[CONTRIBUTION FROM THE WALTER B. JAMES LABORATORY FOR BIOPHYSICS, THE BIOLOGICAL LABORATORY, COLD SPRING HARBOR, L. I., N. Y.]

The Reduction of Chromate Solutions by x-Rays[1]

BY HUGO FRICKE AND EUGENE R. BROWNSCOMBE

Some years ago Dr. S. Morse and one of us[2,3,4] showed that x-rays oxidize ferrous sulfate in acid solutions and that this transformation is due to a primary activation of the water by the rays. Since that time, this study has been extended to other substances, solutions of chromate in sulfuric acid being dealt with in a recent report[5] by Dr. Martha Washburn and one of us. The present investigation is an extension of this work.

Experimental Technique

The solutions irradiated contained potassium dichromate in dilute sulfuric acid. To reduce the possibility of contamination, they were prepared with as little handling as possible. The water from a tin still was passed directly into calibrated Pyrex bottles in which the solutions were kept, and the addition of chromate dissolved in concentrated sulfuric acid served to introduce both chemicals at once. All solutions were saturated with air before irradiation.

Chromate concentrations were determined by electrometric titration with ferrous sulfate.

The solutions were irradiated in glass-stoppered Pyrex flasks (20 to 100 cc.) by means of a 5-inch tungsten tube operated at a maximum potential of 120 kv. and with currents ranging from 10 to 50 ma. The time varied in different experiments from ten minutes to a few hours.

A relative measure of the x-ray intensity was given by a string electrometer connected to an ionization chamber. The dosage in r[6] was determined by irradiating a solution of ferrous sulfate in 0.8 N sulfuric acid under the same conditions as were used for the chromate. The concentration of a solution of ferrous sulfate in 0.8 N sulfuric acid containing excess oxygen is decreased 1/57,400 mols per 1000 cc. for each 1000 r of dosage, independent of the wave length, dosage and ferrous sulfate concentration. The wave length independence holds only when the sulfuric acid is 0.8 N, for which concentration the x-ray absorption is the same function of the wave length as holds for atmospheric air.[2,7,8] The value 1/57,400 is based on the results summarized in Table II of the report referred to,[4] according to which an x-ray dosage producing an ionization of 55,000 electrostatic units in one cubic centimeter of air at 18° and 76 cm. pressure oxidizes one milligram molecule of ferrous sulfate in 1000 g. of solution. Making note of the

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[1] This study, which forms a part of a wider investigation, has been aided by grants from the Carnegie Corporation, the Rockefeller Foundation, and the L. K. and D. W. Elmhirst American Committee. The Committee on Biological Effects of Radiations, of the National Research Council, acting through its chairman, Dr. W. C. Curtis, provided part of the equipment through the courtesy of a group of manufacturers, including The Corning Glass Company, The General Electric Company, The National Carbon Company and The Westinghouse x-Ray Company.

[2] Fricke and Morse, *Am. J. Roentgenol. and Radium Therapy*, **18**, 426 (1927); *Strahlentherapie*, **26**, 749 (1927).

[3] Fricke and Morse, *Am. J. Roentgenol. and Radium Therapy*, **18**, 430 (1927); *Strahlentherapie*, **26**, 757 (1927).

[4] Fricke and Morse, *Phil. Mag.*, **7**, 129 (1929).

[5] Fricke and Washburn, *Phys. Rev.*, **40**, 1033 (1932).

[6] An x-ray dosage of one r produces an ionization of one electrostatic unit in one cubic centimeter of atmospheric air at 0° and 76 cm. pressure.

[7] Fricke and Petersen, *Am. J. Roentgenol. and Radium Therapy*, **17**, 611 (1927).

[8] Fricke and Petersen, *Strahlentherapie*, **26**, 329 (1927).

fact that the *r* unit refers to ionization of air at 0° instead of at 18° and that normalities in the present work refer to one liter instead of one kilogram of solution, the value $55{,}000(291/273)1/1.02 = 57{,}400$ is derived as the number of *r* which oxidizes one milligram molecule of ferrous sulfate in 1000 cc. of solution. The figure 1.02 represents the specific gravity of 0.8 N sulfuric acid.

