

[CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY¹]Photoreduction of Ceric Ion in Sulfuric Acid Solutions. Effect of Thallous Ion^{2a}BY THOMAS J. SWORSKI^{2b}

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Evidence has been obtained for the OH radical as an intermediate in the photoreduction of ceric ion in sulfuric acid solutions. The observed chemical reaction in the photolysis of ceric ion-thallous ion mixtures is the oxidation of thallous ion by ceric ion. The initial quantum yield ($\Phi_{\text{Ce}^{4+}}$) for reduction of ceric ion in the absence of initially added cerous ion is markedly enhanced by thallous ion but is independent of the thallous ion concentration ($2 \times 10^{-4} M$ to $2 \times 10^{-2} M$). At any particular initial cerous ion concentration, the initial $\Phi_{\text{Ce}^{4+}}$ decreases with decreasing initial thallous ion concentration. These data obtained in 0.4 *M* sulfuric acid are quantitatively interpreted by a mechanism in which thallous ion competes with cerous ion for reaction with OH radical. The measured value of 42 for $k_{\text{TI}^+, \text{OH}}/k_{\text{Ce}^{3+}, \text{OH}}$ is in agreement with the value of 38 previously determined in 0.4 *M* sulfuric acid for the radiolysis of ceric ion-cerous ion-thallous ion mixtures with cobalt-60 γ -radiation.

Introduction

When ceric ions in perchloric acid solution absorb ultraviolet radiation, oxygen is evolved with concomitant reduction of ceric ions to cerous ions.^{3,4} Weiss and Porret⁴ postulated the formation of an OH radical in the photochemical primary process. This assumption has been a subject of controversy.^{5,6}

Photoreduction of ceric ions also occurs⁷ in sulfuric acid solutions in disagreement with the observations of Weiss and Porret.⁴ Although no definitive evidence was presented, the OH radical was also postulated⁷ as an intermediate in sulfuric acid solutions. This paper reports the results of a kinetic study of the photolysis of ceric ion-cerous ion-thallous ion mixtures in 0.4 *M* sulfuric acid. These results, when compared with those reported⁸ for the radiolysis of ceric ion-cerous ion-thallous ion mixtures with cobalt-60 γ -radiation also in 0.4 *M* sulfuric acid, yield supporting evidence for the intermediate formation of OH radical in the photoreduction of ceric ion in sulfuric acid solutions.

Experimental

The source of ultraviolet radiation was a G. E. 4-watt germicidal lamp operating from a Sola Electric constant voltage transformer. The light was used without collimation, the solutions being reproducibly placed several centimeters from the light source. The light flux incident upon the solutions was measured with an equal volume of actinometer solution.⁹ The light absorbed from this source by the uranyl actinometer is reported¹⁰ to be almost entirely 253.7 μ . The quantum efficiency for oxalate oxidation was observed to be constant up to 65% of completion.

Solutions of 50-ml. volume were contained in a silica vessel of 3 cm. diameter. The ceric ion solutions in 0.4 *M* sulfuric acid were prepared in the same manner as previously reported⁸ for the radiolysis of ceric ion-cerous ion-thallous ion mixtures with cobalt-60 γ -radiation. Ceric ion concentrations were determined spectrophotometrically with a

Cary model 11 recording spectrophotometer. A molar extinction coefficient for ceric ion at 320 μ of 5580 was used for 0.4 *M* sulfuric acid solutions.¹¹ Molar extinction coefficients of 2440 at 370 μ and 1020 at 395 μ were determined and used for the more concentrated ceric ion solutions. Cerous ion and thallous ion have no measurable effect on these molar extinction coefficients at the concentrations employed.

Results

Ceric ion concentration as a function of time of photolysis, at constant light intensity, was followed in each solution through use of intermittent exposures. Typical data obtained in such experiments are illustrated by Fig. 1. The quantum yield for reduction of ceric ion ($\Phi_{\text{Ce}^{4+}}$) decreased with increasing time of photolysis in all solutions, principally due to an internal filter action of cerous ion and to a smaller extent to an increase in $(\text{Ce}^{3+})/(\text{TI}^+)$. The initial $\Phi_{\text{Ce}^{4+}}$ could not, therefore, be measured with any high degree of accuracy or reproducibility. The initial $\Phi_{\text{Ce}^{4+}}$ obtained under a variety of experimental conditions in air-saturated 0.4 *M* sulfuric acid are listed in Table I.

