recombination of iodine atoms in hexane.[8] Then the maximum possible value of k_α would appear to be 8×10^{10} sec.$^{-1}$. If the temperature-independent term for k_α has the "normal" value of 10^{13} sec.$^{-1}$, the minimum energy of activation for step R1 is 3.0 kcal./mole. This value is undoubtedly minimal, for k_β is almost certainly distinctly less than 10^{13} (mole/ml.)$^{-1}$ sec.$^{-1}$.

The above argument is very qualitative but suggests how some additional information could be obtained. At concentrations of a few moles per liter of bromine, the rates of processes R1 and R2 should be comparable. Under these conditions, kinetic studies of the addition reaction could evaluate k_{CA} and k_α/k_β at various temperatures.[16] Such results could es-

(16) Data of this sort were obtained by Müller and Schumacher for the vapor-phase bromination of dichloroethylene. Unfortunately, they made a mistake in algebra on p. 368 of Reference 13 and thought they could calculate absolute energies of activation for reactions corresponding to our processes R1 and R2.

tablish the constant of proportionality between k_{CA} and k_e and determine whether one or both of the bromines in the dibromoethylene become equilibrated with the entering bromine atom. The results could also provide a better minimum value for the energy difference between Y and A or B. However, all of our studies serve only to provide us fleeting glimpses of the peaks represented by transition states X, Y and Z, and to measure their heights relative to the surrounding plains (C and T) Kinetic measurements alone can never explore the mountain valleys to locate levels A and B. We have a slight hope that the concentration of $C_2H_2Br_3$ radicals might be measurable in an equilibrium or photostationary state, and that the quantitative picture in Fig. 4 could thereby be completed, but we do not see how to make the measurements by any techniques available to us at present.

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# The Molecular Yield in the Decomposition of Water by Hard X-Rays[1]

BY EVERETT R. JOHNSON AND AUGUSTINE O. ALLEN

Dilute aqueous solutions of a number of oxidizing and reducing agents at various concentrations give on irradiation with hard X-rays identical initial yields of hydrogen gas. This yield of molecular hydrogen is therefore characteristic of the action of X-rays on water, and occurs simultaneously with the formation of free radicals which react with solutes. The molecular yield is decreased about 18% by addition of 4% of sulfuric acid to the water.

A number of observations on the radiation chemistry of water and aqueous solutions have been correlated by the idea that the systems behave as though the water were reacting simultaneously in two ways[2-5]—a decomposition into free radicals and also a decomposition into molecules

$$H_2O \longrightarrow H + OH \qquad (1)$$
$$2H_2O \longrightarrow H_2 + H_2O_2 \text{ (or } H_2 + \tfrac{1}{2}O_2 + H_2O) \quad (2)$$
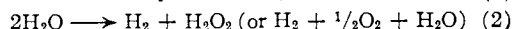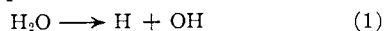
The radicals formed in (1) are assumed to be responsible for most of the reactions undergone by solutes in irradiated solutions. Consequently in the presence of solutes which are sufficiently reactive toward the radicals produced in (1) a constant initial yield of hydrogen gas should appear from reaction (2).

Hydrogen yields from a variety of oxidizing and reducing solutions have been determined with the object of testing this prediction.

Experimental

Reagents and Materials.—The water used in all these experiments was obtained by redistilling ordinary distilled water, first from alkaline permanganate, then acid dichromate, then dilute sodium hydroxide into a Pyrex vessel from which the final distillation was made. The distillate from this last flask was condensed in a silica system and col-

lected in a silica vessel. All reagents were C.P. and were used without further purification, with the exception of ferrous ammonium sulfate which was recrystallized several times.

The sample bulbs (approximately 10-cc. volume) were blown from 2-mm. Pyrex capillary tubing. All sample bulbs were soaked in purified water prior to use.

X-Rays were obtained by bombarding a gold target with 2-Mev. electrons from an electrostatic generator made by High Voltage Engineering Corp. of Cambridge, Mass.

