The Decomposition of Sulfuric Acid by Cobalt γ-Rays

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Some chemical effects of γ-rays on solutions in dilute sulfuric acid have been interpreted as evidence for direct action[1] of the radiation on the acid and for reactions of the acid with the H and OH radicals produced by decomposition of the water.[2,3] It was of interest, therefore, to determine directly the radiation stability of sulfuric acid in aqueous solutions.

The decomposition of sulfuric acid was determined by measurements of the amount of SO_2 that could be swept out of solution during and after irradiation. A steam of purified helium entered the bottom of the radiation vessel through a fritted glass disc, bubbled through the acid, and then bubbled through two absorption cells containing dilute ceric sulfate solutions in series in a Beckman model DU quartz spectrophotometer. Quantitative determinations of SO_2 were made indirectly by measurements of the changes in optical absorption of the ceric sulfate solutions at 320 mμ. SO_2 was qualitatively identified directly in irradiated 95% sulfuric acid by its ultraviolet absorption peak at 280 mμ.

Little or no SO_2 could be detected in irradiated solutions containing less than 60% sulfuric acid. In solutions containing more than 60% sulfuric acid, SO_2 was produced at a rate which increased with increasing acid concentration and decreased with increasing dose as shown in Fig. 1. Each point in Fig. 1 represents the total amount of SO_2 obtained by sweeping with helium for periods up to 30 minutes after irradiation until the optical density of the ceric sulfate solutions was constant. Each curve in Fig. 1 was obtained by successive irradiations of one solution.

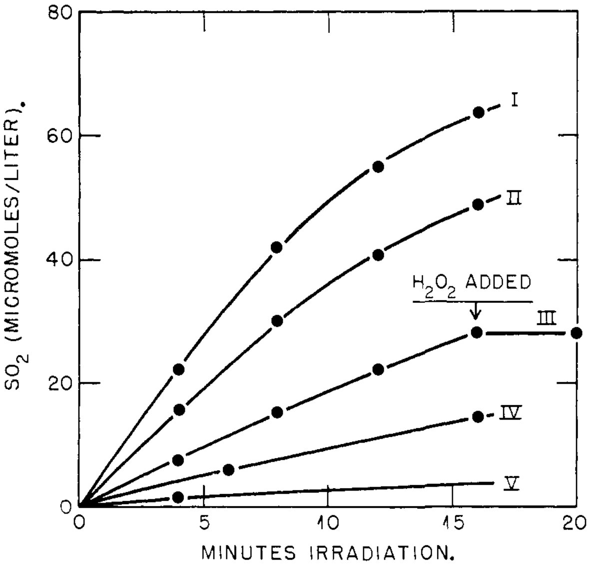

Fig. 1.—SO_2 production from sulfuric acid solutions irradiated with cobalt γ-rays. Acid concentrations in the helium swept solutions: I, slightly fuming; II, 95%; III, 82%; IV 76%; V, oxygen swept 95% sulfuric acid.

Solutions were prepared with J. T. Baker Analyzed Reagent acid, J. T. Baker Analyzed Reagent 20% fuming acid, and Baker and Adamson C.P. acid. Little difference was observed in the decomposition of the different acids. A small amount of SO_2, initially present in all solutions, was removed prior to irradiation by sweeping with helium until a constant optical density was obtained for the ceric sulfate solutions.

Solutions were irradiated with cobalt γ-rays of unvarying intensity distribution within a cylindrical 300 curie cobalt^{60} source.[4] The rate of energy absorption in solution was calculated relative to the rate of ferrous ion oxidation in the same radiation vessel containing a 10^{-3} molar ferrous sulfate solution in air-saturated 0.8 *N* sulfuric acid. The rate of ferrous ion oxidation for this dosimeter was determined by a calorimetric calibration[5] to be 15.6 ± 0.3 ferrous ions oxidized per 100 e.v. absorbed. It was assumed for calculations of the SO_2 yields that γ-ray absorption is entirely by Compton scattering and that the total energy absorbed is therefore proportional to the total number of electrons.

The estimated initial yields of SO_2 are plotted in Fig. 2 as a function of electron fraction for sulfuric acid. A plot of the SO_2 yield as a function of the energy absorbed by the acid would be more significant. This would necessitate correction of the electron fraction to account for the difference in electron stopping powers of the acid and water. The correction, difficult to evaluate, would be small since the ratio of stopping powers per electron for acid and water can be estimated from the data of Gray[6] to be about 0.95 for electrons produced by radium γ-rays.

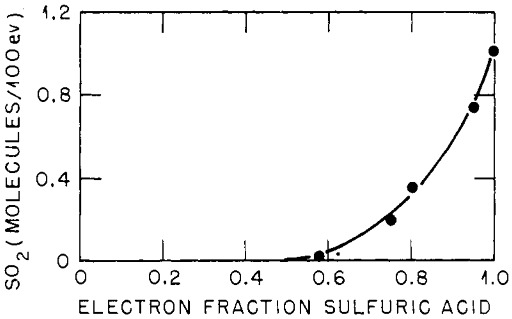

Fig. 2.—Initial yields of SO_2 as a function of the electron fraction sulfuric acid.

Even though the SO_2 was continually swept out of solution during irradiation, the rate of SO_2 production decreased with increasing dose. This indicates either (a) the formation of a non-volatile oxidant in solution which suppresses further SO_2 production or (b) the presence initially of a reductant impurity. Further production of SO_2 was completely inhibited in 82% sulfuric acid by the addition of 0.2 mole/liter of H_2O_2 as shown in Fig. 1. When 95% sulfuric acid was swept with oxygen instead of helium, SO_2 production was greatly reduced as shown in Fig. 1 while sweeping with hydrogen gave the same results as sweeping with helium.

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Halide Films at the Convection Mercury Electrode

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Little is known about the formation and properties of insoluble films on liquid mercury surfaces.[1-4] Current–voltage curves observed at the convection mercury electrode[5] in halide solutions were found to provide conclusive evidence of the forma-

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