[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Hydrogen Yields in the Radiolysis of Aqueous Solutions(1)

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The yield of molecular hydrogen from irradiation of various neutral and alkaline aqueous solutions by γ-rays or hard X-rays is now found to be 0.45 molecule per 100 e.v., independent of temperature from 4 to 65°. It is unchanged by addition of 0.4 M NaCl but is lowered by addition of H_2SO_4. In acid solutions of potassium iodide, additional formation of hydrogen occurs, which is suppressed by the presence of iodine; the additional hydrogen is believed to arise from an acid-dependent oxidation of iodide by H atoms, as postulated by Weiss.

This paper presents new data on the yield of molecular hydrogen in γ-ray or hard X-ray radiolysis of water which extend those of Johnson and Allen(2) and are believed to be more accurate.

Experimental

Two types of radiation were used; X-rays from a 2-Mev. Van de Graaff accelerator (built by High Voltage Engineering Corporation) and γ-rays from a 120-curie cylindrical Co^{60} source described elsewhere.(3) Both sources gave the same results.

The sample bulbs used in the γ-ray source were Pyrex tubes 10 mm. o.d. and approximately 15 cm. long, fitted at one end with a break-off seal and at the other end with a constriction through which the sample was filled and sealed. The sample bulbs for the X-ray exposures were Pyrex cylinders, 2 cm. deep, 4 cm. o.d. and bearing two side-arms, one fitted with a break-off and the other provided for filling. As part of the cleaning procedure, the tubes were filled with water and preirradiated with doses of at least 2.5×10^5 r. The tubes were then flushed with steam for several minutes, sealed to a manifold and filled with degassed solution in a manner similar to that employed by Johnson.(2)

Distilled water was further purified as described by Johnson and Allen.(2) Other chemicals were reagent grade and used without further purification.

To remove gas produced in the irradiation, the break-off was sealed to the analysis system and the sample admitted into an evacuated 50-cc. bulb where it was stirred vigorously by a glass-enclosed magnet, then frozen while the gas was removed by a Toepler pump. This procedure was repeated once or twice to ensure removal of all the gas. Other degassing methods (refluxing the sample and shaking) were tried and gave the same results. The gas was analyzed by combustion of the hydrogen in oxygen on a platinum filament, and measurement on a McLeod gage of the pressure decrease, a similar method to that employed by Johnson.(2) A cold finger in the system was kept in liquid nitrogen before and after combustion to remove the water vapor.

The volume of the analysis system was determined by pressure measurement when a known amount of gas was let into the system with the mercury just below the point at which it cut the McLeod gage off from the system. The McLeod gage was calibrated in a similar way and also by mercury and water weighings. The combined standard deviations in the calibration amounted to 1.6%.

The cobalt source and the Van de Graaff X-rays were calibrated by determining the rate of oxidation of 10^{-3} M ferrous sulfate in 0.4 M H_2SO_4. The solutions were made millimolar in sodium chloride in order to protect the reaction from interference by organic matter. Calibrations have been made in this manner for the Co^{60} source over a period of five months, the results indicating decay of the activity with the accepted half-life of 5.2 years. The rate of oxidation on October 10, 1953, was 10.9 ± 0.1 micromoles/l. of ferrous ion oxidized per minute. The intensities employed with the X-rays were (in the same units) 56.6 and 16.6.

Results and Discussion

The irradiation unit in Figs. 1–3 is the number of micromoles/l. of Fe^{++} ion in 0.4 M H_2SO_4 that would be oxidized by the dose applied. This unit facilitates the comparison of results obtained with different radiation sources.

The ratio of the hydrogen gas yield at 25° from various dilute neutral or alkaline solutions to the yield of ferrous sulfate oxidation is 0.0280 with a standard deviation of 0.0007 (Fig. 1). Since the standard deviation of the calibration of the analysis line is 1.6% and the standard deviation of the measurement of the rate of oxidation of ferrous sulfate is 0.9%, the total standard deviation of the hydrogen yield is ±0.009. Using a G (molecules converted per 100 e.v.) of 15.8 for the oxidation of ferrous sulfate and a γ-ray stopping power ratio of 0.4 M H_2SO_4 to water of 1.025, $G_{H_2} = 0.452$.