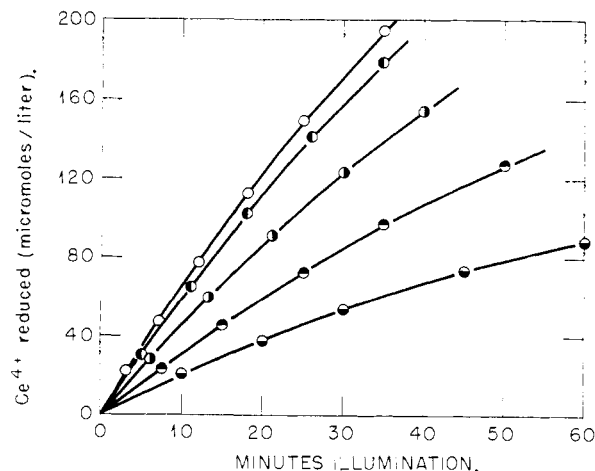


Fig. 1.—Effect of variation in initial thallous ion concentration on the rate of photoreduction of ceric ion at constant initial ceric and cerous ion concentrations. Initial cerous ion concentration in all solutions was $10^{-3} M$. Initial ceric ion concentration in all solutions was $3.64 \times 10^{-4} M$. Initial thallous ion concentrations were: \circ , $10^{-2} M$; \bullet , $10^{-3} M$; \circ , $4 \times 10^{-4} M$; \bullet , $2 \times 10^{-4} M$; \bullet , $10^{-4} M$.

(1) Operated by Union Carbide Nuclear Company for the Atomic Energy Commission.

(2a) Paper presented before the Division of Physical and Inorganic Chemistry, 131st Meeting of the American Chemical Society at Miami, Fla., April 7-12, 1957.

(2b) Sterling Forest Nuclear Center, Union Carbide Nuclear Company, Union Carbide Corporation, New York, N. Y.

(3) E. Bauer, *Z. physik. Chem.*, **63**, 583 (1908).

(4) J. Weiss and D. Porret, *Nature*, **139**, 1019 (1937).

(5) L. J. Heidt and M. E. Smith, *THIS JOURNAL*, **70**, 2476 (1948).

(6) M. G. Evans and N. Uri, *Nature*, **166**, 602 (1950).

(7) T. J. Sworski, *THIS JOURNAL*, **77**, 1074 (1955).

(8) T. J. Sworski, *Radiation Research*, **4**, 483 (1956).

(9) W. G. Leighton and G. S. Forbes, *THIS JOURNAL*, **52**, 3130 (1930).

(10) J. P. Hunt and H. Taube, *ibid.*, **74**, 5999 (1952).

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

TABLE I
EFFECT OF CERIC, CEROUS AND THALLOUS ION CONCENTRATIONS ON THE QUANTUM YIELD FOR PHOTOREDUCTION OF CERIC ION^a

| (Ce ⁴⁺), μmoles/l. | (Ce ⁺⁺⁺), moles/l. | (Tl ⁺), mole/l. | Initial Φ _{Ce⁺⁺⁺} |
|-----------------------------------|-----------------------------------|--------------------------------|--|
| 242 | 0 | 5 × 10 ⁻³ | 0.200 |
| 478 | 0 | 5 × 10 ⁻³ | .205 |
| 962 | 0 | 5 × 10 ⁻³ | .201 |
| 1907 | 0 | 5 × 10 ⁻³ | .200 |
| 460 | 0 | 2 × 10 ⁻² | .204 |
| 460 | 0 | 5 × 10 ⁻³ | .204 |
| 460 | 0 | 2 × 10 ⁻⁴ | .212 |
| 325 | 0 | 2 × 10 ⁻² | .199 |
| 325 | 0 | 2 × 10 ⁻³ | .212 |
| 325 | 0 | 2 × 10 ⁻⁴ | .206 |
| 325 | 2 × 10 ⁻² | 2 × 10 ⁻² | .0292 |
| 325 | 2 × 10 ⁻² | 2 × 10 ⁻³ | .0263 |
| 325 | 2 × 10 ⁻² | 8 × 10 ⁻⁴ | .0197 |
| 325 | 2 × 10 ⁻² | 4 × 10 ⁻⁴ | .0158 |
| 325 | 2 × 10 ⁻² | 2 × 10 ⁻⁴ | .00947 |
| 364 | 10 ⁻² | 10 ⁻² | .0490 |
| 364 | 10 ⁻² | 10 ⁻³ | .0400 |
| 364 | 10 ⁻² | 4 × 10 ⁻⁴ | .0313 |
| 364 | 10 ⁻² | 2 × 10 ⁻⁴ | .0204 |
| 364 | 10 ⁻² | 10 ⁻⁴ | .0146 |

^a Quantum yields are based on total light absorbed by the solutions.

