

Photochemical Reduction with X Rays and Effects of Addition Agents

George L. Clark and Wesley S. Coe

Citation: [The Journal of Chemical Physics](#) **5**, 97 (1937); doi: 10.1063/1.1749999

View online: <http://dx.doi.org/10.1063/1.1749999>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/5/2?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Xray tube noise and vibration reduction](#)

J. Acoust. Soc. Am. **98**, 3026 (1995); 10.1121/1.413836

[Reduction of driver energy for xray lasers](#)

AIP Conf. Proc. **332**, 423 (1995); 10.1063/1.47932

[Proximity effect reduction in xray mask making using thin silicon dioxide layers](#)

J. Vac. Sci. Technol. B **10**, 3062 (1992); 10.1116/1.585929

[Xray induced reduction effects at CeO₂ surfaces: An xray photoelectron spectroscopy study](#)

J. Vac. Sci. Technol. A **9**, 1416 (1991); 10.1116/1.577638

[A study of proximity effects at high electronbeam voltages for xray mask fabrication. I. Additive mask processes](#)

J. Vac. Sci. Technol. B **8**, 1763 (1990); 10.1116/1.585155

A promotional banner for the 2014 Special Topics in AIP APL Materials. The banner has an orange background with a white border. At the top, the text '2014 Special Topics' is written in a large, white, sans-serif font. Below this, there are five circular icons, each containing a different material structure and a label: 'PEROVSKITES' (red and black), '2D MATERIALS' (blue and red), 'MESOPOROUS MATERIALS' (green and yellow), 'BIOMATERIALS/ BIOELECTRONICS' (yellow and black), and 'METAL-ORGANIC FRAMEWORK MATERIALS' (brown and black). At the bottom left, the AIP APL Materials logo is displayed. At the bottom right, a red banner with white text says 'Submit Today!'.

Photochemical Reduction with X-Rays and Effects of Addition Agents

GEORGE L. CLARK AND WESLEY S. COE

Department of Chemistry, University of Illinois, Urbana, Illinois

(Received November 10, 1936)

Ceric sulfate solution was reduced by exposure to x-radiation. In order to follow this reaction a very accurate method was developed for the determination of ceric sulfate in dilute solutions by the use of orthophenanthroline indicator. The amount of reduction of ceric sulfate by x-rays was found to be practically independent of concentration. Reduction was shown to be directly proportional to time of exposure up to 50 percent and slightly less efficient beyond that point. Silver perchlorate and silver nitrate decreased the amount of reduction of ceric sulfate by x-rays. Mercuric nitrate and acetic acid increased the amount of reduction caused by x-rays. Curves are also presented to show the effect of changing the concentration of these addition agents. Indications are that the mercuric nitrate was truly a catalyst to the reduction of ceric sulfate by x-rays and that the acetic acid increased the amount of reduction by direct action on the ceric sulfate under the influence of x-rays. Perchloric and nitric acids increased the reduction of ceric sulfate appreciably but not to as great an extent as did $\text{Hg}(\text{NO}_3)_2$. Sodium nitrate, perchlorate and sulfate showed no effect. Various organic substances were tried and found to increase the reduction by varying amounts. Experiments were carried out with

various combinations of the catalysts and inhibitors to determine their relative efficiencies. The reduction of potassium permanganate by x-rays proceeded to manganese dioxide for low acid concentrations and to manganous ion at higher acidity. The reaction was greater than for ceric sulfate but not as nearly proportional to dosage. The effect of addition agents was similar to that for ceric sulfate. X-rays did not produce the same reaction in solutions of uranyl sulfate-oxalic acid as does ultraviolet radiation. Solutions of potassium iodate were reduced by x-rays but to a less degree than ceric sulfate or potassium permanganate. Hydrogen peroxide was formed in samples during radiation but did not effect the potassium iodate. Solutions of potassium bromate were not reduced by x-rays but even larger amounts of hydrogen peroxide were formed. Calculations were made for: ions reduced per r unit absorbed, r units necessary for reduction of one equivalent, ions reduced per ion pair formed by x-rays, and calories of absorbed energy necessary for reduction of one equivalent, by two independent methods. A mechanism was proposed for the formation of hydrogen peroxide by x-rays in the presence of dissolved oxygen.

PHOTOCHEMICAL reduction of inorganic compounds by x-rays is an interesting field of investigation which already has received some attention. Chamberlain¹ has reported the reduction of potassium permanganate and potassium iodate by x-rays. These results were only qualitative. Clark and Pickett² made the same observation and did quantitative work on the photolysis of potassium nitrate and potassium iodide by x-rays. Fricke and Brownscombe,³ and Fricke and Washburn⁴ have noted the reduction of potassium dichromate by x-rays and attributed it to the formation of hydrogen peroxide. These workers have also observed large effects of impurities in the irradiated solution.