Preparation of Samples and Methods of Analyses.—The procedure for filling the bulbs is as follows: The solution to be irradiated is placed in bulb A (Fig. 1), outgassed at room temperature, and frozen with liquid nitrogen while the entire system is being pumped down. When the pressure is less than 1×10^{-5} mm. (as measured by an ion gage), the liquid nitrogen trap is removed from the solution bulb and solution boiled (about 40–50°) and refrozen. When the pressure is again less than 1×10^{-5} mm., that part of the line containing the solution and reaction bulbs is sealed off from the remaining portion by means of the heavy-walled
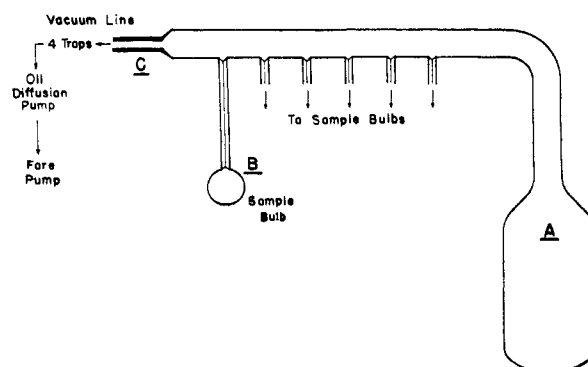
(1) Research carried out under the auspices of the U. S. Atomic Energy Commission.

(2) (a) A. O. Allen, J. Phys. Colloid Chem., 52, 479 (1948); (b) A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, Report AECU-1413; J. Phys. Chem., 56, 601 (1952).

(3) C. J. Hochanadel, ibid., 56, 587 (1952).

(4) E. J. Hart, THIS JOURNAL, 73, 1891 (1951).

(5) E. J. Hart, Reports AECU-1250 and ANL-4636; J. Phys. Chem., 56, 594 (1952).

Fig. 1.—Arrangement for filling sample bulb.

tubing (C). The solution is then brought to room temperature and poured into the reaction bulbs under vacuum. The individual bulbs are sealed off about 4–5 cm. above the liquid level. The bulb stem is then fitted with a brass cup and the bulb placed in an ice-bath, as shown in Fig. 2. When the bulb has come to ice-water temperature, liquid nitrogen is poured into the metal cup and the capillary sealed off about 8–9 mm. above the frozen liquid level. When the bulb is raised to room temperature, little or no vapor volume remains.
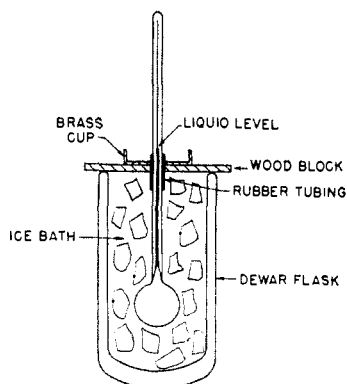

Fig. 2.—Arrangement for sealing off sample bulbs.

The irradiated samples are analyzed in the vacuum system shown in Fig. 3. The sample is placed in trap (A), and when a vacuum of better than 1×10^{-6} mm. is obtained, stopcock 1 is closed, a *n*-butyl bromide-bath (−118°) is placed on trap (B) and a Dry Ice–acetone-bath on trap (A); the freezing mixture causes the sample bulb to break in about 30 minutes. After the bulb has broken, the sample is degassed by pumping with the Toepler, boiling the liquid, freezing with Dry Ice and acetone, and repeating until the solution is gas-free. The *n*-butyl bromide trap removes the water vapor and does not trap out any CO_2 that may be present.
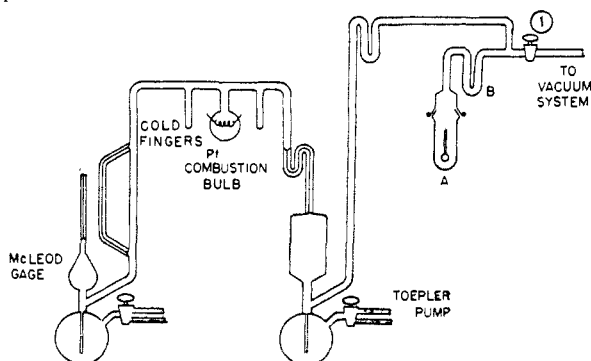

Fig. 3.—System for opening bulbs and determining dissolved gases.

The gas analyses were done by measuring the pressure before and after combustion in the McLeod section of the line, with the cold fingers cooled with liquid nitrogen. The method relies entirely on diffusion and works satisfactorily for pressures up to 20 microns. Condensable gases such as CO_2 may be determined by the pressure drop occurring when a *n*-butyl bromide-bath on the cold fingers is replaced by liquid nitrogen.

Methods of degassing and analysis of the gaseous products were checked with known samples and found to be reproducible within a few per cent. for the pressure range studied. Table I gives results on degassing and on combustion analyses of known synthetic samples.