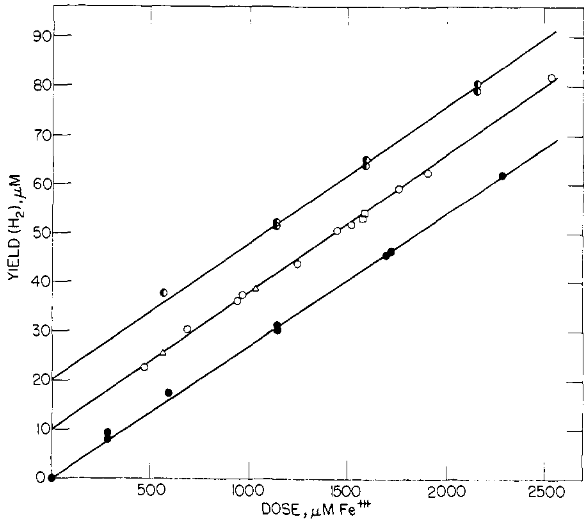

Fig. 1.—Hydrogen yields from aqueous solution as a function of temperature and composition: ●, 2×10^{-3} M KI at 4.5°; ◐, 2×10^{-3} M KI at 65°; ○, 5×10^{-4}–2×10^{-3} M KBr at 25°; Δ, 10^{-3} M KNO_2, $pH \sim 11$ at 25°; □, 2×10^{-3} M $NaAsO_2$, pH 10.4 at 25°. The origins of the three curves are raised progressively by 10 μM in order to facilitate comparison.

The yields reported by Johnson and Allen(2) showed somewhat more scattering, but the mean value of the yield was considerably higher. An important source of error in their data may have been the presence of traces of nitrogen in the gas. They usually ran a combustion on the gas sample and assumed the residue was excess hydrogen. In all runs presented here, a final combustion was run with excess oxygen added to the sample, thus ensuring that hydrogen was specifically determined. Despite careful deaeration, we find up to 7 micro-

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) E. R. Johnson and A. O. Allen, THIS JOURNAL, **74**, 4147 (1952).

(3) H. A. Schwarz and A. O. Allen, *Nucleonics*, **12**, No. 2, 58 (1954).

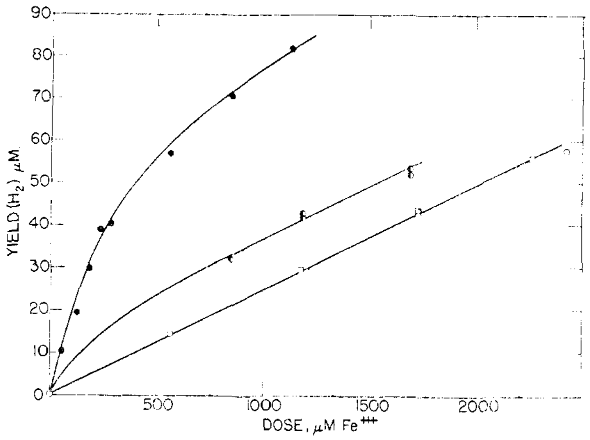

Fig. 2.—Hydrogen production from KI solutions in 0.4 *M* H_2SO_4 at 25°: ●, 1×10^{-2} *M* KI; ◐, 2×10^{-3} *M* KI; ○, 1×10^{-3} *M* KI + 1×10^{-3} *M* I_2; ⊐, 5×10^{-4} *M* I_2.

moles/l. of inert gas, presumably nitrogen, in the irradiated solutions. It is not impossible that the radiation may release, from the vessel walls, small amounts of gas normally held firmly in the glass.

The yield of hydrogen gas in basic $NaAsO_2$ and basic KNO_2 (Fig. 1) is seen to be the same as found in neutral solutions of KBr, KI, etc. This observation is in disagreement with the results of Haissinsky and Lefort[4] who found $G_{H_2} \sim 3.6$ in arsenite solutions at a *p*H of 10.5, but agrees with Fricke and Hart,[5] who report G_{H_2} independent of *p*H from *p*H 2 to *p*H 11.

