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RADIOLYSIS OF CITRIC ACID SOLUTIONS

By

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ABSTRACT

Radiolysis of citric acid in solutions of HNO_3 - $\text{Sr}(\text{NO}_3)_2$ by a cobalt-60 gamma source has a G value of 0.80. For each mole of citric acid destroyed, an average of 7.00 moles of hydrogen ion disappear. Concentrations of citric acid and nitric acid at which dark-brown radiolysis products and/or solids formed were also determined.

RADIOLYSIS OF CITRIC ACID SOLUTIONS

INTRODUCTION

Strontium-90 recovered from radioactive wastes must be purified before being converted to strontium fluoride for permanent storage. Two methods of purification are under consideration at Hanford: (1) precipitation as strontium sulfate, and (2) an additional solvent extraction cycle in the B Plant. In the solvent extraction process, ^{90}Sr is extracted into an 0.3M di(2-ethylhexyl) phosphoric acid (HDEHP)-0.2M tributyl phosphate (TBP)-n-paraffin hydrocarbon (NPH) solvent. Impurities are scrubbed from the organic with a citric acid-diethylenetriaminepentaacetic acid (DTPA) solution. Strontium-90 is then stripped from the organic phase with 1.0M citric acid (H_3Cit).

The citric acid concentration in the product solution must be lowered sufficiently to avoid formation of radiolysis products which would interfere with subsequent operations. A chemical means of destroying citric acid has been investigated by Buckingham⁽¹⁾ and used in the Hot Semiworks Strontium Recovery Program. Radiation will also decompose citric acid, but little is known of the applicability of radiolysis to the purification of strontium product. The purpose of this study was to investigate the conditions under which the radiolytic destruction of citric acid takes place. The parameters of main interest were the amount of hydrogen ion destroyed in relation to the amount of citric acid destroyed, the concentrations at which the solutions became visibly contaminated with nongaseous radiolysis products, the concentrations at which precipitation of tars or

solids took place, and an average G value[†] for the radiolysis of citric acid.

SUMMARY AND CONCLUSIONS

The radiolysis of citric acid (H_3Cit) in strontium solutions proceeds slowly over a period of days at megarad/hr dose rates, and undesirable by-products can be eliminated by proper adjustment of the hydrogen ion concentration.

Synthetic strontium product solutions with varying concentrations of citric acid, nitric acid, and strontium nitrate were irradiated by a ^{60}Co source. On the average, 7.00 moles of hydrogen ion were destroyed for every mole of citric acid destroyed. Reaction rates were on the order of $10^{-3}M/hr$ at dose rates of 2.66×10^6 rads/hr. The average G value for the radiolytic destruction of citric acid is 0.80 molecule/100 eV or 3550 watt-hr per mole.

Formation of dark-brown radiolysis products takes place when the ratio of hydrogen ion concentration to citric acid concentration is less than 4:1. When this ratio is less than 3:1, precipitation of solids takes place.

Solids formed by solution with low hydrogen ion concentration were found to contain an average of 44.0 percent strontium and, in some cases, accounted for all the strontium originally present in solution.

The radiolysis rate of nitric acid in the absence of citric acid was negligible when compared with the rate in the presence of citric acid.

[†] G value = number of molecules formed or destroyed per 100 eV absorbed.

EXPERIMENTAL

REAGENTS

Analytical grade reagents were used throughout.

SAMPLE IRRADIATION PROCEDURE

Samples were contained in specially constructed Pyrex vials and irradiated by one of two ^{60}Co gamma sources. The smaller source had a dose rate of 7.0×10^5 rads/hr and operated at room temperature. The larger source had a dose rate of 2.66×10^6 rads/hr. A specially constructed sample holder with a cooling coil was used to hold sample temperatures in the 10 to 25 °C range. During the course of irradiation, thief samples were taken for analysis. All samples were open to the atmosphere.

ANALYTICAL PROCEDURE

Total hydrogen ion concentration was determined by titration with standardized NaOH solution using a Beckman Automatic Titrator in derivative mode for end-point determination.

Nitrate ion activities were determined by an Orion nitrate specific ion electrode and Orion Model 801 pH meter. Nitrate concentrations were calculated from these nitrate ion activities.

Strontium was determined with a Techtron Model AA-5 atomic absorption spectrometer.

