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by

M. L. Hyder

Savannah River Laboratory
E. I. du Pont de Nemours & Company
Aiken, South Carolina 29801

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M. L. Hyder

Savannah River Laboratory
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ABSTRACT

Uranyl ion was reduced to U^{4+} by ionizing radiation in deoxygenated solutions containing organic solutes. This reduction is effected by free radical species formed from the organics and perhaps in part by H atoms from H_2O decomposition. A detailed study of uranyl oxalate solutions showed that the role of H_2O_2 in this system is complex and that chain-type reactions involving this species can occur.

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INTRODUCTION

Uranyl ion in aqueous solution reacts rapidly with the aqueous electron produced by radiation,¹ and might also react with H atoms. However, the radiolysis of solutions of uranyl salts normally does not reduce uranyl ion significantly. Indeed, radiolysis of solutions containing U^{4+} causes rapid oxidation of this ion.² This oxidation results from reaction of the oxidizing species (OH , H_2O_2) formed by radiolysis of water, together with other reactions involving dissolved O_2 .²

These observations suggested that UO_2^{2+} might be reduced by radiation in deoxygenated solutions containing a scavenger for OH radicals. A series of experiments using simple organic molecules as scavengers was therefore performed to confirm this hypothesis. These experiments showed that U^{4+} was formed in greater amounts than the maximum anticipated in some cases. Therefore, a more thorough study was made using uranyl oxalate solutions to establish the reaction mechanisms involved.

EXPERIMENTAL

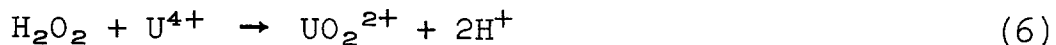
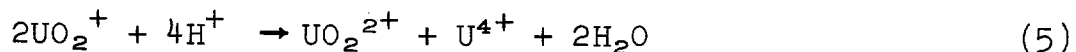
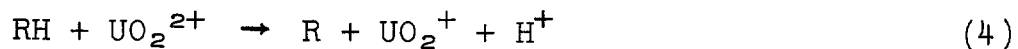
Solutions were prepared from reagent-grade chemicals and triply distilled water. A ^{60}Co source of approximately 1.2×10^6 rad/hr was used for the irradiations. The source was calibrated with a Fricke dosimeter. Solutions were deoxygenated before irradiation by extensive purging with argon which had previously been bubbled through triply distilled water. CO_2 production was measured on samples which had been thoroughly degassed by freezing-pumping-melting cycles on a vacuum line. These samples were sealed in "Pyrex" under vacuum for irradiation and broken open in another vacuum apparatus for analysis. The total amount of gas produced was determined by manometry, and the composition measured by mass spectrometry.

Uranyl ion was analyzed by colorimetry using the thiocyanate complex. The amount of U^{4+} produced was calculated from the decrease in UO_2^{2+} concentration. In several cases, U^{4+} was determined separately as a check, either by spectrophotometry or by separating it (ion exchange or fluoride precipitation) and reoxidizing it with peroxide for analysis as UO_2^{2+} . Both determinations of U^{4+} agreed satisfactorily.

Oxalate ion was determined either by permanganate titration (with a suitable correction for the U^{4+} content of the solution), or by the method of Bricker.³ The two methods agreed well, and the less laborious permanganate method was used preferentially.

RESULTS AND DISCUSSION

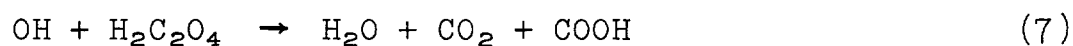
Table I summarizes the reduction of uranyl ion in deoxygenated uranyl solutions containing a variety of organic solutes. UO_2^{2+} was reduced to U^{4+} generally with good yields — sometimes exceeding 2.5 molecules (6 equivalents) per 100 ev. This was somewhat surprising on the basis of the anticipated mechanism, which involved Reactions 1-6:



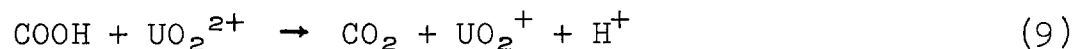
If these were the only reactions which occurred, the yield of U^{4+} from radiolysis would be given by $\frac{1}{2}(G_H + G_{OH} - 2G_{H_2O_2})$. Using the

known yields of radiolytic species in acidic solutions,⁴ the maximum value for U^{4+} production derived from this mechanism is 2.45 molecules per 100 ev.