The formation and decomposition of hydrogen peroxide by x-rays have been the subject of much investigation because of the possibility of its influence on any x-ray photochemical reaction in aqueous medium. Glocker and Risse^{5, 6} studied the effect of wave-length and concentration upon the decomposition of hydrogen peroxide. Risse reported the formation of hydrogen peroxide by

x-rays in water containing dissolved oxygen. Fricke⁷ and Brownscombe⁸ confirmed his report and showed that no hydrogen peroxide was formed in pure air-free water.

The purpose of the present work was to contribute to the knowledge of the quantitative aspects of reductions by x-rays of familiar inorganic reagents in dilute aqueous solution and the catalytic or inhibitory effects of various substances added voluntarily to these solutions.

EXPERIMENTAL

The x-ray tube used for the irradiation of solutions during this investigation was one designed by the authors and constructed in the machine shop at the University of Illinois. It was designed with a metal body for self-protection from stray radiation, a water-cooled copper or tungsten anode to allow a high tube current, and a special aluminum-beryllium alloy window for the efficient transmission of x-rays but not light or heat. A complete description of this tube will appear elsewhere.

Determination of intensity of radiation

Intensity measurements were taken with a Victoreen R meter and corrections made for temperature and atmospheric pressure to give values in terms of the internationally accepted r unit⁹ of x-radiation. The effective wave-length of x-rays emitted from both copper and tungsten targets operating at 55 kilovolts was determined by the method of Duane, Hudson and Sterling¹⁰ involving the determination of percent transmission by a 2 mm aluminum plate. Values of 0.62A for the copper target and 0.60A for the tungsten target were obtained. The general experimental procedure for irradiation was to expose 10 cc of the solution in a 50 cc beaker at a distance of 15 or 20 cm from the focal spot, with the tube operating at 55 kilovolts. Some exposures were made with a tube current of 20 and others with 30 milliamperes.

Absorption coefficients calculated for water for the two effective wave-lengths used ($\mu=0.826$ for $\lambda=0.62A$ and $\mu=0.746$ for $\lambda=0.60A$) agree satisfactorily with interpolations from a series given by Glocker and Risse.⁵

Method for estimation of ceric sulfate

Since it was desired to determine quantitatively the amount of ceric sulfate reduced by reasonably short exposures to x-rays a very precise method of titration had to be developed. Potentiometric titration with 0.001 *N* ferrous sulfate was tried but found to be only partially satisfactory. Since orthophenanthroline¹¹ has been widely used as an oxidation-reduction indicator in solutions of ordinary concentration and found to give a very sharp end point, it was thought probable that application might be made of this indicator even in dilute solutions. The following procedure has been used and found very satisfactory: the orthophenanthroline ferrous complex was made up to one-fifth the usual concentration (0.005 *M* instead of 0.025 *M*) and one drop of the solution used for a 10 cc sample. Sufficient sulfuric acid was added to the sample to make it approximately 1 *N* and titration carried out with 0.001 *N* ferrous sulfate. Under these conditions the end point was detected as the first appearance of a permanent pink color in contrast to the colorless solution before the end point. This change was

noticeable with 0.01 cc of 0.001 *N* ferrous sulfate and very pronounced with 0.02 cc, particularly when illuminated with a strong light on a white table and with a white background. It is evident that the indicator correction was very large since the indicator contained 0.005 *N* Fe^{++} . However, nonirradiated controls were always titrated at the same time as the irradiated samples so the difference due to x-radiation did not depend on indicator correction as long as it was kept constant. The proper correction was made when direct comparison of the two solutions was necessary.

The procedure finally adopted for the preparation of these ceric sulfate solutions was to recrystallize the ceric ammonium sulfate until a very pure product was assured; then it was ignited in a muffle furnace at 900 to 1000°C for eighteen hours to convert it to the oxide. Decomposition took place at a lower temperature but also some reduction was caused by the ammonia liberated. The prolonged heating in the presence of oxygen of the air reoxidized the product to ceric oxide. This oxide was then treated with a small amount of concentrated sulfuric acid (9 parts H_2SO_4 to 1 part H_2O) to convert it to the sulfate. The purified ceric sulfate was finally dissolved in water and diluted to convenient stock concentration. The solutions were always strongly acidic with the excess sulfuric acid necessary to react with the oxide.

These solutions, as well as all others used for irradiation in this investigation, were prepared from "conductivity" water redistilled from alkaline permanganate.

Reduction of ceric sulfate solutions by x-radiation

Experiments showed that the amount of reduction was practically independent of the concentration of ceric sulfate for dilute solutions. This is consistent with most photochemical effects of x-rays. The amount of reduction did increase slightly for more concentrated solutions of ceric sulfate (above 0.001 *M*).