Citric acid was determined as carbon using the method of Van Hall, Safranko, and Stenger⁽²⁾ on a Beckman carbonaceous analyzer. It must be pointed out that in subsequent references to citric acid, a total carbon content was actually analyzed for rather than the H_3Cit molecule specifically.

Radiolysis products are thus included as citric acid.

RESULTS AND DISCUSSION

CITRIC ACID-NITRIC ACID SOLUTIONS

To determine the moles of hydrogen ion destroyed for each mole of citric acid, a series of samples with initial concentrations shown in Table I were irradiated, and changes in the citric acid and total hydrogen ion concentration were measured. A plot of citric acid concentration versus total hydrogen ion concentration during radiolysis is nearly linear except at low hydrogen ion concentrations where large amounts of dark-colored reaction products are present. A few representative cases are shown in Figure 1. The slope of the plot is the ratio, $\Delta[H^+]/\Delta[H_3Cit]$, shown in Table I.

Of the samples listed in Table I, the ones which had initial ratios of $[H^+]$ to $[H_3Cit]$ greater than the average value of 7.00 calculated for the ratio $\Delta[H^+]/\Delta[H_3Cit]$ were the samples in which citric acid concentration was reduced to low values without forming visible, discolored reaction products or precipitation of solids. A borderline case with an initial $[H^+]$ to $[H_3Cit]$ ratio of 7.15 remained colorless after a dose of 10^9 rads, but a small amount of solids precipitated.

When a large amount of dark-colored decomposition products is present in the solution, the ratio, $\Delta[H^+]/\Delta[H_3Cit]$, tends to become smaller. Two cases in Table II illustrate this effect, which can also be seen as a bending of the lower part of the curves in Figure 1. Contrary to what one might expect, Figure 1 shows that no abrupt change occurs when the molar ratio of hydrogen ion to citric acid becomes less than three. At this point it would be expected that the total hydrogen ion present is due only to the three

TABLE I

INITIAL CONCENTRATIONS AND $\frac{\Delta[H^+]}{\Delta[H_3Cit]}$ RATIOS

<u>Initial</u> <u>[H₃Cit]</u>	<u>Initial</u> <u>[H⁺]</u>	<u>Total Dose</u> <u>Rads</u>	<u>$\frac{\Delta[H^+]}{\Delta[H_3Cit]}$</u>
1.050	6.412	4.38 x 10 ⁸	6.52
1.031	4.913	4.38 x 10 ⁸	6.97
0.511	3.329	3.09 x 10 ⁸	7.75
*1.031	4.932	8.12 x 10 ⁷	8.48
1.560	5.909	4.38 x 10 ⁸	6.93
0.545	5.032	2.97 x 10 ⁸	7.13
0.534	2.717	2.97 x 10 ⁸	6.77
0.541	2.151	2.97 x 10 ⁸	6.32
1.039	3.715	3.64 x 10 ⁸	6.96
1.043	4.312	2.97 x 10 ⁸	7.12
1.564	5.279	2.97 x 10 ⁸	7.96
0.496	4.975	1.39 x 10 ⁹	7.87
0.499	2.711	1.39 x 10 ⁹	6.84
0.517	2.166	1.39 x 10 ⁹	6.41
1.030	6.498	1.46 x 10 ⁹	6.60
1.019	4.790	1.46 x 10 ⁹	6.46
1.030	3.730	1.46 x 10 ⁹	5.82
1.534	6.370	1.39 x 10 ⁹	7.54
0.508	6.549	1.39 x 10 ⁹	7.36
1.239	4.239	1.39 x 10 ⁹	7.16
1.019	4.312	1.46 x 10 ⁹	6.43
0.817	4.312	1.46 x 10 ⁹	6.43
0.608	4.348	1.46 x 10 ⁹	7.16
0.412	4.322	1.46 x 10 ⁹	6.95
Average			7.00

Initial [Sr(NO₃)₂] was 0.14M in all samples except *, which was 0.28M.

acidic protons associated with citric acid. Nitrate ion was present in excess of the amount necessary to combine with strontium, which suggests that not all of the nitric acid had been destroyed. Since it is total carbon which was actually being determined and not "citric acid" *per se*, the "citric acid" in these low-ratio solutions must consist partly of radiolysis by-products, some of which have less than three acidic protons per molecule.