This discrepancy between the observed quantity of UO_2^{2+} reduced and the predictions of the simple mechanism above required further study for its explanation. It was also of interest to determine whether Reaction (1) competes with Reaction (2). Accordingly a number of studies were made of the radiolysis of uranyl solutions containing oxalic acid. The irradiation of oxalic acid has been studied extensively by Draganic and coworkers,⁵ and the radiolytic reactions involved are fairly well understood. In the absence of oxygen, oxalic acid reacts with both H atoms and OH radicals:⁵



The COOH radical and the addition product from Reaction (8) undergo various complex reactions leading eventually to CO_2 and H_2O plus other minor products. In the presence of UO_2^{2+} , the organic radicals formed are expected to react with UO_2^{2+} by reactions of the general type of Reaction (4), thus



Uranyl Ion Reduction

A number of measurements were made of uranyl ion reduction as a function of concentration in acidified solutions containing either 0.4M H_2SO_4 or 0.8M $HClO_4$, and also in solutions containing only $UO_2C_2O_4$ and $H_2C_2O_4$. (The UO_2^{2+} concentration could not be varied greatly due to the limited solubility of uranyl oxalate.) Typical results are presented (1) in Figure 1, showing the apparent $G(-UO_2^{2+})$ as a function of initial $H_2C_2O_4$ concentration at a given total dose; and (2) in Figure 2, where the UO_2^{2+} concentration is

shown as a function of total dose for two different initial concentrations of $\text{H}_2\text{C}_2\text{O}_4$. It is apparent from the latter figure that the uranyl reduction rate falls off with increasing dose, especially at lower oxalate concentrations. This observation is most easily explained by assuming that the oxidation of U^{4+} by OH is competing with Reaction (7). This would account for the rapid drop in $G(-\text{UO}_2^{2+})$ with oxalate concentration as indicated in Figure 1. The equilibrium concentration of U^{4+} is reached for low oxalate concentrations at doses much lower than that used in these experiments. From these results the rate constant for reaction of OH with U^{4+} is estimated to be several hundred times greater than that for its reaction with oxalic acid. Since the rate constant for reaction of OH with oxalate ion (pH 9) is 5.0×10^8 ,⁶ and OH reacts with very many inorganic ions at rates $>10^9$,⁷ this explanation of the variations in U^{4+} production seems reasonable. It is additionally substantiated by other results given below.

No significant difference was found between solutions acidified with perchloric and sulfuric acids, but the reduction of UO_2^{2+} in solutions containing only oxalate was always somewhat higher than in either of these. This may in part be due to the precipitation in these solutions of U(IV) oxalate, which would tend to inhibit the reoxidation of this uranium.

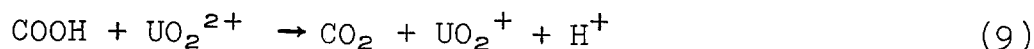
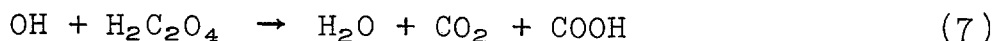
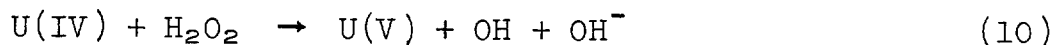
Oxalate Decomposition

Some measurements of oxalate decomposition are presented in Table II. These values show the same trends as the uranyl data, as would be expected from the mechanism suggested above; at higher dose or lower oxalic acid concentrations some OH is reacting to reoxidize U^{4+} . High absolute values of oxalate decomposition

are found for higher oxalate concentrations — above 7 molecules per 100 ev in one case. The maximum value predicted from the mechanism previously postulated is about 6.7 molecules per 100 ev.