The chemical change which occurs during photolysis is oxidation of thallos ion by ceric ion. This was experimentally established by two different methods. (I) In a solution containing initially 10⁻³ *M* ceric ion and 2.67 × 10⁻⁴ *M* thallos ion, the rate of photoreduction markedly decreased when 5.40 × 10⁻⁴ mole/l. of ceric ion had been reduced. (II) For a solution containing initially 10⁻³ *M* ceric ion and 2.67 × 10⁻³ *M* thallos ion, equal volumes of either the original solution or a portion in which 85% of the ceric ion concentration

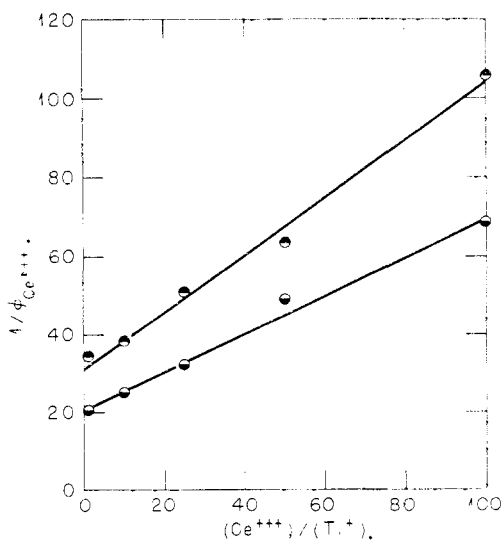


Fig. 2.—Effect of (Ce⁺⁺⁺)/(Tl⁺) ratio on the initial rate of photoreduction of ceric ion in air-saturated 0.4 *M* sulfuric acid solutions. Initial cerous ion concentrations were: ●, 2 × 10⁻² *M* and ◻, 10⁻² *M*. Initial ceric ion concentrations were: ●, 3.25 × 10⁻⁴ *M*; ◻, 3.64 × 10⁻⁴ *M*.

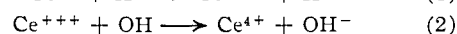
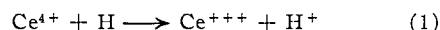
had been photochemically reduced oxidized equal amounts of ferrous ion.

In ceric ion-thallos ion mixtures, the initial Φ_{Ce⁺⁺⁺} is independent of the ceric ion concentration (2.4 × 10⁻⁴ *M* to 1.9 × 10⁻³ *M*). This indicates that essentially all the incident light is absorbed by these solutions. These results in sulfuric acid solutions differ markedly with those obtained in perchloric acid solutions by Heidt and Smith⁶ where Φ_{Ce⁺⁺⁺} increases with increasing ceric ion concentration.

The initial Φ_{Ce⁺⁺⁺} is also independent of thallos ion concentration (2 × 10⁻⁴ *M* to 2 × 10⁻² *M*) but only in the absence of initially added cerous ion. At any particular initial cerous ion concentration, the initial Φ_{Ce⁺⁺⁺} decreases with decreasing thallos ion concentration. Since cerous ion acts as an internal filter, dependence of initial Φ_{Ce⁺⁺⁺} on (Ce⁺⁺⁺)/(Tl⁺) was investigated at constant concentration of ceric and cerous ions.

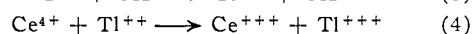
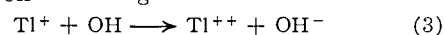
Discussion

The reactions of ceric and cerous ions with radicals in aqueous solution have been elucidated by recent studies in radiation chemistry. *G*(Ce⁺⁺⁺)¹² in the radiolysis of sulfuric acid solutions containing ceric ions was postulated¹³ to be equal to 2*G*_{H₂O₂} + *G*_H - *G*_{OH}. The following radical reactions were assumed



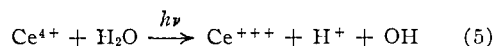
This mechanism was confirmed¹⁴ by a demonstration of ceric ion reduction with concomitant oxidation of radioactive cerous ion.