Experimental Results

An acid solution of potassium dichromate is reduced by irradiation with x-rays, a sufficiently prolonged irradiation causing a complete reduction to the trivalent state. The transformation takes place solely during the irradiation. The amount of chromate reduced varies with the acidity, except in strong acid. The effect of acidity is dealt with in one of the following sections, in the rest the medium is 0.8 N sulfuric acid, which is within the range of acidity independence.

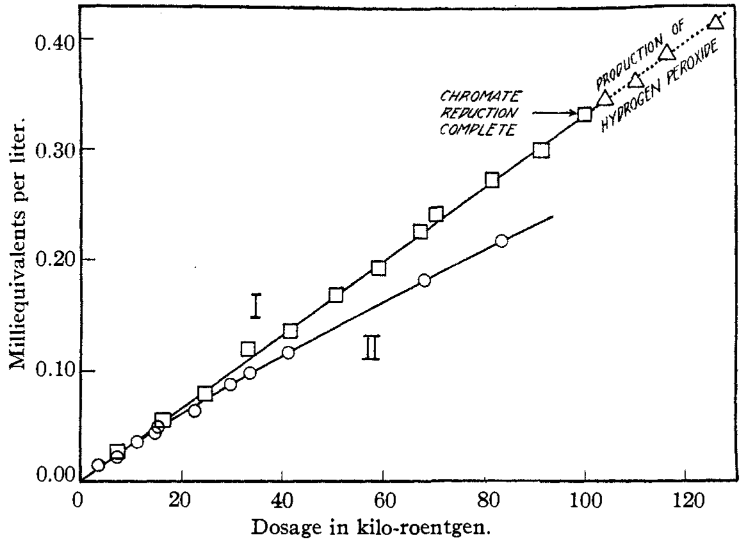

Fig. 1.—Dosage curves for (I) reduction of chromate by irradiation of $0.000333N$ potassium dichromate in $0.8N$ sulfuric acid and (II) production of hydrogen peroxide by irradiation of $0.8N$ sulfuric acid.

Variation of Dosage and Chromate Concentration.—Irradiation of chromate solutions ranging in concentration from $N/500$ to $N/9000$ showed that the amount of chromate reduced is proportional to the dosage and independent of the chromate concentration. This indicates that the primary action of the rays is on the solvent rather than on the chromate. A dosage curve for $N/3000$ chromate is given in Fig. 1 (Curve I). (The dotted extension represents the formation of hydrogen peroxide after the chromate is completely reduced, as discussed below.)

The amount of chromate reduced is 3.31×10^{-6} equivalents per 1000 cc. for each 1000*r* of dosage.

Temperature Coefficient.—Irradiation of $N/9000$ chromate at 5 and 90° gave a temperature coefficient (per ten degrees) of 1.000 ± 0.005. To detect any spurious effect, samples irradiated at 5° were first heated to 90°, and those irradiated at 90° were first cooled to 5°. Controls heated to 90° without irradiation showed no spontaneous reduction.

Production of Hydrogen Peroxide.—It is well known[4,9,10] that hydrogen peroxide is formed by irradiation of water with x-rays, or with radioactive rays. In order to determine if the amount of chromate reduced is to be accounted for by this production of hydrogen peroxide, 0.8 *N* sulfuric acid was irradiated with different dosage, chromate added in surplus, and the solutions titrated with ferrous sulfate. The result of one such series of experiments is shown by Curve II in Fig. 1. The amount of hydrogen peroxide formed is not proportional to the dosage, but the rate of production falls off at higher dosages. This decrease may be accounted for by a decomposition of the hydrogen peroxide by the rays, since it is well known[10,11] that irradiation of aqueous solutions of hydrogen peroxide results in its decomposition. The initial rate of formation of hydrogen peroxide is equal to the rate of reduction of chromate. This fact indicates that the reduction of chromate is related to the production of hydrogen peroxide. The following experiments in which the acidity of the solutions irradiated was varied lead to a more definite formulation of this hypothesis.