Since the ceric sulfate stock solution was quite acidic with sulfuric acid the dependence of reduction upon acid concentration was determined. Increasing the sulfuric acid concentration from 0.05 *N* to 1.2 *N* decreased the amount of reduc-

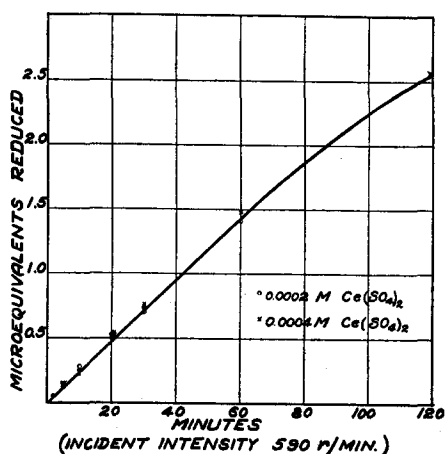


FIG. 1.

tion by a given dosage of x-rays in 0.0002 M $Ce(SO_4)_2$ by approximately 10 percent.

The next step was to determine the function of reduction with time of radiation. This series of experiments was carried out with 10 cc samples of 0.0002 M and 0.0004 M $Ce(SO_4)_2$ in 0.1 N H_2SO_4 . Fig. 1 is a curve showing the microequivalents reduced against minutes irradiation (20 milliamperes, 590 $r/min.$ incident intensity). It can be seen that the amount of reduction is very nearly proportional to dosage up to 50 percent. The sixty minute value for 0.0002 M $Ce(SO_4)_2$ which corresponds to approximately 75 percent reduction is somewhat low indicating that the rate of reaction has decreased slightly. The one hundred and twenty minute value for 0.0004 M $Ce(SO_4)_2$ shows a similar behavior.

Effect of added substances upon reduction of ceric sulfate

During the investigation of the effect of various dosages upon amount of reduction one sample was exposed after a drop of the orthophenanthroline indicator had been added. The amount of reduction in that sample was almost double that of samples given the same irradiation without the indicator present. Further experiments with Fe^{++} added to the concentration present in the indicator failed to cause any irregularity in results. The increased reduction, then, must have been due to the organic part of the indicator.

It was thought of interest to determine what effect small amounts of Ag^+ might have on the amount of the reduction of ceric sulfate by

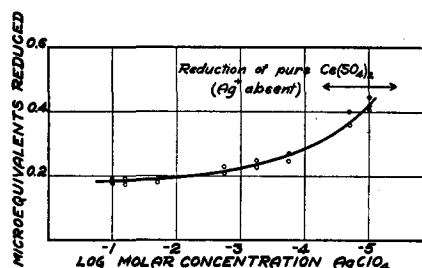


FIG. 2.

x-rays. Inasmuch as the Ag^+ would cause the solution to absorb a larger percentage of x-rays it might be predicted that a greater amount of reaction would take place. On the contrary Ag^+ was actually found to be a very efficient inhibitor for the reaction. Fig. 2 is a curve showing amount of reduction in 10 cc of 0.0002 M $Ce(SO_4)_2$, 0.1 N H_2SO_4 against the log of the concentrations of $AgClO_4$ present. $AgNO_3$ was also used and the values agree within experimental error with those for $AgClO_4$. These values were taken with copper target radiation with the tube operating at 55 peak and 30 milliamperes for fifteen minute exposures. The solutions were placed 15 cm from the focal spot and the incident intensity of radiation was 775 $r/min.$ From the curve it is seen that even $10^{-5} M$ $AgClO_4$ has a definite inhibitory effect upon the course of the reduction and 0.1 M $AgClO_4$ decreases the amount of reduction to approximately one-third of its ordinary amount.

Since silver salts were found to have such a marked effect, other salts of heavy metals were tried to see if they might behave in a similar way. However, mercuric nitrate was found to show a very strong behavior in the *opposite* direction, that is, increasing the amount of reduction of

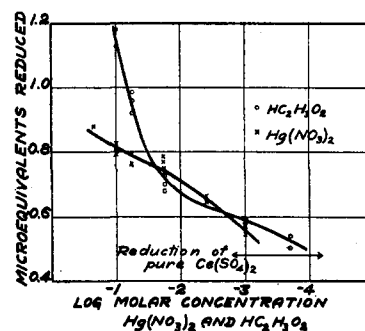


FIG. 3.

TABLE I

ADDITION AGENT (CONCN. APPROX. 0.02 M)	MICROEQUIVALENTS $\text{Ce}(\text{SO}_4)_2$ REDUCED
None	0.48
Ethyl alcohol	.61
Diethyl ether	.71
Dibutyl ether	.73
Acetone	.51
Carbon tetrachloride	.57
Ethyl acetate	.51
Dioxane	.55
Benzene	1.12

ceric sulfate. One curve of Fig. 3 shows the amount of reduction in $0.0002 M \text{ Ce}(\text{SO}_4)_2$, $0.1 N \text{ H}_2\text{SO}_4$ plotted against the logarithm of molar concentration of $\text{Hg}(\text{NO}_3)_2$ for the same conditions of irradiation as used for sample represented by Fig. 2. A curve is also shown for acetic acid which has been found to have an effect similar to that of mercuric nitrate. It is well to mention again that the values given for amount of reduction are differences in amount of standard FeSO_4 necessary to titrate the irradiated sample and a similar nonirradiated control. The values recorded are then due to the action of x-rays and independent of any direct action between ceric sulfate and the added substance.

