The Decomposition of Sulfuric Acid by Cobalt γ-Rays

By C. J. Hochanadel, J. A. Ghormley and T. J. Sworski

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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.

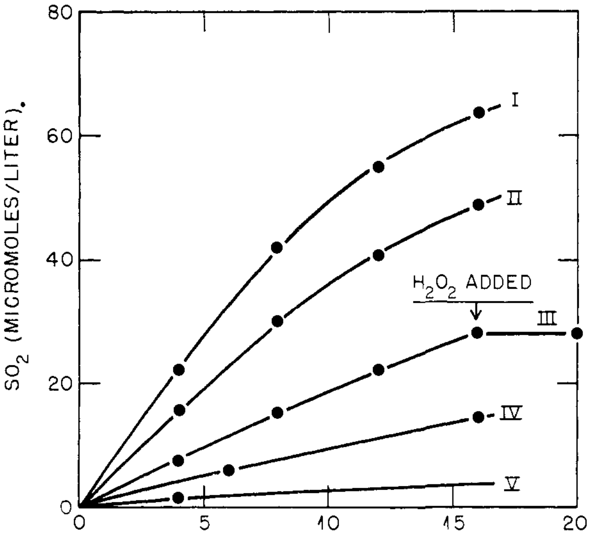

Fig. 1.—SO_2 production from sulfuric acid solutions irradiated with cobalt γ-rays. Acid concentrations in the helium swept solutions: I, slightly fuming; II, 95%; III, 82%; IV 76%; V, oxygen swept 95% sulfuric acid.

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.

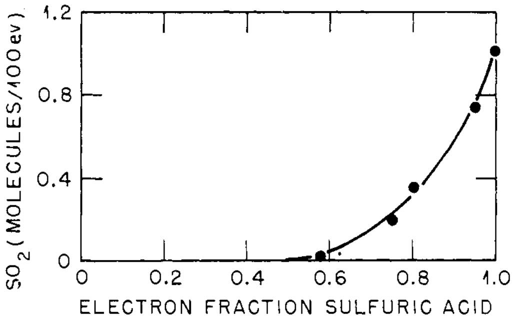

Fig. 2.—Initial yields of SO_2 as a function of the electron fraction sulfuric acid.

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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[1] E. R. Johnson and A. O. Allen, This Journal, **74**, 4147 (1952).

[2] A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, *J. Phys. Chem.*, **56**, 575 (1952).

[3] T. J. Sworski, *J. Chem. Phys.*, **21**, 375 (1953).

[4] J. A. Ghormley and C. J. Hochanadel, *Rev. Sci. Instr.*, **22**, 473 (1951).

[5] C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **21**, 880 (1953).

[6] L. H. Gray, *Brit. J. Radiology*, **22**, 677 (1949).

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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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[1] V. Majer, *Collection Czechoslov. Chem. Communs.*, **7**, 215 (1935).

[2] I. M. Kolthoff and C. Barnum, This Journal, **62**, 3061 (1940).

[3] I. M. Kolthoff and C. S. Miller, *ibid.*, **63**, 1405 (1941).

[4] J. J. Lingane and L. W. Niedrach, *ibid.*, **71**, 196 (1949).

[5] I. M. Kolthoff, J. Jordan and S. Prager, *ibid.*, **76**, 5221 (1954).

tion of insoluble mercurous halide films, between 50 and 500 Å. thick, which adhered to the mercury surface with remarkable tenacity while the ambient solution was being stirred vigorously by forced convection.

The experimental setup of the convection mercury electrode (CME) was the same as described in a previous paper.[5] The effective area of our indicator electrode was 0.023 sq. cm. and the sensitivity[6] 24.0 μa./milliequivalent per l. Current-voltage (c.v.) curves and current-time (c.t.) curves were recorded with a Sargent XXI Polarograph at a chart speed of 2.53 cm./min. The rate of change of applied potential, $\Delta v/\Delta t$, was 2.47 mv./sec. in all c.v. experiments. An acetate buffer of *p*H 5.0, 0.1 *M* in total acetate, was selected as supporting electrolyte because it yielded negligible residual currents in the working range of potentials. The volume of solution was 150 ml. in all experiments.