Variation of Acidity.—It has already been noted by earlier investigators[10,12] that the hydrogen-ion concentration is a factor in the reactions produced by irradiating aqueous solutions, but no accurate determinations of the relationship are on record. So far our own experiments are preliminary, but because of the pertinent implication of the results it is desirable to include them here.

The irradiations were not carried out in buffered solutions, but potassium dichromate was dissolved in a series of sulfuric acid solutions ranging in concentration from 0.8 *N* to pure water. The chromate concentration was *N*/9000. In the lower concentrations of sulfuric acid it should be noted that the chromate is an appreciable factor in determining the *P*H of the solution, and that the *P*H is changed considerably by the irradiation.

In one set of experiments these chromate solutions of different acidity were irradiated with a dosage sufficient to reduce half the chromate of the 0.8 *N* solution. After irradiation, sulfuric acid was added to bring the concentration to 0.8 *N* and the solutions analyzed for chromate as usual. The amount of chromate reduced, given as percentage of the reduction observed at 0.8 *N* sulfuric acid, is shown in Curve I, Fig. 2. As cited above, the reduction becomes constant at high acidities. The sharp minimum a little below 10^{-3} *N* sulfuric acid is a salient feature. It is probable that this minimum extends down to the zero line, but in the absence of direct experimental verification, we have left the curve open at this point.

A similar set of irradiations was run on sulfuric acid of the same concentrations containing no chromate. After irradiation, chromate was added to *N*/9000, then sulfuric acid to 0.8 *N*, and the solutions titrated for chromate as before. The results, which are shown in Curve II (points ⊡) in Fig. 2, agree with those of the preceding experiments in strongly acid and in neutral solutions, but not in the intermediate range. There is no trace of the minimum seen in Curve I. However, as might have been anticipated from facts known[13] about hydrogen peroxide, a time factor is involved in these last experiments. The amount of chromate reduced depends on the difference in time between the addition of the chromate and the addition of the strong acid. Allowing sixteen hours to pass between these two additions, Curve III (points △) is obtained. A minimum now appears at the same place as in Curve I.

This last set of experiments may be explained on the basis of a primary production of hydrogen peroxide and its subsequent catalytic decomposition by chromate at a rate depending upon the acidity, with a maximum near 10^{-3} *N* sulfuric acid.[13] In order to

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(9) Kernbaum, *Le Radium*, **6**, 225 (1909).

(10) Risse, *Z. physik. Chem.*, **A140**, 133 (1929).

(11) Kailan, *Sitzb. Akad. Wiss. Wien*, [IIa] **120**, 1213 (1911).

(12) Ref. 11, p. 1273.

(13) Spitalsky and Koboseff, *Z. physik. Chem.*, **127**, 129 (1927).

test this hypothesis directly, $N/18{,}000$ hydrogen peroxide in $N/9000$ chromate at the different acidities used above was allowed to stand sixteen hours, then acidified to 0.8 N sulfuric acid and analyzed for chromate. This set of experiments is similar to the previous one, except that the addition of hydrogen peroxide replaces irradiation. The results are shown by points ▽ in Fig. 2, and are seen to fit Curve III.

The similarity of Curves I and III suggests that the decrease in x-ray effect on chromate in the intermediate range of acidities is due to the decomposition of hydrogen peroxide. The fact that the decomposition observed for normal hydrogen peroxide is negligible during the length of time an irradiation lasts presents an apparent inconsistency which may be solved by assuming that the x-rays produce the hydrogen peroxide initially in an activated form. This reasoning implies that this active form is involved also in the decomposition of normal hydrogen peroxide, lending an additional interest to the study of the action of x-rays from the bearing it may have in the purely chemical field.

