Elementary Processes in the Radiolysis of Aqueous Sulfuric Acid Solutions. Determinations of Both G_{OH} and $G_{SO_4^-}$[1,2]

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Kinetic evidence is presented for concurrent production of two oxidizing radicals in the radiolysis of aqueous sulfuric acid solutions: OH and SO_4^- radicals that are presumed to result from direct action of ionizing radiation on water and sulfuric acid anions, respectively. The evidence was obtained from the dependence of $G(Ce^{III})$ on cerium(III) and either formic acid or 2-propanol concentrations in the radiolysis of cerium(IV)–cerium(III)–formic acid mixtures and cerium(IV)–cerium(III)–2-propanol mixtures. Determinations of G_{OH} and $G_{SO_4^-}$ required the use of a computer for least-squares fit of experimental data to complex kinetic equations containing up to 22 dependent variables. Applicability of the kinetic equations is indicated by the excellent agreement for two determinations in 4.0 *M* sulfuric acid: $G_{OH} = 1.76 \pm 0.19$ and $G_{SO_4^-} = 0.95 \pm 0.18$ with 2-propanol solutions; $G_{OH} = 1.78 \pm 0.03$ and $G_{SO_4^-} = 0.94 \pm 0.03$ with formic acid solutions. A small but significant yield of SO_4^- was determined in 0.4 *M* sulfuric acid: $G_{OH} = 2.60 \pm 0.04$ and $G_{SO_4^-} = 0.20 \pm 0.04$. No evidence was obtained for oxidation of sulfuric acid anions by precursors of OH radical such as H_2O^+, since G_{OH} was found to be proportional to electron fraction water.

Introduction

The importance of the SO_4^- radical as an intermediate in the radiolysis of aqueous sulfuric acid solutions has been the subject of numerous investigations. Three different processes have been proposed for the production of SO_4^- radicals: reaction of OH radical with sulfuric acid anions,[4,5] direct action of ionizing radiation on sulfuric acid anions,[6] and reaction of sulfuric acid anions with H_2O^+, a commonly assumed precursor of the OH radical.[7]

The proposal that OH radical reacts with sulfuric acid anions has been substantiated. Rate constant ratios for reaction of OH radical with cerium(III), formic acid, and sulfuric acid anions were determined from the dependence of $G(Ce^{III})$ on cerium(III) and formic acid concentrations in the radiolysis of cerium(IV)–cerium(III)–formic acid mixtures in air-saturated 0.4 *M* sulfuric acid with ^{60}Co γ radiation.[8] More direct evidence for the reaction of OH radical with sulfuric acid anions was obtained by pulse radiolysis techniques.[9]

Boyle[6] proposed the concurrent production of OH and SO_4^- radicals in the radiolysis of aqueous sulfuric acid solutions with G_{OH} proportional to electron fraction water and $G_{SO_4^-}$ proportional to electron fraction sulfuric acid. The evidence, though convincing, was indirect: the formation of hydrogen peroxide, peroxosulfuric acid, and peroxodisulfuric acid in the spur was attributed to combination reactions of some OH and SO_4^- radicals before the remainder escaped by diffusion into the bulk of the solution. No evidence was presented, however, for those SO_4^- radicals that escaped by diffusion into the bulk of the solution.

The energy absorbed by each component in the radiolysis of mixtures is commonly assumed to be proportional to its electron fraction. It has long been recognized, however, that the *G* values for intermediates that are characteristic of each component may not be proportional to the energy absorbed by each component, owing to either ionization transfer or excitation transfer.[10] The suggestion[7] that SO_4^- radical may result from reaction of sulfuric acid anions with H_2O^+, an example of ionization transfer, has been neither substantiated nor refuted. Our interest in this suggestion is due to the recent model for the radiolysis of water in which hole trapping by anions is postulated to occur.[11]

This paper reports an extension of the previous kinetic study[8] to include the radiolysis of cerium(IV)–cerium(III)–formic acid mixtures in air-saturated 0.04, 0.4, and 4.0 *M* sulfuric acid solutions and cerium(IV)–

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cerium(III)-2-propanol mixtures in air-saturated 0.4 and 4.0 M sulfuric acid solutions. As reported in our preliminary communication,[12] kinetic evidence is presented for the concurrent production of OH and SO_4^- radicals in the radiolysis of aqueous sulfuric acid solutions. The proposal of Boyle[6] is substantiated. The suggestion[7] that sulfuric acid anions react with H_2O^+ to yield SO_4^- is refuted, since G_{OH} is proportional to electron fraction water.

Experimental Section

Materials. Fisher purified ceric ammonium sulfate, G. Frederick Smith Co. reagent cerous sulfate, Matheson Coleman and Bell spectroquality reagent 2-propanol, Baker Analyzed reagent formic acid, Baker and Adamson reagent ferrous ammonium sulfate, and Du Pont reagent sulfuric acid were used without further purification. All solutions were prepared with water from a Barnstead still that was further purified by successive distillations from an acid dichromate solution, from an alkaline permanganate solution, and finally from an all-silica system into silica storage vessels.