The shape of the c.v. curves depended on whether they were recorded from negative to positive potentials or *vice versa*. In Fig. 1 are plotted examples of c.v. curves of 10^{-4} *M* halide solutions recorded from positive to negative potentials starting at +0.3 v. (*vs.* SCE). The c.v. curves of all three halides exhibit cathodic "dissolution patterns."[7] Iodide (curve IV) yields a well-defined anodic convection current in a range of potentials between zero and +0.23 v. and bromide (curve III) an ill-defined one at about +0.2 v. No convection current was observed in 0.0001 *M* chloride (curve II) as the anodic chloride current, which starts at +0.23 v. overlaps at about 3 μa. with the dissolution current of mercury in the halide-free supporting electrolyte. "Zero current potentials" *versus* the SCE observed in the 0.0001 *M* halide solutions are: +0.23 v. for chloride, +0.12 v. for bromide and −0.07 v. for iodide. The corresponding thermodynamic equilibrium potentials, calculated from Latimer's data[8] for the mercury-mercurous halide couples, are +0.25, +0.13 and −0.05 v., respectively. The agreement within 0.02 v. between the reversible potentials of the mercury-mercurous halide electrodes and our zero current potentials identifies the films on the CME as Hg_2Cl_2, Hg_2Br_2 and Hg_2I_2, respectively.

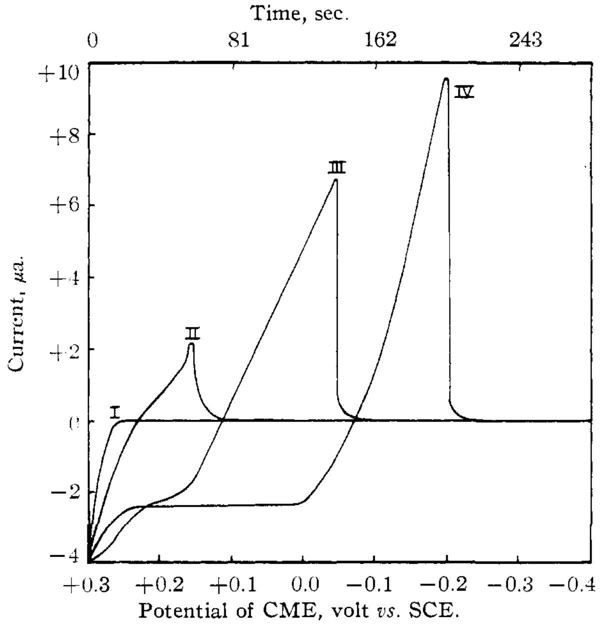

Fig. 1.—Current-voltage curves of 10^{-4} *M* halide solutions, recorded from positive to negative potentials. Supporting electrolyte: acetate buffer of *p*H 5.0, 0.1 *M* in total acetate. Lower abscissa represents potential, upper abscissa gives time. I, residual current; II, KCl; III, KBr; IV, KI.

Since the rate of change of applied potential was constant, the abscissa in Fig. 1 can represent potential or time. Thus, the amount of electricity in the anodic area and in the cathodic dissolution area can be readily evaluated. The values obtained have approximate significance only, especially when short times are involved, because the response of our recording instrument has a time-lag between about $^1/_2$ and 5 sec. The anodic and cathodic areas, expressed in faraday, for the 0.0001 *M* halide solutions were 5.3×10^{-10} and 3.3×10^{-10} for chloride, 2.3×10^{-9} and 2.2×10^{-9} for bromide, and 3.5×10^{-9} and 2.4×10^{-9} for iodide. The characteristic quasi-triangular shape of the dissolution patterns is accounted for by the increase in the rate of dissolution of the film as the potential is made more negative, followed by an abrupt decrease to zero of the reduction current when the film is completely removed.[7]

C.v. curves run from negative to positive potentials gave only anodic waves similar in shape to the anodic portion of the curves in Fig. 1.