Thallos ion increases¹⁵ *G*(Ce⁺⁺⁺) to 2*G*_{H₂O₂} + *G*_H + *G*_{OH} according to the reaction mechanism



A value of 38 was measured⁸ for the ratio *k*₃/*k*₂ in 0.4 *M* sulfuric acid.

If the postulate is correct that an OH radical is formed in the primary photochemical process in sulfuric acid solutions



then the experimental data should be fully described by a reaction mechanism containing only reactions 5, 2, 3 and 4. From this reaction mechanism, the following kinetic relationship can be derived

$$\frac{1}{\Phi_{\text{Ce}^{+++}}} = \frac{1}{2\Phi_{\text{OH}}} + \frac{k_2(\text{Ce}^{+++})}{2\Phi_{\text{OH}}k_3(\text{Tl}^+)}$$

Φ_{OH} is the quantum yield for the OH radicals formed in the primary photochemical process.

A linear relationship does exist between 1/Φ_{Ce⁺⁺⁺} and (Ce⁺⁺⁺)/(Tl⁺) as shown in Fig. 2. Treatment of the data by the method of least

(12) In the decomposition of water by ionizing radiation, 100 e.v. yields of the intermediates H, OH, H₂ and H₂O₂ are denoted by *G*_H, *G*_{OH}, *G*_{H₂} and *G*_{H₂O₂}. The 100 e.v. yield of any measurable product in radiolysis of aqueous solutions is denoted by *G*(product).

(13) A. O. Allen, *Radiation Research*, **1**, 85 (1954).

(14) G. B. Challenger and B. J. Masters, *THIS JOURNAL*, **77**, 1063 (1955).

(15) T. J. Sworski, *ibid.*, **77**, 4689 (1955).

squares yields the equations

$$1/\Phi_{\text{Ce}^{+++}} = 31.2 + 0.730(\text{Ce}^{+++})/(\text{Ti}^+) \quad (\text{I})$$

$$1/\Phi_{\text{Ce}^{+++}} = 20.5 + 0.495(\text{Ce}^{+++})/(\text{Ti}^+) \quad (\text{II})$$

Equation I is obtained from the data with $2 \times 10^{-2} M$ cerous ion solutions while eq. II is obtained from the data with $10^{-2} M$ cerous ion solutions.

From eq. I and II, k_3/k_2 is evaluated by division of the intercept by the slope. From eq. I, k_3/k_2 is equal to 31.2/0.73 or 42.7. From eq. II, k_3/k_2 is equal to 20.5/0.495 or 41.4. The average value of 42 is in excellent agreement with the value of 38 measured⁸ for the radiation chemistry of the same chemical system using cobalt-60 γ -radiation.

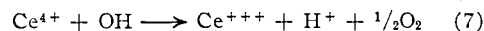
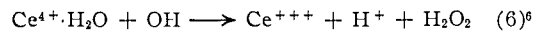
This comparison of the photochemistry with the radiation chemistry of ceric ion-cerous ion-thal-ous ion mixtures thus yields convincing evidence for the postulated formation of OH radical in the photoreduction of ceric ion in sulfuric acid solutions.

Let us assume that OH is an intermediate in perchloric acid and that OH radical can reduce⁶

ceric ion in perchloric acid. Then, the following kinetic relationship can be derived

$$\frac{1}{\Phi_{\text{Ce}^{+++}}} = \frac{1}{x\Phi_{\text{OH}}} + \frac{k_2(\text{Ce}^{+++})}{x\Phi_{\text{OH}}k_y(\text{Ce}^{++})}$$

The value of x would be either 2 or 4 and k_y would be either k_6 or k_7 depending whether ceric ion oxidized OH radical according to reaction 6 or reaction 7



Heidt and Smith⁵ report that for $1.1 \times 10^{-2} M$ ceric ion solutions in perchloric acid $1/\Phi_{\text{Ce}^{+++}} = 5 + 670(\text{Ce}^{+++})$. Thus, k_y/k_2 would have a value of 0.68. Whether reaction 6 or reaction 7 occurs could be determined if Φ_{OH} were known. This would have required a study of the effect of added solutes, such as reported here, which was not investigated by Heidt and Smith.⁵