The large observed G values for uranyl reduction indicate that the role of molecular H_2O_2 differs from that anticipated (Reaction 6). The high value for oxalate reduction also suggests the inadequacy of the postulated mechanism. Control experiments confirmed that H_2O_2 is formed in approximately normal yield in oxalate solutions containing no uranium; but, as expected, no H_2O_2 was present in solutions containing U(IV). Evidently the H_2O_2 is reacting in some manner which does not lead to the oxidation of U(IV).

In explanation of the results, the following chain sequence is proposed:



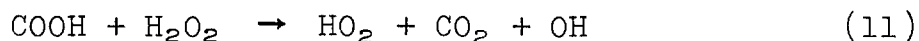
These reactions together with the disproportionation of UO_2^+ (Reaction 5) would lead to the oxidation of oxalate by peroxide with no net oxidation or reduction of uranium species.

This hypothesized chain sequence was tested by experiments designed to observe the effect of H_2O_2 added to the uranyl oxalate solution before irradiation. The results, described below, substantiate the chain mechanism. The only uncertain point is whether the reacting uranium species in Reaction (10) is U(IV) as written, or UO_2^+ , which will be present in small amounts in the solution during radiolysis. In either case, the one-electron

oxidation Reaction (10), which is the key to the chain reaction, appears reasonable. Experiments with added peroxide:

I. A solution containing $5 \times 10^{-2} \text{M H}_2\text{C}_2\text{O}_4$, $2 \times 10^{-3} \text{M UO}_2\text{SO}_4$, and $5 \times 10^{-4} \text{M H}_2\text{O}_2$ was irradiated and the H_2O_2 and UO_2^{2+} concentrations monitored periodically. Peroxide was destroyed at about 18 molecules per 100 ev. UO_2^{2+} was reduced negligibly until all the peroxide was destroyed. A similar solution containing no uranyl ion was irradiated and values of $G(-\text{H}_2\text{O}_2)$ measured were < 1.0 .

Husain and Hart⁸ have postulated that at $\text{pH} > 2$, COOH can react with H_2O_2 by



This reaction coupled with Reaction (7) could produce the chain oxidation of oxalate by peroxide. However, the above experiment indicates that this does not occur in these solutions at $\text{pH} \sim 1$. A radiation-initiated chain reaction of oxalate with peroxide was observed in an oxalate solution buffered to $\text{pH} 4$ with sodium oxalate; $G(-\text{H}_2\text{O}_2)$ exceeded 20.

II. CO_2 production was measured in uranyl-oxalate solutions with and without added H_2O_2 (Table III). Due to the quantity of product required for analysis, it was not possible to determine $G(\text{CO}_2)$ at very low doses; but appreciably larger quantities of CO_2 were nevertheless observed in the solutions with H_2O_2 , as the postulated mechanism would require.

CONCLUSIONS

The experiments offer good evidence that the radiation chemistry of uranyl oxalate solutions can be described by Reactions (7), (8), (4), (9), and (5), and perhaps also by Reaction (1).

Uranyl ion is reduced in deoxygenated solutions containing organic materials until the concentration of U^{4+} is high enough to compete with the organic solute for OH radicals. These conclusions may have significance for the processing of irradiated uranium fuels by solvent extraction; in the absence of oxygen some U^{4+} should be formed by radiolysis in such systems.

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TABLE I

URANYL REDUCTION IN IRRADIATED URANYL-ORGANIC
SOLUTIONS CONTAINING 0.4M H₂SO₄

| <u>Additive</u> | <u>Dose, rad</u> | <u>G(-UO₂²⁺), molecules per 100 ev</u> |
|--------------------|-----------------------|--|
| Methanol, 0.10M | 3.5 x 10 ⁵ | 2.6 |
| HCOOH, 0.10M | 3.5 x 10 ⁵ | 2.3 |
| Oxalic acid, 0.10M | 3.5 x 10 ⁵ | 2.6 |
| Oxalic acid, 0.30M | 5.0 x 10 ⁵ | 3.0 |