Characteristics of the c.v. curves of iodide—the only halide which yielded a well-defined convection current—were investigated at several concentrations. The convection current, i_{conv}, of iodide at +0.1 v. was proportional to concentration in a range between 5×10^{-6} and 10^{-4} *M*, i_{conv}/C being equal to (24.3 ± 0.9) μÅ./millimole per l. At concentrations larger than 10^{-4} *M* iodide gave a limiting current, i_l, which was smaller than the convection current. For instance, in 2.32×10^{-4} and 1.77×10^{-3} *M* iodide solutions i_l/C was equal to 22.0 and 1.41 μa./millimole per l. C.t. curves recorded at a constant potential of +0.1 v. indicated that in a range of concentrations between 5×10^{-6} and 10^{-4} *M* the convection current of iodide did not vary for at least 15 min., whereas the limiting current in 2.32×10^{-4} *M* iodide solution decayed linearly with time in about 5 min. from 5.56 to 4.05 μa. The 10^{-4} *M* iodide solution yielded dissolution patterns after electrolysis at +0.1 v. for periods as short as 1-5 seconds. The area of dissolution patterns of 2.32×10^{-4} and 1.77×10^{-3} *M* iodide solutions, obtained from c.v. curves recorded under the same conditions as in Fig. 1, corresponded to 5×10^{-10} and 10^{-9} Faraday, respectively.

Discussion

From the current-time area of the cathodic dis-

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[6] I. M. Kolthoff and J. Jordan, THIS JOURNAL, **76**, 3843 (1954).

[7] I. M. Kolthoff and J. Jordan, *ibid.*, **74**, 510 (1952).

[8] W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Second Edition, Prentice-Hall, Inc., New York, N. Y., 1952, p. 175-176.

solution patterns, the molecular weights, the density of the solid mercurous halides and the effective area of our indicator electrode, were calculated the thickness of the halide films expressed in Å. and also in molecular diameters. Diameters were evaluated from interatomic distances given by Wyckoff[9] for linear molecules of the type X–Hg–Hg–X of which the tetragonal crystals of the mercurous halides are built.[10] The data are presented in Table I.

TABLE I

THICKNESS OF MERCUROUS HALIDE FILMS ON THE MERCURY CONVECTION ELECTRODE

Halide	Concn. (moles/l.)	Approximate thickness of film Å.	Mol. diameter
Chloride	1.00×10^{-4}	50	7
Bromide	1.00×10^{-4}	370	48
Iodide	1.00×10^{-4}	440	55
Iodide	2.32×10^{-4}	90	11
Iodide	1.77×10^{-3}	180	22

The most striking result in Table I is that the film obtained in 10^{-4} *M* iodide was about 5 times and 2.5 times as thick as those observed in 2.3×10^{-4} and 1.8×10^{-3} *M* solutions. In spite of this, in 10^{-4} *M* solution the true convection current was measured which remained constant with time, while the limiting currents in the more concentrated solutions were much smaller than the convection currents and decayed with time. In agreement with Majer[1]) and Müller, *et al.*,[11] it is concluded that the resistance exhibited by the film is not determined by its thickness but by its structure which in turn determines its permeability to the electroactive species. According to Müller, this permeability is determined by the structure of the first molecular layer which is formed. The convection electrode appears to be ideally suited for a systematic study of the permeability of films formed under various conditions. Our estimates of between 5 and 50 molecular diameters (Table I) are of the same order of magnitude as Majer's value[1] of 23 to 29 molecules for films of mercurous chloride and bromide at the dropping mercury electrode.

Acknowledgment.—This investigation was supported by research grants from the National Science Foundation and the Graduate School of the University of Minnesota.

[9] R. W. G. Wyckoff, "Crystal Structures," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1951, Chapter III, table, page 43.

[10] R. J. Havighurst, THIS JOURNAL, **48**, 2113 (1926).

[11] W. J. Müller, *Z. Elektrochem.*, **38**, 854 (1932); **40**, 119 (1939); **41**, 83 (1935); W. J. Müller and K. Konopicky, *Monatsh.*, **48**, 711 (1927); W. J. Müller and L. Holleck, *ibid.*, **52**, 409, 425 (1929).