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TOLEDO]

A Study of the Kinetics of the Reaction between Oxalate Ion and Cerium(IV) in Aqueous Sulfuric Acid Solution

BY VANCE H. DODSON AND ARTHUR H. BLACK

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The kinetics of the reaction between cerium(IV) and oxalate ion, bioxalate ion and oxalic acid in aqueous sulfuric acid has been studied over the temperature range of 19 to 35°. The reaction appears to be second order, and the rate of the reaction is dependent upon the concentration of sulfuric acid. The experimental energy of activation is 16.5 ± 0.4 kcal./mole in 0.5, 1.0 and 2.0 M sulfuric acid solutions.

Kinetic studies of the reactions between cerium(IV) and tin(II),¹ arsenic(III)² and oxalic acid³ have been reported in the literature. In a recent examination of the reaction between cerium(IV) and oxalate ion⁴ in aqueous sulfuric acid, it was noted that the rate of the reaction decreased as the concentration of the sulfuric acid was increased. Since the previously published work³ merely established the order of the reaction, it was of interest to re-examine the kinetics of the reaction and attempt to establish a mechanism for it.

Experimental Part

Equipment and Reagents.—Reaction rates were determined by using a Bausch and Lomb Spectronic 20 colorimeter. The solutions were kept in a constant temperature bath, then mixed and immediately transferred to the cell and placed in the instrument. In all of the experiments conducted, the cell and its contents were never in the instrument longer than one minute. Over the temperature range of 19 to 35° this short exposure to the heat of the excitor lamp produced no deviations greater than $\pm 0.1^\circ$ in the reaction mixtures.

The reagents were prepared by dissolving anhydrous cerium(IV) acid sulfate (G. Frederick Smith Chemical Co.) and C.P. Special Grade anhydrous sodium oxalate (Baker Chemical Co.) in aqueous sulfuric acid of known molarity. The cerium(IV) solutions were standardized with iron(II).

(1) C. H. Brubaker, Jr., and A. J. Court, *THIS JOURNAL*, **78**, 5530 (1956).

(2) J. S. Yates and H. C. Thomas, *ibid.*, **78**, 3950 (1956).

(3) S. D. Ross and C. G. Swain, *ibid.*, **69**, 1325 (1947).

(4) A. H. Black and V. H. Dodson, *J. Chem. Ed.*, **33**, 562 (1956).

Ferrous *o*-phenanthroline was used as the indicator. The concentrations of the oxalate solutions were checked against the cerium(IV) solutions. Reagent grade sulfuric acid and distilled water were used in the preparation of the aqueous acid solutions. A series of 2.0, 1.0 and 0.5 M solutions was prepared. These were used as solvents in the cerium(IV) and oxalate solutions and as diluents in the reaction rate measurements. No special precautions were taken to protect the solutions from light and air.⁶

Spectrophotometric Determination of the Rate of Reaction.—The per cent. transmission of the standard cerium(IV) solutions was measured at 425, 450 and 475 $m\mu$ and found to obey Beer's law. The calibration curve at 450 $m\mu$ over the range of concentrations 0.0055 to 0.00025 M was the one most often used in these experiments. No significant variation in per cent. transmission of the cerium(IV) solutions was observed at any of these three wave lengths when the concentration of sulfuric acid was varied from 0.5 to 2.0 M .⁶

The following procedure was followed in measuring the reaction rates. The oxalate solution of known concentration, prepared by diluting a portion of the stock solution with sulfuric acid of appropriate molarity, was placed in a stoppered wide-mouth conical flask. The cerium(IV) solution of known concentration (in sulfuric acid of the same molarity as that in the oxalate solution) was placed in a stoppered soft glass test-tube whose bottom had been blown to form a thin-walled bulb. Both the bulb and flask were then placed in the constant temperature bath. At time zero the bulb of cerium(IV) solution was broken in the conical flask and the solutions were mixed by rapid swirling. A portion of the reaction mixture was immediately transferred to the colorimeter cell and per cent. transmission readings were taken at various time intervals.

(5) H. H. Willard and P. Young, *THIS JOURNAL*, **51**, 149 (1929).

(6) E. G. Jones and F. G. Soper, *J. Chem. Soc.*, 802 (1935).