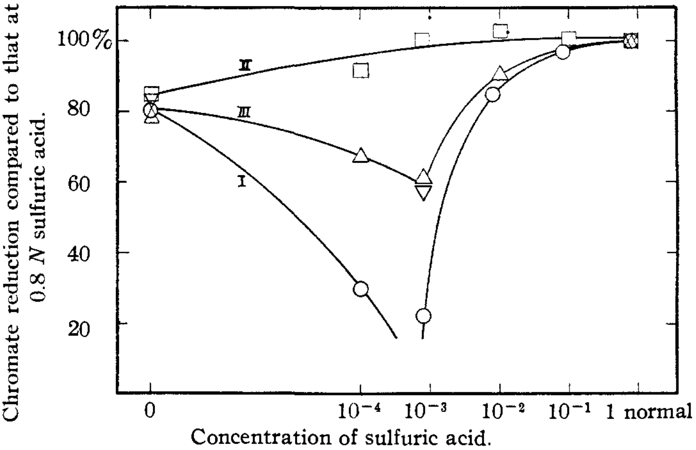

Fig. 2.—The reduction of chromate by x-rays as a function of acidity; Curve I, ⊙, irradiation of $N/9000$ chromate; Curve II, ⊡, irradiation of sulfuric acid and addition of chromate and strong acid immediately; Curve III, △, irradiation of sulfuric acid, addition of chromate immediately, and of strong acid sixteen hours later; Curve III, ▽, addition of hydrogen peroxide to $N/9000$ chromate and of strong acid sixteen hours later.

Influence of Foreign Substances.—That impurities played an important role in the action of the rays was indicated by the irregularity of early results. Experiments were therefore carried out in which substances likely to be active and to be present as impurities were added to chromate solutions, and the effect of irradiation determined. So far, the ammonium, mercuric, and ferric ions, and a number of organic substances, have been tested.

Ammonium sulfate, mercuric sulfate and ferric sulfate were each added in a concentration of 1/10,000 N and were all found to be without effect.

As previously reported,[5] traces of organic substances increase the amount of chromate reduced by irradiation. This has been found to be true for all of some thirty different substances tested, including especially acids, alcohols and aldehydes of the paraffin series. The effect is not peculiar to chromate, but is of a more general nature, the primary production of hydrogen peroxide itself being increased. Although not previously recognized, it was probably responsible for the irregularity of results characteristic of earlier work on chemical effects of x-rays in aqueous solutions.

In plotting the increase in chromate reduction as a function of the concentration of organic substances curves are obtained which are similar at high dilution, but which show characteristic differences at higher concentrations. In particular, for substances of higher reducing power the curves continue to rise at high concentrations, while those for inactive substances come to a constant level. Some of the latter may be represented by the function $\alpha C/(\beta + C)$, where C is the concentration of organic substance, and α and β are constants, α being the same for the different substances while β varies from one substance to another. Most substances begin to give noticeable effects within the concentration range 10^{-5} to 10^{-7} molar. This high dilution indicates the operation of a catalytic action The fact that in the presence of organic substances the reduction remains a linear function of the dosage confirms this inference. The results point to one effect of a general nature predominating at low concentrations with others more specific coming into play at higher concentrations.