FIGURE I
CITRIC ACID CONCENTRATION VERSUS HYDROGEN ION
CONCENTRATION DURING RADIOLYSIS FOR DIFFERENT
INITIAL CONCENTRATIONS

TABLE II

EFFECT OF DECOMPOSITION PRODUCTS ON THE RATIO $\frac{\Delta[H^+]}{\Delta[H_3Cit]}$

<u>Exposure, rads</u>	<u>$\frac{\Delta[H^+]}{\Delta[H_3Cit]}$</u>	<u>Solution Appearance</u>
<i>Initial</i> $\frac{[H^+]}{[H_3Cit]} = 3.62$		
6.3 x 10 ⁷	8.24	Brown
1.91 x 10 ⁸	7.53	Brown, solids began to form
3.70 x 10 ⁸	6.95	Brown, contained solids
5.72 x 10 ⁸	4.32	Brown, contained solids
8.15 x 10 ⁸	3.96	Brown, contained solids
1.02 x 10 ⁹	3.76	Brown, contained solids
1.26 x 10 ⁹	3.00	Brown, contained solids
1.46 x 10 ⁹	~4.0	Brown, contained solids
<i>Initial</i> $\frac{[H^+]}{[H_3Cit]} = 4.15$		
4.41 x 10 ⁸	7.79	Brown, few fine solids
6.98 x 10 ⁸	7.83	Brown, contained solids
8.93 x 10 ⁸	5.74	Brown, contained solids
1.14 x 10 ⁹	4.68	Brown, contained solids
1.39 x 10 ⁹	4.45	Brown, contained solids

From Figure 1 and similar plots, the following conclusions appear valid:

- Dark-brown discoloration due to radiolysis products occurs when the ratio of hydrogen ion concentration to citric acid concentration is less than four to one.
- Precipitation of solids occurs when the ratio of hydrogen ion concentration to citric acid concentration is less than three to one.
- Since an average of 7.00 moles of hydrogen ion disappears for every mole of citric acid destroyed, destruction of citric acid will proceed without

forming troublesome products or precipitates as long as the HNO_3 molarity is at least four-fold greater than the citric acid molarity.

G VALUE

An initial rate for the radiolytic destruction of citric acid is the slope of a linear least squares analysis of the data for citric acid concentration versus time up to the point where colored and/or solid reaction products formed. A G value for the disappearance of citric acid was calculated from this initial rate. Table III summarizes the results of these calculations. The average G value, 0.80, is low compared with the Fricke dosimeter. This G value does not represent the citric acid (H_3Cit) molecule alone, but includes the carbon in all non-gaseous radiolysis products of citric acid, since it is total organic carbon that is analyzed for and not the H_3Cit molecule.

It is not possible to formulate a kinetic expression for the reaction. As can be seen from Figure II, which shows several representative cases, citric acid concentration is not a linear function of dose. It appears that above citric acid concentrations of 0.5M, the rate of destruction is proportional only to the dose rate, but the presence of decomposition products and/or solids causes a deviation from a linear function. No definite effect on the initial rate could be attributed to citric acid, hydrogen ion, or strontium concentrations. Holm and Sehested⁽³⁾ have described a similar condition in an oxalic acid system. They concluded that up to 30 percent destruction, the oxalic acid is a linear function of the dose; above 30 percent destruction, the function takes the form:

$$\log (\text{dose}) = a \log (\text{oxalic acid decrease}) + b.$$

FIGURE 2
CITRIC ACID CONCENTRATION VERSUS DOSE
FOR DIFFERENT INITIAL CONCENTRATIONS

TABLE III
G VALUES

<u>Initial [H₃Cit]</u>	<u>Initial [H⁺]</u>	<u>G(-H₃Cit), molecules/100 eV</u>
1.050	6.412	0.95
1.031	4.913	1.10
0.511	3.329	0.85
*1.031	4.932	1.10
1.560	5.909	1.08
0.545	5.032	0.74
0.534	2.717	0.90
0.541	2.151	0.90
1.039	3.715	0.93
1.043	4.312	1.10
1.564	5.279	0.98
0.496	4.975	0.36
0.499	2.711	0.55
0.517	2.166	0.47
1.030	6.498	0.80
1.019	4.790	0.79
1.030	3.730	1.10
1.534	6.370	0.83
0.508	6.539	0.32
1.239	4.239	0.59
1.019	4.312	0.83
0.817	4.312	0.79
0.608	4.348	0.73
0.412	4.322	0.45
Average		0.80

* Initial [Sr(NO₃)₂] was 0.14M in all samples except *, which was 0.28M.