Fe^{+++} was determined by the thiocyanate method using a Beckman model DU spectrophotometer. Exactly 0.4 cc. of NH_4CNS solution (12 g. dissolved in 100 cc. of H_2O) is added to 2 cc. of the unknown solution, mixed and then diluted to 5 cc. with 0.8 N H_2SO_4. After thorough shaking the optical density at 480 mμ is read. (Concentration of

TABLE I

TESTS OF DEGASSING AND COMBUSTION PROCEDURES

Degassing (cc. NTP)		Combustion (H_2–O_2 mixtures) % H_2	
Observed	Theoretical	Observed	Theoretical
0.260	0.261	37.3	38.3
.322	.333	46.6	46.5
.507	.518	42.3	42.8

ferric iron in original solution in μM. = 462 × o.d. by our calibration curve for 1-cm. cells.) Readings are made within 10 minutes from time of mixing. Blank consists of 0.4 cc. of NH_4CNS solution diluted to 5 cc. with 0.8 N H_2SO_4.

An alternate procedure was the direct determination of the absorption of Fe^{+++} in 0.8 N H_2SO_4 at 305 mμ (concentration of ferric iron in μM. = 457 × o.d.).

Hydrogen peroxide was determined by the method described in reference (2).

Results

All irradiations were done at a constant dose rate (about 16 r./sec. as measured by Victoreen thimble chambers) at a temperature of 24 ± 1°; the results are expressed as micromoles per liter of product against time (in seconds) of irradiation. The hydrogen yields may be compared with the oxidation yield of ferric iron obtained by irradiating air-saturated ferrous ammonium sulfate solutions (approximately millimolar) in 0.8 N H_2SO_4 (Fig. 4). The least squares value of the oxidation rate was 231.2 ± 1.5 μM. Fe^{III} per 1000 sec.
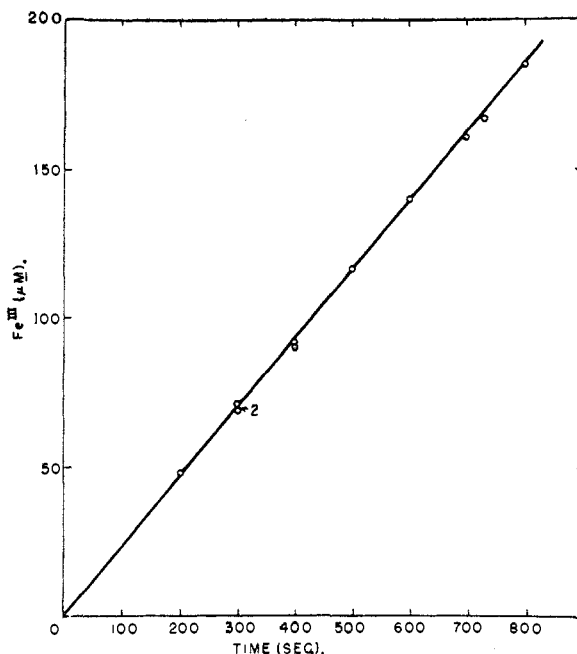

Fig. 4.—Oxidation of ferrous sulfate solution by X-rays

All rates given were obtained by least squares, using those points shown on the graphs which lie on the initial linear portions of the curves. The precision values given are the standard deviations of the slopes. Four aberrant runs on ferrous sulfate oxidation were rejected by application of Chauvenet's criterion[6]; all data obtained on hydrogen yields are included.

(6) A. G. Worthing and J. Geffner, "Treatment of Experimental Data," John Wiley & Sons, Inc., New York, N. Y., 1943.

Bromide and Iodide Solutions.—The hydrogen formed from the irradiation of neutral deaerated KBr and KI solutions, in the concentration range 1×10^{-7} M to 5×10^{-4} M, is shown in Fig. 5. The curve extends linearly up to the maximum dose (about 900 seconds), except in the more dilute solutions where it levels off and reaches a steady state. The rate of hydrogen evolution was 8.75 ± 0.36 μM./1000 sec. The dotted lines extending through the solid points indicate steady-state hydrogen values for 10^{-6} M and 10^{-7} M KI solutions. These steady states are believed to result from competition for the radicals produced in reaction (1), between the iodide or bromide ion and the decomposition products formed in reaction (2). With the more concentrated solutions the dosages employed were not sufficient to reach a steady state level.
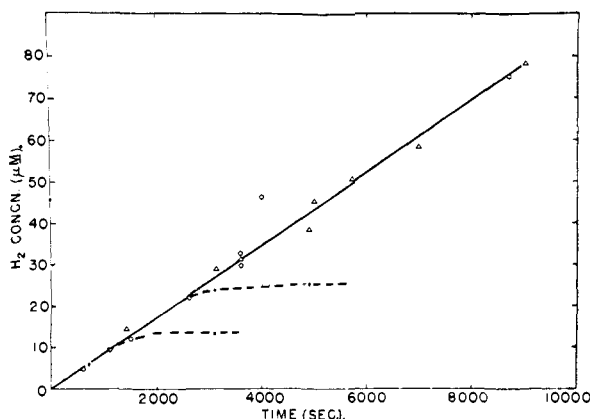

Fig. 5.—Hydrogen produced by X-rays in KBr and KI solutions: O, KBr (10–400 μM.); △, KI (10–500 μM.); ●, KI (0.1 or 1.0 μM.).