The effects of HClO_4 and HNO_3 on the reduction of $\text{Ce}(\text{SO}_4)_2$ by x-rays were also determined. In each case the amount of reduction was increased but not to as great an extent as for $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{Hg}(\text{NO}_3)_2$. Whereas, 0.48 microequivalents of $0.0002 M \text{ Ce}(\text{SO}_4)_2$, $0.1 N \text{ H}_2\text{SO}_4$ were reduced under conditions stated above, $0.1 M \text{ HClO}_4$ increased this value to 0.57 microequivalents and $0.1 M \text{ HNO}_3$ to 0.59 microequivalents. Bismuth nitrate was also found to increase the amount of reduction considerably but the separation of bismuthyl sulfate prevented an exact quantitative estimate under the same conditions as used for the other substances. On the other hand, $0.05 M \text{ CuSO}_4$ acted more like AgClO_4 and decreased the amount of reduction to 0.38 microequivalents. NaNO_3 , NaClO_4 , and Na_2SO_4 were also tried but found to give no appreciable effect.

Various organic substances were also tried. Some were found to increase the amount of reduction very markedly and others to a lesser extent. Table I shows the substances studied and gives the microequivalents reduced under the

same conditions of irradiation as preceding experiments.

Since both catalytic and inhibitory effects were noticed for single substances added to ceric sulfate solutions, it was of interest to see if these behaviors would be additive when two substances were present in the same solution. Experiments with $0.06 M \text{ Hg}(\text{NO}_3)_2$, $0.06 M \text{ HC}_2\text{H}_3\text{O}_2$, and $0.02 M \text{ Hg}(\text{NO}_3)_2$, $0.02 M \text{ HC}_2\text{H}_3\text{O}_2$ indicated that the reduction was increased to a greater extent than by either single substance but not as much as to be directly additive. The next combination tried was one catalyst and one inhibitor such as $\text{HC}_2\text{H}_3\text{O}_2$ and AgClO_4 , or $\text{Hg}(\text{NO}_3)_2$ and AgClO_4 . Curves in Fig. 4 show the amount of reduction for a constant concentration of the catalysts ($0.02 M \text{ HC}_2\text{H}_3\text{O}_2$; $0.06 M \text{ Hg}(\text{NO}_3)_2$) in $0.0002 M \text{ Ce}(\text{SO}_4)_2$, $0.1 N \text{ H}_2\text{SO}_4$ for varying concentrations of the inhibitor AgClO_4 . In both cases AgClO_4 was found to be much more efficient as an inhibitor than the other substance as a catalyst. This is easily seen on the graph since the points where the curves intersect the line drawn to indicate reduction in pure $\text{Ce}(\text{SO}_4)_2$ represent the condition of balance between catalyst and inhibitor. Thus, $0.0001 M \text{ AgClO}_4$ ($\log = -4$) neutralizes the effect of $0.02 M \text{ HC}_2\text{H}_3\text{O}_2$ and $0.002 M \text{ AgClO}_4$ ($\log = -2.7$) corresponds to $0.06 M \text{ Hg}(\text{NO}_3)_2$.

Experiments with potassium permanganate and added substances

The reduction of potassium permanganate has been noted by other investigators; Chamberlain¹ reported reduction to Mn^{++} and Clark and Pickett² reported the formation of MnO_2 . These results were only qualitative, probably because a satisfactory method for estimation of dilute solutions of potassium permanganate was not available. Preliminary qualitative investigation confirmed the observations cited and showed that MnO_2 was formed by irradiation of solutions of potassium permanganate less than $0.1 N$ with respect to H_2SO_4 . Solutions of higher acidity ($1.0 N \text{ H}_2\text{SO}_4$) were reduced directly to Mn^{++} and varying amounts of MnO_2 and Mn^{++} were formed for intermediate concentrations.

Quantitative determination of reduction was found possible by a procedure similar to that used for ceric sulfate. However, the orthophenan-

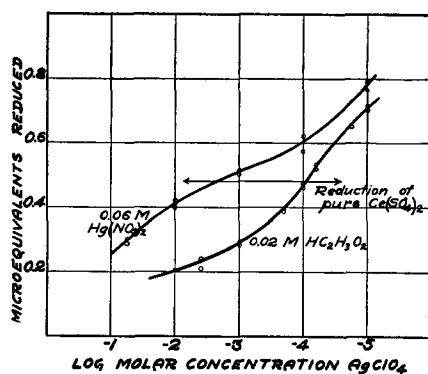


FIG. 4.

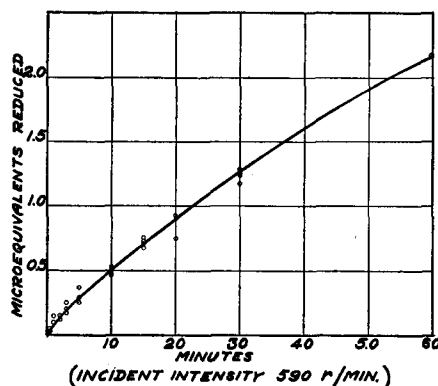


FIG. 5.

throline end point with 0.001 N FeSO_4 was neither as sharp nor as permanent as for ceric sulfate and a titration error of approximately ± 0.03 cc was thus introduced.

