_2O_2 production in air saturated acid solutions is described by equation 3, the primary H_2O_2 yield in equation 1 plus one-half the difference between the H atom and OH radical yields.

$$G(H_2O_2)_{air} = G_{H_2O_2} + \frac{(G_H - G_{OH})}{2} \qquad (3)$$

Eight heavy water runs indicated a $G(D_2O_2)$ of 1.24 with a standard deviation of ± 0.005. Six light water runs indicated a $G(H_2O_2)$ of 1.17 $\pm$ 0.017. In each run hydrogen peroxide was produced linearly with dose over the range studied, 0–10^{22} e.v., $l.^{-1}$. A run consisted of a series of individual analytical determinations made on the same solution after given intervals of irradiation time.

Ferric Yields in Aerated Solutions.—In the generally accepted ferrous oxidation mechanism[6] each H_2O_2 molecule oxidizes two ferrous ions, each OH radical oxidizes one ferrous ion and each H atom oxidizes three ferrous ions.

$$G(Fe^{+++})_{air} = 2G_{H_2O_2} + G_{OH} + 3G_H \qquad (4)$$

The oxidation of ferrous ion was determined in air-saturated 0.4 M sulfuric acid light and heavy water solutions containing 2×10^{-3} M $FeSO_4$-$(NH_4)_2SO_4$ and 10^{-3} M NaCl. The $G(Fe^{+++})_{air}$ for six heavy water runs averaged 16.72 with a standard deviation of ± 0.17 whereas the $G(Fe^{+++})_{air}$ for five light water runs normalized about the assumed yield of 15.60 had a standard deviation of ± 0.13.

The average value $G(Fe^{+++})_{air} = 16.72$ is in agreement with Hardwick[7] (17.06)[8] and McDonell[9] (16.36)[10] but in disagreement with Trumbore and Aten (18.6).[11] Hardwick[7] also observed $G(D_2) = 0.288$[8] and calculated $G_D = 4.12$.[8]

The measured rates and the molecular and free radical yields, calculated using equations 1, 2, 3 and 4, are presented in Table I for both light and heavy water. The differences in yields, presented in the last column, have been evaluated statistically at the 95% confidence limit.

In light water the observed yields of radiolysis products indicated that there were 4.58 molecules of water decomposed for each 100 e.v. of energy absorbed by a 0.4 M sulfuric acid solution whereas in heavy water there were 4.75 molecules decomposed. Slower diffusion rates or slower reaction rates may be the cause for the greater decomposition of heavy water. Kirchenbaum[12] has cited numerous references illustrating that generally slower reaction rates are observed in heavy water than in light water. If initially the same number of light and heavy water molecules are decomposed for each 100 e.v. then a relatively slower rate of recombination of D with OD in heavy water would cause an increase in the calculated number of water molecules decomposed.

TABLE I

YIELDS[a] IN THE DECOMPOSITION OF D_2O AND H_2O BY COBALT-60 γ-RADIATION IN 0.4 M SULFURIC ACID

Product	D_2O	H_2O	Difference[b]
$(Fe^{+++})_{air}$	16.72	15.60	1.12 ± 0.16
$(H_2O_2)_{air}$	1.24	1.17	0.07 ± .01
$(H_2)_{Br^-}$	0.38	0.45	.07 ± .01
H	3.99	3.68	.31 ± .03
OH	3.14	2.96	.18 ± .08
H_2O_2	0.81	0.81	.00 ± .02
H_2	0.38	0.45	.07 ± .01
$-H_2O$	4.75	4.58	.17 ± .09

[a] Based upon 15.60 molecules of ferrous oxidized per 100 e.v. of energy absorbed. [b] Presented as the 95% confidence limits.

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[6] A. O. Allen, *Rad. Res.*, **1**, 85 (1954).

[7] T. J. Hardwick, PR-CM-8, Progress Report for the Period October 1, 1956, to December 31, 1956, for the Chemistry and Metallurgy Division, Chalk River, Ontario, Canada.

[8] Corrected to a ferrous oxidation rate of 15.6 molecules oxidized per 100 e.v.

[9] W. R. McDonell, ANL-5206, January 12, 1954.

[10] Corrected for the change in the molar extinction coefficient of Fe^{+++} in 0.4 M H_2SO_4 heavy water solution at 25°.

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[12] I. Kirchenbaum, "Physical Properties and Analysis of Heavy Water," National Nuclear Energy Series III, Vol. IVA, McGraw-Hill Book Co., Inc., New York, N. Y., 1951.