The products from the irradiation of neutral bromide and iodide solutions are hydrogen, oxygen and a small amount of hydrogen peroxide. Material balances were within a few per cent. No detectable amount of any oxidized form of bromide or iodide was produced by radiation in the solutions studied.

Solutions of Hydrogen Peroxide and Oxygen.—Hydrogen yields from solutions of oxygen in water, and from deaerated solutions of hydrogen peroxide with and without added 10^{-4} M KI, are shown in Fig. 6. The hydrogen concentration levelled off at 27 μM. for a solution initially 95 μM. in H_2O_2, and at 52 μM. for a solution initially 2300 μM. in H_2O_2, but did not level off in the dose range studied for solutions containing 10^{-4} M KI. The initial hydrogen yield appears to be the same for all the solutions, and is equal to 9.08 ± 0.35 μM./1000 sec., which agrees with the value found for bromide and iodide solutions. The mean rate from water solutions is then 8.9 ± 0.25. It is especially striking that the rate of hydrogen evolution is the same for solutions showing great differences in rate of peroxide decomposition[7] and that while the peroxide was being converted largely to oxygen in the course of the reaction the rate of hydrogen evolution remained unchanged.

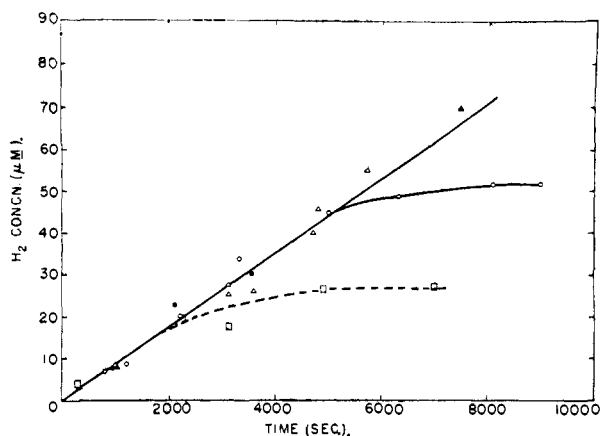Solutions of air or oxygen often gave low and ir-

(7) E. R. Johnson, *J. Chem. Phys.*, **19**, 1204 (1951).

Fig. 6.—Hydrogen produced by X-rays in solutions of H_2O_2 and O_2 in water: O, H_2O_2 (2300 μM.); □, H_2O_2 (95 μM.); △, H_2O_2 (45–5000 μM.) with KI (100 μM.); ⊗, oxygen-saturated water.

reproducible hydrogen yields, but this difficulty seems to have been overcome by pre-irradiating the reaction vessels. Pre-irradiation was performed by exposing the bulbs, filled with water, to X-rays until they showed a faint brown color (about 70,000 r.).

Solutions in 0.8 N H_2SO_4.—Figure 7 shows hydrogen yields from the irradiation of air-saturated 0.8 N H_2SO_4, deaerated 10^{-3} M ceric sulfate in 0.8 N H_2SO_4, and oxygen-saturated 10^{-3} M ferrous ammonium sulfate in 0.8 N H_2SO_4. The initial rate of hydrogen production is the same in all three solutions, and equal to 7.24 ± 0.51 μM./1000 sec., which is significantly lower than the value from solutions in pure water.
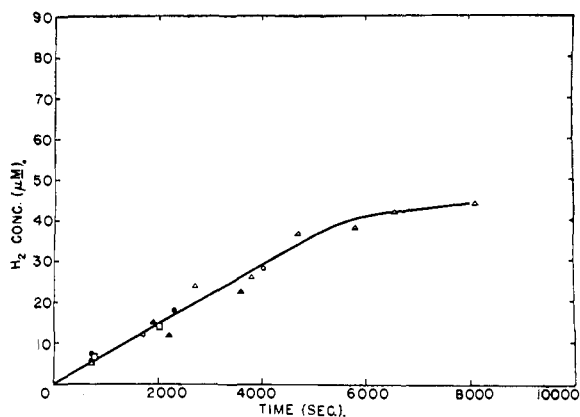

Fig. 7.—Hydrogen produced by X-rays in solutions in 0.8 N H_2SO_4: O, oxygen-saturated ferrous ammonium sulfate; △, deaerated ceric sulfate; □, air-saturated only.