A study of the amount of reduction of KMnO_4 by different dosages of x-rays was carried out in a manner similar to that for $\text{Ce}(\text{SO}_4)_2$. Ten cubic centimeter samples of 0.0004 N KMnO_4 , 1.0 N H_2SO_4 were used. Fig. 5 is a curve showing microequivalents reduction plotted against minutes radiation, 20 cm from tungsten target, operating at 55 peak and 20 milliamperes (incident intensity 590 r/min.).

From the curve it is seen that the relation between reduction of potassium permanganate and dosage is not so nearly linear as was the case for ceric sulfate. The curve shows a sharp rise for the first few minutes; this may indicate that x-rays catalyze the reduction of KMnO_4 by slight traces of organic materials remaining in the solution in spite of precautions taken to prevent such contamination. This is further borne out by the fact that slight amounts of added organic substances were found to increase the reduction to a great extent. Orthophenanthroline as dilute as 0.00002 M increased the reduction for a ten minute exposure to three times its normal amount.

Mercuric nitrate and acetic acid increased the reduction of potassium permanganate in the same manner as for ceric sulfate. Whereas, approximately 0.49 microequivalents were reduced by a ten minute exposure of 0.0004 M KMnO_4 , 1 N H_2SO_4 solution, the presence of 0.05 M $\text{Hg}(\text{NO}_3)_2$ or 0.05 M $\text{HC}_2\text{H}_3\text{O}_2$ augmented this value to 1.09 and 1.12, respectively.

The reduction of KMnO_4 was inhibited by AgClO_4 and AgNO_3 as would be expected by comparison with their behavior with $\text{Ce}(\text{SO}_4)_2$. This reduction was decreased from 0.49 microequivalents to 0.18 in the presence of 0.05 M AgClO_4 and to 0.22 for 0.05 M AgNO_3 .

Experiments with uranyl sulfate-oxalic acid solution

Uranyl sulfate-oxalic acid solutions have been widely used as an actinometer for sunlight or ultraviolet radiation.^{12, 13} The procedure usually employed is to titrate radiated samples and controls with standard potassium permanganate to a faint pink color, the difference in amount of permanganate being a measure of the amount of oxidation of $\text{H}_2\text{C}_2\text{O}_4$ by radiation, catalyzed by uranyl sulfate. Since the reaction is quite large with ultraviolet, it was thought that some reaction might be noted by x-rays.

A solution of 0.005 M $\text{H}_2\text{C}_2\text{O}_4$, 0.002 M UO_2SO_4 was prepared and samples exposed to x-radiation. No reaction could be detected, so again it was found that behavior with ultraviolet was not safe evidence for prediction of the action of x-rays. Further experiments using a very large dosage of x-rays (17 cm, Cu target, 30 milliamperes, 55 kv, 2 hours) even showed that approximately 0.10 cc more 0.01 N KMnO_4 was necessary for the titration of the radiated samples than for the controls. However, the titration reaction was very slow near the end point for the radiated samples; this was probably due to the fact that a small amount of hydrogen peroxide had been formed by x-radiation and was re-

sponsible for the extra amount of KMnO_4 necessary.

Experiments with potassium iodate and potassium bromate

Since this investigation was primarily concerned with reduction effects of x-rays, it was desirable to examine the effect upon potassium iodate and potassium bromate. Stock solutions were carefully prepared from reagent quality chemicals and redistilled water. Solutions for exposure to x-rays were diluted to 0.0006 N and enough sulfuric acid added to make the solutions 0.1 N . Ten cubic centimeter samples were placed 15 cm from the copper target tube operated at 55 peak and 30 milliamperes (incident intensity 720 $r/\text{min.}$).

The samples were examined by adding excess potassium iodide and titrating almost to the disappearance of the liberated iodine with 0.001 N $\text{Na}_2\text{S}_2\text{O}_3$. Starch was then added and the titration continued to the disappearance of the blue color. This end point is capable of detection to ± 0.01 cc of 0.001 N $\text{Na}_2\text{S}_2\text{O}_3$. It was necessary to add more sulfuric acid for the titration of the bromate samples.

Preliminary experiments with potassium iodate showed that reduction did take place but to a less extent than for ceric sulfate and potassium permanganate. The time of exposure was increased to one hour and several measurements taken on the amount of reduction for that time. An average of 0.55 microequivalents was reduced. Titration of these samples seemed to proceed to a sharp and stable end point but upon standing thirty minutes or longer the radiated samples become blue again while the controls remained unchanged. Further titration with sodium thiosulfate solution after two hours gave another sharp end point which was stable over a

long period except as atmospheric oxidation caused a gradual change for the acidity used. (0.1 N H_2SO_4). Repeated experiments revealed that the second titration of the radiated samples depended on time of radiation in the same manner as the reduction noted by the first titration. This second titration averaged 0.42 microequivalents for one hour exposures.