At high decomposition values, a systematic deviation from this relation was observed and no description of the system was attempted above 60 percent decomposition. Holm and Sehested attributed this deviation to the buildup of radiolytic by-products which take part in the process. The similarity of citric acid to oxalic acid can be seen in the dotted portions of the curves in Figure 2, which represent formation of darkly colored or solid radiolysis by-products. Note the change in slope as decomposition products build up and compete in the degradation process.

Since radiolysis is generally considered a free radical process, the process of polymerization must also be taken into account. Some of the dark-brown radiolysis products may be organic polymers which would decrease significantly the rate of disappearance of organic substances. This could also explain the observation that while low concentrations of citric acid could be reached, total removal of organic carbon was not possible, even by large doses. For example, one sample after a dose of 8.15×10^8 rads assayed 650 ppm carbon. An additional dose of 2.03×10^8 rads brought this value down to 134 ppm carbon. A further dose of 2.44×10^8 rads lowered carbon to only 80 ppm; and a further dose of 2.01×10^8 rads was required to lower it 5 ppm to 75 ppm carbon.

RADIOLYSIS OF NITRIC ACID

A sample of dilute nitric acid only was irradiated by the ^{60}Co gamma source. Table IV shows that the effect of radiation on nitric acid was negligible. An estimated G value for the radiolysis of nitric acid is about 0.02, over two orders of magnitude lower than in the presence of citric acid. Proskurnin and co-workers⁽⁴⁾ have found that in acidic nitrate solutions the total yield of nitrite formation falls rapidly, reaching zero at large irradiation doses.

TABLE IV
EFFECT OF RADIATION ON NITRIC ACID

<u>Dose, rads</u>	<u>[H⁺]</u>
0	1.412
4.41×10^8	1.412
6.98×10^8	1.405
8.93×10^8	1.402
1.14×10^9	1.405
1.39×10^9	1.402

LOSS OF STRONTIUM

The precipitates formed in various low-acid samples contained strontium. When the solids first formed, they were white and crystalline; but upon further irradiation they became more powdery and grayish-to-brown in color, depending upon contamination from other radiolysis products. These solids were insoluble in water, dilute HNO_3 , NaOH , and several organic solvents. Upon treating with concentrated HNO_3 followed by dilution with water, they would dissolve. Seven samples of the precipitate contained an average of 44.0 percent strontium and 10.3 percent carbon. Comparison of infrared (IR) spectra with that of potassium oxalate indicates that these solids are mostly strontium oxalate. The effect of precipitation of these solids on the strontium concentration of the solution is shown in Table V.

TABLE V
LOSS OF STRONTIUM

<u>Initial</u> <u>[Sr]</u>	<u>[Sr]</u> <u>After</u> <u>Irradiation</u>	<u>grams Sr in</u> <u>Solids from</u> <u>35 ml Sample</u>
0.144	0.001	0.380
0.142	0.005	0.370
0.143	0.050	0.193
0.144	0.004	0.295
0.142	0.002	0.421
0.143	0.122	0.055
0.145	0.146	No precipitate

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REFERENCES

1. J. S. Buckingham. *The Destruction of Citric Acid with Peroxide*, HW-80992, General Electric Company, Richland, Washington, February 24, 1964.
2. C. E. Van Hall, John Safranko, and V. S. Stenger. *Anal. Chem.*, 35, 315 (1963).
3. Niels W. Holm and K. Sehested. "Oxalid Acid Dosimeter Procedure," *Radiation Chemistry*, R. F. Gould, ed., American Chemical Society Publications, Washington, D.C., 1968, pp. 568-578.
4. M. A. Proskurnin, V. D. Orekhov, and A. I. Chernova. "The Action of Radiation on Aqueous Solutions of Potassium Nitrate and Nitrite," *Symposium on Radiation Chemistry*, Academy of Sciences of the USSR, Moscow, 1955, p. 79 (Engl. trans.).

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