TABLE II

DESTRUCTION OF OXALIC ACID IN IRRADIATED
URANYL-SULFATE-OXALIC ACID SOLUTIONS ($\text{H}_2\text{SO}_4 = 0.40\text{M}$)

| <u>UO_2^{2+},</u> <u>moles/sec</u> | <u>$\text{H}_2\text{C}_2\text{O}_4$,</u> <u>moles/sec</u> | <u>Dose, rad</u> | <u>$G(-\text{H}_2\text{C}_2\text{O}_4)$,</u> <u>molecules</u> <u>per 100 ev</u> |
|---|---|-------------------|--|
| 0.02 | 0.02 | 2.5×10^5 | 3.2 |
| 0.02 | 0.02 | 5×10^5 | 2.7 |
| 0.02 | 0.05 | 5×10^5 | 4.1 |
| 0.01 | 0.10 | 9×10^5 | 7.5 |

TABLE III

CO₂ PRODUCTION IN IRRADIATED URANYL-OXALATE SOLUTIONS

| <u>Solution</u> | <u>Dose, rad</u> | <u>G(CO₂), molecules per 100 ev</u> |
|---|-----------------------|--|
| A. UO ₂ SO ₄ , 0.005M; H ₂ C ₂ O ₄ , 0.05M | 1 x 10 ⁶ | 5.1 |
| B. As A but 5 x 10 ⁻⁴ M H ₂ O ₂ added | 2.5 x 10 ⁵ | 9.0 |
| C. UO ₂ SO ₄ , 0.001M; H ₂ C ₂ O ₄ , 0.05M | 2.5 x 10 ⁵ | 6.0 |
| D. As A but 0.4M H ₂ SO ₄ added | 1 x 10 ⁶ | 4.3 |

Fig. 1

UO₂²⁺ REDUCTION AS A FUNCTION OF H₂C₂O₄ CONCENTRATION

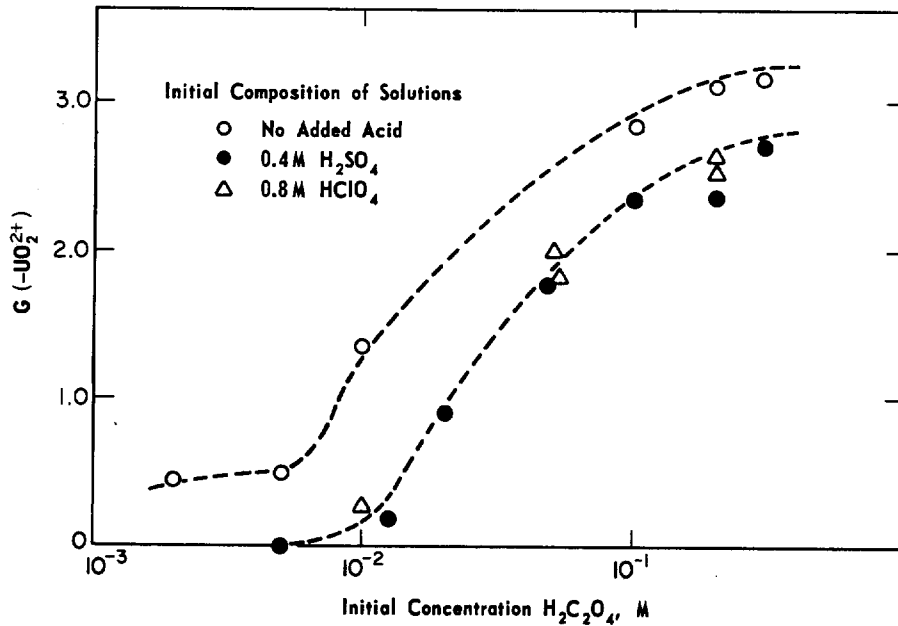


Fig. 2

REDUCTION OF UO₂²⁺ IN OXALATE SOLUTIONS AS A FUNCTION OF DOSE
 UO₂²⁺ Initially 2 × 10⁻³ M; 0.40 M H₂SO₄ Present