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Rates of Neutralization of C_1 to C_4 Nitroparaffins

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The kinetics of neutralization of the C_1 to C_3 nitroparaffins by hydroxide ion

$$R_1R_2CHNO_2 + OH^- = R_1R_2CNO_2^- + H_2O \quad (1)$$

have been studied by 1000-cycle conductivity[1a,b] at 0 and 5° and by polarography[1c] in buffered solution at 25°. The mechanism of the reaction has been thoroughly discussed.[1] The C_4 nitroparaffins have apparently not been investigated; neither have the compounds been studied at 25° in unbuffered medium.

The present investigation describes measurement of the neutralization rates of six lower C_1 to C_4 primary and secondary nitroparaffins by a megacycle frequency oscillator circuit, using an insulated cell. Such application is possible because of the large change in solution conductivity as the reaction of equation 1 occurs, and hydroxide ion is replaced by the anion. If equivalent conductances do not change over the range of ionic concentration encountered in an experiment (as was assumed by Pearson[1b] and others for higher concentrations than those used here), the changes in reaction (1) can be expressed in terms of measured items which are linear functions of conductance.[2]

Kinetic Data.—The data are summarized in Table I; standard deviations of the mean of the second-order rate constant range from 0.8 to 5.6% with only one exceeding 3.2%.

TABLE I

RATE DATA FOR CONVERSION OF NITROPARAFFINS TO THE ANION

Compound and concn. m*M*	NaOH concn., m*M*	No. of runs	Av. second-order rate constant, *k*, l. mole^{-1} min.$^{-1}$	Av. $t_{1/2}$, min.
Nitromethane, 2.42	0.514	2	1026 ± 8.5 (0.8%)	0.280
Nitroethane, 9.14	.919	3	236 ± 7.6 (3.2%)	0.321
1-Nitropropane, 9.20	.999	3	195 ± 2.1 (1.1%)	0.384
2-Nitropropane, 9.11	.999	5	16.4 ± 0.92 (5.6%)	4.44
1-Nitrobutane, 9.11	.999	4	192 ± 6.2 (3.2%)	0.397
2-Nitrobutane, 9.31	.999	5	8.78 ± 0.162 (1.8%)	8.49

Effect of Possible Reverse Reaction.—The present treatment, which does not make explicit allowance for the effect of opposing reactions, is strictly valid only when the equilibrium in equation 1 lies so far to the right that secondary effects become negligible; consequently, the slopes of the curves have been calculated from the initial values so as to minimize the influence of the reverse reaction. However, when the equilibrium concentration is explicitly introduced in the calculations, a first-order expression is observed for a reversible reaction with the effective rate constant being the sum of the constants for the forward and reverse directions.[3] It is possible to estimate, at least qualitatively, the effect of the reverse reaction for the specific compounds studied.

Miller, Arnold and Astle,[1c] using polarographic measurements, found the fraction of the nitroparaffin remaining in the nitro form in the equilibrium mixture at *p*H 8.9 to be 0.71, 0.20, 0.42 and 0.78 for nitromethane, nitroethane, 1-nitropropane

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[1] (a) S. H. Maron and V. K. La Mer, THIS JOURNAL, **60**, 2588 (1938); (b) R. G. Pearson, *ibid.*, **70**, 204 (1948); (c) E. W. Miller, P. A. Arnold and M. J. Astle, *ibid.*, **70**, 3971 (1948); (d) D. Turnbull and S. H. Maron, *ibid.*, **65**, 212 (1943); (e) C. M. Drew, J. R. McNesby and A. S. Gordon, *ibid.*, **75**, 3098 (1954).

[2] Applicability of megacycle frequency oscillator circuits to reaction rate measurement with emphasis on moderately fast reactions is discussed in P. J. Elving, *Faraday Soc. Discs.*, **17**, 156 (1954). See also D. G. Flom and P. J. Elving, *Anal. Chem.*, **25**, 541, 544, 546 (1953).

[3] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 173.