Since hydrogen peroxide might have been formed in the radiated samples the next procedure was to see if hydrogen peroxide added to the control samples would cause them to behave in the same manner as those that had been radiated. This was at first thought doubtful because the H_2O_2 might be oxidized by the KIO_3 or at least be destroyed during the first titration. However, a series of samples was prepared and the results are indicated in Table II.

It is noted that H_2O_2 did not affect the KIO_3 and did not disturb the titration since the controls necessitated the same amount of $\text{Na}_2\text{S}_2\text{O}_3$ as did those containing H_2O_2 . There is a difference of approximately 0.54 microequivalents between the controls and radiated samples corresponding to the reduction by x-rays. After the first titration the solutions were allowed to stand. After ten minutes the radiated samples and those to which H_2O_2 had been added became slightly blue due to the slow liberation of I_2 as the H_2O_2 reacted with HI formed by previous addition of excess KI to the 0.1 N H_2SO_4 . The blue color continued to develop in both solutions at the same rate proving beyond a doubt that H_2O_2 had been formed in the radiated samples. The second titration was carried out after about two hours and corresponded to the amount of H_2O_2 formed or added. The amount of oxidation of the control samples by air was equivalent to 0.02 cc of $\text{Na}_2\text{S}_2\text{O}_3$. In more concentrated H_2SO_4 solutions the reaction between HI and H_2O_2 was more rapid and consequently the end point for the first titration could not be detected as accurately.

The effect of x-rays upon solutions of potassium bromate was tried in a manner similar to that for potassium iodate but *no* reduction could be detected. However, the second titration showed that even larger amounts of H_2O_2 had been formed than in the case of potassium iodate. Approximately 1.01 microequivalents of H_2O_2

TABLE II.

SAMPLES 10 cc, 0.0006 N KIO_3 , 0.1 N H_2SO_4	FIRST TITRATION cc 0.001 N $\text{Na}_2\text{S}_2\text{O}_3$	SECOND TITRATION cc 0.001 N $\text{Na}_2\text{S}_2\text{O}_3$
Controls	5.91	0.02
	5.93	.02
Radiated one hour	5.35	.45
	5.38	.43
0.42 microequiv. H_2O_2 added (not radiated)	5.92	.44
	5.94	.45

TABLE III.

	Ce(SO ₄) ₂ Reduced (0.1 N H ₂ SO ₄)	KMnO ₄ Reduced (1.0 N H ₂ SO ₄)	KIO ₃ Reduced (0.1 N H ₂ SO ₄)	H ₂ O ₂ Formed (0.1 N H ₂ SO ₄)
"Equivalents" converted per r unit absorbed	4.42×10^{12}	7.45×10^{12}	1.27×10^{12}	2.30×10^{12}
r units absorbed per equivalent converted	1.37×10^{11}	0.81×10^{11}	4.78×10^{11}	2.63×10^{11}
Ions converted per ion pair	2.0	3.7	0.62	1.1
Calories of absorbed energy per equivalent reduced*	379,500	205,135	1,224,193	690,000
Calories electronic energy for conversion of one equivalent†	344,000	204,000	1,095,000	602,000

Note: "Equivalents" equal gram equivalents times 6.06×10^{23} .

* Calculated from ions per ion pair, electron volts per ion pair, and heat equivalence of electron volts.

† Calculated from total heat equivalence of r unit, and total heat dissipated as electronic energy.

were formed for a one hour exposure. Further experiments revealed that about the same amount of H₂O₂ was formed by same radiation of 0.1 N H₂SO₄ (not air-free).

An attempt was made to study the effect of x-rays upon solutions of potassium chlorate but a satisfactory method for the accurate determination of dilute solutions could not be found.

Energy relationships

Ceric ions reduced per r unit.—Values are given in Fig. 1 for amount of reduction of 0.0002 M and 0.0004 M ceric sulfate in 0.1 N H₂SO₄ by tungsten radiation (effective $\lambda = 0.60$) for varying periods of exposure. From the straight portion of the curve it can be seen that forty-one minutes were necessary for the reduction of 1.0 microequivalent weight or 6.06×10^{17} ceric ions. Since the incident intensity was 590 r /min. per sq. cm, $590 \cdot 11.94 = 7050$ per min. incident radiation on the total surface. Of this amount 47.5 percent was absorbed by 0.1 N H₂SO₄; the absorption due to the small amount of Ce(SO₄)₂ present is negligible. From this it is calculated that 137,000 r units were absorbed in forty-one minutes. Therefore, 6.06×10^{17} ions per 137,000 r units or 4.42×10^{12} ions per r unit absorbed were reduced; 1.37×10^{11} r units were necessary for complete reduction of one mole of ceric ions.