The least mean square values of the H_2 yield from 2×10^{-3} *M* KI solutions (relative to $FeSO_4$ oxidized at 25°) were 0.027 at 4.5° and 0.028 at 65° (Fig. 1), thus showing no change with temperature within experimental error.

The hydrogen yield in solutions of KI in 0.4 *M* H_2SO_4 is seen from Fig. 2 to be dependent on the KI concentration and on the total dose. Iodine was found to be a prominent reaction product. Similar effects were noted by Rigg and Weiss[6] in the photolysis of acid iodide solutions and were attributed to the reactions

$$H + H^+ \rightleftarrows H_2^+ \qquad (1)$$

$$H_2^+ + I^- \longrightarrow H_2 + I \qquad (2)$$

Such reactions would lead in the case of γ-rays to an extra yield of H_2 in acid solution, beyond the normal molecular yield found in all solutions. A similar explanation was offered by Weiss[7] for the high yields of hydrogen found on irradiation of acid ferrous sulfate solutions. In the present case, the rate of hydrogen production is seen to drop and eventually attain a constant value as the reaction proceeds and iodine accumulates in the solution. The drop is attributed to the reaction

$$H + I_2 \longrightarrow H^+ + I^- + I \qquad (3)$$

which competes with 1 and 2. Then at sufficiently high concentration ratios of iodine to iodide, the extra H_2 arising from atomic H will be suppressed. The limiting slope of the curves at large doses is then interpreted as the true molecular yield of H_2 coming from water in these solutions. The lowest curve in Fig. 2 shows that if I_2 is added to the KI solution before irradiation, this limiting slope appears from the beginning, in agreement with this explanation.

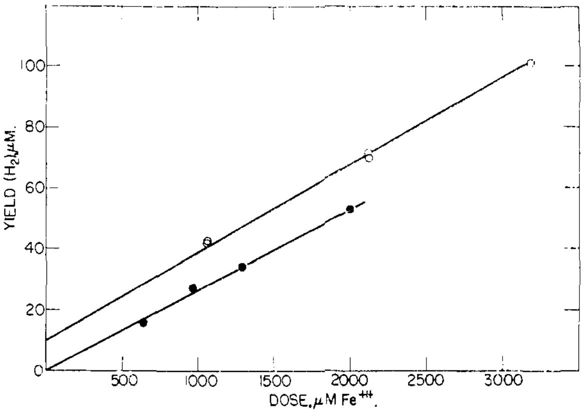

Fig. 3.—Hydrogen yields from aqueous solutions: ●, 5×10^{-4} *M* I_2 in 1 *M* H_2SO_4; ○, 5×10^{-4} *M* KBr in 0.4 *M* NaCl (the origin of this curve is raised 10 µ*M*).

The molecular yield in 0.4 *M* H_2SO_4 from Fig. 2 (with KI and I_2 added) is 0.0248 or $G_{H_2} = 0.392$. This is about 13% smaller than in neutral solutions, and is the same as that observed by Hochanadel[8] in aerated ferrous sulfate solutions in 0.4 *M* H_2SO_4. Miller[9] found a 16% smaller yield of H_2 in the $FeSO_4$, O_2 solution in 0.4 *M* H_2SO_4 than in neutral solutions, although the absolute values of his yields are about 14% larger than ours.

The hydrogen yield in 1 *M* H_2SO_4 (Fig. 3) is 0.0263, which, when corrected for electron density, gives $G_{H_2} = 0.376$ or slightly lower than in 0.4 *M* H_2SO_4. The difference in yields between 0.4 *M* H_2SO_4 and 1 *M* H_2SO_4 is slight (4%) compared to that between neutral solutions and 0.4 *M* acid. The lowering of the yield is not first order in H_2SO_4 concentration.

In 0.4 *M* NaCl with 10^{-4} *M* KBr added (Fig. 3), $G_{H_2} = 0.456$. Thus the addition of NaCl does not produce a lowering of the molecular yield; the lowering produced by sulfuric acid is not merely an effect of ionic strength. Further work is in progress on effects of electrolytes at relatively high concentrations.

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