As expected, excess oxygen appears along with hydrogen in the irradiated ceric sulfate solutions, and oxygen is consumed in the ferrous ammonium sulfate solutions.

Attempts were also made to obtain hydrogen yields from deaerated 10^{-3} M KMnO$_4$ solutions in 0.8 N H_2SO_4, but the results were erratic. However, the hydrogen yield at any dose never exceeded that anticipated from Fig. 7. The low yields were believed due to adsorption of hydrogen, or its catalytic recombination with oxygen, by the MnO$_2$ which is formed during the irradiation.

Discussion

The initial hydrogen yield is the same in a given medium for a variety of solutions, irrespective of the concentration or of the oxidizing or reducing character of the solute. The hydrogen cannot be formed by combination of randomly diffusing H atoms, for if it were the yield would depend on the concentration of active solutes which react with atoms. A direct decomposition of the medium to molecular hydrogen must thus be occurring, as shown in Eq. (2) above.

To evaluate the yield of the molecular decomposition, we have used ferrous ammonium sulfate in 0.8 N H_2SO_4 as an actinometer, in conformity with common practice. The ratios we find of hydrogen produced per unit volume to iron oxidized per unit volume, on exposure to equal doses of X-rays, are 0.0385 ± 0.0011 for water solutions and 0.0313 ± 0.0022 for 0.8 N H_2SO_4 solutions. Considering the yield ratio on the basis of unit energy absorption, we remember that volume absorption coefficients for such hard X-rays as we have used are proportional to the density of the material. The ratio of the yield, per unit energy input, of hydrogen molecules from water to that of ferric ions from ferrous sulfate solution in 0.8 N H_2SO_4 is therefore equal to 0.0385 multiplied by the specific gravity of the acid solution (1.0257), or 0.0395 ± 0.0011.

Fricke and Hart,[8] using X-rays of effective wave length 0.3 Å., obtained a constant hydrogen yield from dilute solutions of bromide, iodide, nitrite, arsenite, ferrocyanide and selenite, and give 0.0316 for the ratio of the yield of hydrogen produced to that of iron oxidized in the $FeSO_4$, 0.8 N H_2SO_4 actinometer, per unit volume, for equal radiations. Since the effective mass absorption coefficient at 0.3 Å. is 12% greater for 0.8 N H_2SO_4 than for H_2O,[9]

(8) H. Fricke and E. J. Hart, J. Chem. Phys., 3, 365, 596 (1935).
(9) D. E. Lea, "Actions of Radiations on Living Cells," The Macmillan Co., New York, N. Y., 1947, pp. 345–348.

their yield ratio on the energy basis is 0.0316 × 1.12 × 1.0257 = 0.0364. Hochanadel[3] determined the molecular yield from the peroxide formed in acid bromide solutions, and his ratio to the ferrous sulfate actinometer on the energy basis is 0.0297.

To determine the absolute molecular yield in water decomposition, the ratios discussed above must be multiplied by the absolute yield of the ferrous sulfate actinometer. Authorities unfortunately disagree on the yield of the actinometer; Hochanadel[3] gives a value of 15.5 ferrous ions oxidized per 100 e.v. energy input, while Miller[10] gives 20.6.

The molecular decomposition probably occurs in the regions of high density of energy release (hot spots) which appear along the track of a fast electron as a result of the formation of relatively slow secondary electrons. (In cloud chamber photographs these regions appear as clusters of ions.[11,12]) If water molecules in these regions are regarded as decomposing first to radicals H and OH, many of these radicals must immediately combine in like pairs to H_2 and H_2O_2. Since millimolar solutes have no effect on the molecular yield, the diameters of the hot spots must not be larger than the average distance between solute molecules in a millimolar solution (about 120 Å.).

In 0.8 N H_2SO_4 solutions, about 4% of the energy expended in the solution is initially taken up by HSO_4^- ions rather than by H_2O. Any sulfate groups initially broken up must regenerate themselves spontaneously, since no reduction of sulfate appears to occur in these solutions. The net result is to give a lower yield of hydrogen in H_2SO_4 solutions than in more dilute water solutions.

(10) N. Miller, J. Chem. Phys., 18, 79 (1950).
(11) E. Kara-Michailova and D. E. Lea, Proc. Camb. Phil. Soc., 36, 101 (1940).
(12) W. J. Beekman, Physica, 15, 327 (1949).

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