By definition one r unit corresponds to an ionization such that a current of 1 e.s.u. flows in 1.0 cc of air under saturation potential. The number of ion pairs in air is therefore:

$$\frac{\text{total energy}}{\text{charge on electron}} = \frac{1}{4.774 \times 10^{-10}} \\ = 2.1 \times 10^9 \text{ ion pairs/cc}$$

in air and $2.1 \times 10^9 \cdot 795^* = 1.7 \times 10^{12}$ ion pairs per cc per r unit incident radiation on the water surface. These calculations assume a very thin layer of fluid so that the incident intensity is the same on all portions. Since this was not the case for the experimental conditions used, it is necessary to calculate the average incident intensity compared to that at the surface. Using the absorption equation $I = I_0 e^{-\mu x}$ and allowing I_0 to be 100 percent, the area under the curve of intensity against depth of solution can be found as $\int_0^{0.84} 100 e^{-\mu x} dx$. Dividing this value by 0.84 gives an average for all portions of the solution of 73.3 percent of the intensity incident upon the surface. There were, then, $590 r/\text{min.} \cdot 0.733 \cdot 1.7 \times 10^{12} = 7.35 \times 10^{14}$ ion pairs per cc per min. in the solution under the conditions used. But, one microequivalent (6.06×10^{17} ions) of ceric ions was reduced for a forty-one minute exposure in 10 cc; this gives:

$$\frac{6.06 \times 10^{17}}{7.35 \times 10^{14} \cdot 10 \cdot 41} = 2.01 \text{ ions reduced per ion pair.}$$

Energy of reduction in calories per equivalent of ceric ions.—This calculation comes out directly from the ions reduced per ion pair (2.01), the energy in electron volts to produce an ion pair (33 volts) and the heat equivalence per mole of the electron volt (23,000). The result is 379,000 calories per mole of ceric sulfate. By an entirely independent method based on the best data available on total heat equivalence of the r unit (148 ergs per r unit at the given wave-length) and the proportion of total heat dissipated as electronic energy (0.71), the value 344,000 calories is

* The best value correlating the number of ion pairs in water and in air in terms of density difference.

obtained. A check within 10 percent for these two different calculations would seem to be highly satisfactory.

Discussion of results

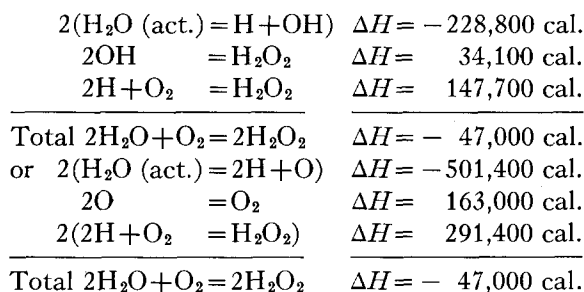
Table III shows the results for ceric sulfate in tabular form and also values for KMnO_4 , KIO_3 , and H_2O_2 as computed from similar calculations. It should be noted that all values are in terms of oxidation-reduction equivalents instead of moles. The values would be the same for ceric ion but would differ by a factor of 5 for KMnO_4 , 6 for KIO_3 and 2 for H_2O_2 . This method of tabulation allows direct comparison of the oxidation-reduction change brought about by x-rays in the different substances. An appropriate term, "equivalents," has been used to indicate a single "equivalent" ion and bears the same relation to gram equivalent as does the molecule to the gram mole. The values given for $\text{Ce}(\text{SO}_4)_2$, KMnO_4 , and KIO_3 are for amount of reduction by x-rays and the values for H_2O_2 designate the amount formed in 0.1 *N* H_2SO_4 in the presence of dissolved oxygen.

The reduction of ceric sulfate and potassium permanganate by x-rays is undoubtedly a complicated process involving both the formation of H_2O_2 and direct reduction by activated water. The importance of the activated water molecule in x-ray photochemistry has been repeatedly shown by Fricke¹⁴ and co-workers. This accounts for the fact that most effects of x-rays are independent of concentration of reactant.

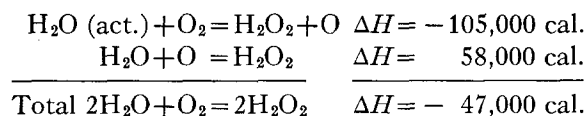
Since all solutions irradiated were open to the air, dissolved oxygen was present in solution and the production of H_2O_2 by x-rays proceeded according to the over-all equation:



The mechanism for this reaction has never been established although various ones have been suggested. Risse¹⁵ postulated two mechanisms for the decomposition of H_2O by x-rays and subsequent formation of H_2O_2 . These mechanisms with added values for heats of reaction (H = heat evolved) as calculated from data given by *International Critical Tables* and Lewis and von Elbe¹⁶ are as follows:

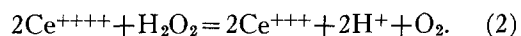


These mechanisms require very large activation energies and also have the disadvantage of requiring collision between two groups that could not be present in large amounts, such as 2 OH's in the first case and 2 O's in the second. In view of these facts a more logical mechanism would seem to be:

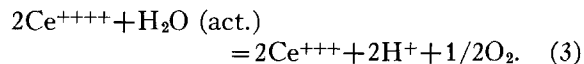


This is also consistent with the fact that the formation of H_2O_2 has not been observed in pure (O_2 free) water. The activation energy involved is moderate and the water molecule itself is a reactant in each step.