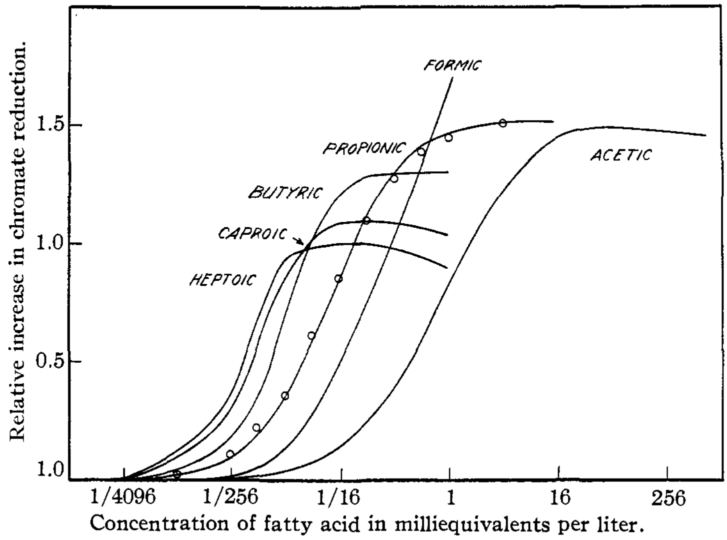

Fig. 3.—The reduction of chromate by x-rays as increased by the presence of fatty acids. The circles are calculated for propionic acid from $1.52C/(0.000052 + C)$.

Figure 3 shows concentration curves for some of the fatty acids in $N/3000$ chromate. The ordinate is the increase in chromate reduction due to the presence of organic substance compared to the reduction found for pure chromate as unity. The circles were calculated from the function given above, the values for α and β being chosen to fit the curve for propionic acid. The abnormality of formic acid is in line with its reducing properties.

Summary

In 0.8 N sulfuric acid 3.31×10^{-6} equivalents of potassium dichromate are reduced per 1000 cc. for each 1000r of x-ray dosage, independent of chromate concentration and of temperature (between 5 and 90°). The dependence on sulfuric acid concentration has been determined. The

results indicate that the reduction is due to a primary production of an activated form of hydrogen peroxide from the water. Traces of organic substances increase the action of the rays catalytically.

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The Photolysis of Gaseous Acetone and the Influence of Water[1]

BY GLENN H. DAMON AND FARRINGTON DANIELS

The action of ultraviolet light on the simplest ketone offers interesting material in the study of kinetics and photochemistry. Quantitative measurements recorded here show that only about one quantum out of every five or six absorbed produces chemical change in gaseous acetone and that this ratio is affected by pressure, intensity of radiation and other factors. Activated acetone molecules may undergo chemical decomposition, but if water is present as a catalyst they are more apt to undergo a condensation reaction.

Henri and Wurmser[2] and Porter and Iddings[3] found that acetone absorbs between 3400 and 2200 Å. with a maximum at about 2800 Å. Porter and Iddings found also that the rate of decomposition into ethane and carbon monoxide was independent of wave length in this region.

Bowen and Watts[4] using light that was not monochromatic reported a quantum yield of 1.8 molecules per quantum. In the present investigation with better apparatus a much smaller yield was obtained.

Apparatus

Monochromatic light at intensities up to 100,000 ergs per second was obtained with a large quartz monochromator[5] and quartz capillary lamps[6] of high intensity. The monochromator was adjusted to give a sharp focus of a line (3130 Å. for example) on a piece of fluorescent uranium glass placed directly behind the slit. The entrance and exit slits were set at 0.6 mm., a width slightly less than the image of the arc. Back of the slit at a distance of 5 cm. a double convex lens of quartz rendered the monochromatic beam parallel. The beam then passed through a quartz window, into a water thermostat controlled to 0.01°. Here it passed through a narrow, rectangular quartz cell and onto a large thermopile connected to a sensitive galvanometer.

The all-quartz reaction cell, made by the Hanovia Chemical Manufacturing Company, is shown in Fig. 1. It consisted of a rectangular box 10 × 1 × 5 cm. with the

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[1] More complete details of this investigation are contained in part of a Ph.D. thesis by Glenn Damon filed in the Library of the University of Wisconsin in June, 1932.

[2] Henri and Wurmser, *Compt. rend.*, **156**, 1013 (1913).

[3] Porter and Iddings, THIS JOURNAL, **48**, 40 (1926).

[4] Bowen and Watts, *J. Chem. Soc.*, 1607 (1926).

[5] Heidt and Daniels, THIS JOURNAL, **54**, 2384 (1932).

[6] *Ibid.*, p. 2381.