Since hydrogen peroxide reduces ceric sulfate in acid solution, any H_2O_2 formed by x-rays reacted immediately, according to:



However, it can be seen from Table III that such a reaction could not account for the amount of reduction noted. Therefore, an additional direct reaction must have been caused by other activated water molecules. The actual mechanism of reduction was probably a direct combination with secondary electrons liberated from water molecules by x-ray photons, but the over-all reaction would be:

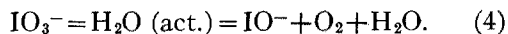


It is recognized, of course, that the production of H_2O_2 is determined in cerium-free solutions and that in this case part of the H_2O_2 produced is again decomposed by x-rays.¹⁷ From the data of Fricke under the conditions of the experiment, nearly half of the H_2O_2 would be decomposed. Hence, the reduction of ceric ions can more nearly

be accounted for by allowance for the initial production of H_2O_2 . Further proof for the type of direct reaction mentioned above is furnished by the fact that KIO_3 solutions were reduced by x-rays but not affected by H_2O_2 added or formed by irradiation. This is also consistent with the smaller amount of reduction noted for KIO_3 than for $\text{Ce}(\text{SO}_4)_2$. KMnO_4 was reduced to an even greater extent than $\text{Ce}(\text{SO}_4)_2$, probably due to a higher efficiency of the direct reduction by activated water or secondary electrons.

From Eq. (3) it is to be noted that the liberation of oxygen accompanies the process of reduction in solutions irradiated by x-rays. Therefore, conditions for formation of hydrogen peroxide are soon established even if irradiation is executed in air free solutions in closed containers. A few exposures with freshly boiled solutions showed that the reaction proceeded a little more slowly at the beginning.

The reduction of IO_3^- apparently proceeded only to the stage of IO^- because no free I_2 was detected by the addition of starch for the titration until excess KI was added. The over-all equation would be:



It is impossible to state whether the O_2 liberated came from H_2O or IO_3^- . The answer may be that one O came from each.

As yet, no logical explanation has been found to interpret the fact that BrO_3^- was not reduced by x-rays in a manner similar to that for IO_3^- . It is even more puzzling in view of the fact that the reaction, $\text{BrO}_3^- = \text{BrO}^- + \text{O}_2$, is slightly exothermic while the similar one for IO_3^- is endothermic.

The decrease in amount of reduction of ceric

sulfate by x-rays in the presence of Ag^+ indicates that the heavy silver ion absorbed the activation energy from H_2O before it was effective in producing reduction. On the other hand, Hg^{++} seemed to act as an efficient acceptor for the activation energy from the water or for secondary electrons and brought about increased reduction of ceric sulfate by intermediate reduction to Hg_2^{++} and reoxidation by Ce^{++++} .

Acetic acid also increased the amount of reduction of ceric sulfate by x-rays, but as pointed out previously, the difference in the shape of the curves of reduction versus concentration of $\text{Hg}(\text{NO}_3)_2$ and $\text{HC}_2\text{H}_3\text{O}_2$ (Fig. 3) would seem to indicate that x-rays produced the necessary activation energy to promote direct reaction between the acetic acid and ceric sulfate. Since no method was available for the accurate determination of the amount of acetic acid remaining, this could not be proven definitely.

BIBLIOGRAPHY

- ¹ Chamberlain, Phys. Rev. **26**, 525 (1925).
- ² Clark and Pickett, J. Am. Chem. Soc. **52**, 465-479 (1930).
- ³ Fricke and Brownscombe, J. Am. Chem. Soc. **55**, 2358-2363 (1933).
- ⁴ Fricke and Washburn, Phys. Rev. **40**, 1033 (1932).
- ⁵ Glocker and Risse, Zeits. f. Physik **48**, 845-851 (1928).
- ⁶ Risse, Zeits. f. physik. Chemie **A140**, 133-157 (1929).
- ⁷ Fricke, J. Chem. Phys. **2**, 349 (1934).
- ⁸ Fricke and Brownscombe, Phys. Rev. **44**, 240 (1933).
- ⁹ Clark, *Applied X-Rays* (McGraw-Hill, 1932), p. 163.
- ¹⁰ Duane, Hudson and Sterling, Am. J. Roentgenol. Radium Therapy **20**, 241-245 (1928).
- ¹¹ Smith, *Ortho-Phenanthroline* (The G. Frederick Smith Chemical Co., Columbus, Ohio).
- ¹² Leighton and Forbes, J. Am. Chem. Soc. **52**, 3139-3152 (1930).
- ¹³ Mayerson, Am. J. Hyg. **22**, 106-136 (1935).
- ¹⁴ Fricke, Sym. Quant. Biol. **3**, 55-65 (1935).
- ¹⁵ Risse, Strahlentherapie **34**, 578-581 (1929).
- ¹⁶ Lewis and von Elbe, J. Chem. Phys. **3**, 63 (1935).
- ¹⁷ Fricke, J. Chem. Phys. **3**, 364 (1935).