Irradiations. Solutions in a 2-cm Pyrocell cylindrical absorption cell were irradiated in ^{60}Co sources of the Ghormley-Hochanadel design.[13] The cell had S18-260 silica windows that did not become colored enough during irradiations to interfere with spectrophotometric analyses of the solutions with a Cary recording spectrophotometer. Dose rates were determined with the ferrous sulfate dosimeter using $G(\mathrm{Fe^{III}}) = 15.6$.[14] The energy absorbed in solutions relative to the ferrous sulfate dosimeter was assumed to be in the ratio of electron densities.

Analyses. Changes in cerium(IV) concentration with absorbed dose were determined spectrophotometrically in the irradiation cell. Molar extinction coefficients for cerium(IV) at 320 nm of 5580 in 0.4 M sulfuric acid[14] and 6590 in 4.0 M sulfuric acid[15] were used. The molar extinction coefficient of cerium(IV) at 320 nm in 0.04 M sulfuric acid was markedly affected by the high concentrations of cerium(III) sulfate that we used (ranging from 5099 in its absence to 5446 for 0.058 M) and was determined for each concentration of cerium(III) sulfate. A molar extinction coefficient for iron(III) at 305 nm of 2210 in 0.4 M sulfuric acid[16] was used for ferrous sulfate dosimetry. While all irradiations were made at ambient room temperature, all spectrophotometric analyses were made thermostatically at 25°.

Results

$G(\mathrm{Ce^{III}})$ is markedly dependent on both cerium(III) and formic acid concentrations in the radiolysis of cerium(IV)-cerium(III)-formic acid mixtures in air-saturated sulfuric acid solutions.[8] Figure 1 shows the results obtained in 4.0 M sulfuric acid solutions. Similar results were obtained in both 0.4 M and 0.04 M sulfuric acid solutions.

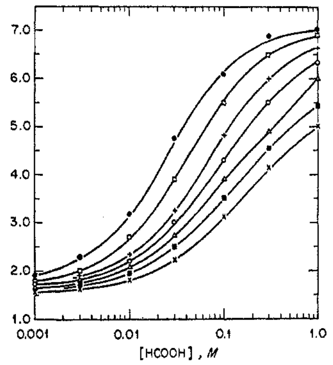

Figure 1. Dependence of $G(\mathrm{Ce^{III}})$ on [$\mathrm{Ce^{III}}$] and [HCOOH] in the reduction of cerium(IV) in air-saturated 4.0 M sulfuric acid solutions induced by ^{60}Co γ radiation. Initial [$\mathrm{Ce^{III}}$]: (×) 3.0×10^{-2} M, (■) 1.5×10^{-2} M, (△) 6.0×10^{-3} M, (○) 3.0×10^{-3} M, (+) 1.5×10^{-3} M, (□) 6.0×10^{-4} M, (●) 3.0×10^{-4} M. Curves are theoretical and represent least-squares fit of the data to eq III.

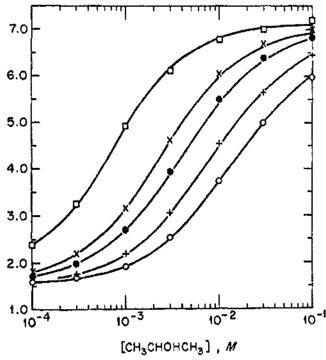

Figure 2. Dependence of $G(\mathrm{Ce^{III}})$ on [$\mathrm{Ce^{III}}$] and [$CH_3CHOHCH_3$] in the reduction of cerium(IV) in air-saturated 4.0 M sulfuric acid solutions induced by ^{60}Co γ radiation. Initial [$\mathrm{Ce^{III}}$]: (○) 2.92×10^{-2} M, (+) 1.46×10^{-2} M, (●) 5.86×10^{-3} M, (×) 2.92×10^{-3} M, (□) 6.10×10^{-4} M. Curves are theoretical and represent least-squares fit of the data to eq III.

$G(\mathrm{Ce^{III}})$ is also markedly dependent on both cerium(III) and 2-propanol concentrations in the radiolysis of cerium(IV)-cerium(III)-2-propanol mixtures in air-saturated sulfuric acid solutions. Figure 2 shows the results obtained in 4.0 M sulfuric acid solutions. Similar results were obtained in 0.4 M sulfuric acid solutions.

The initial concentration of cerium(IV) in all solutions was about 10^{-4} M. Changes in cerium(IV) concentrations with dose were determined in each solution

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(13) J. A. Ghormley and C. J. Hochanadel, *Rev. Sci. Instrum.*, **22**, 473 (1951).

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by five to six successive irradiations. In most cases, the cerium(IV) concentration changed linearly with dose within experimental error. In some cases, the initial rate of reduction was determined by extrapolation from a plot of the rate of cerium(IV) reduction as a function of dose.

There is reportedly[17] no effect of oxygen on $G(Ce^{III})$. The absence of an oxygen effect was attributed to reduction of cerium(IV) by either H atom or the HO_2 radical that results from reaction of H atom with oxygen. A small effect of oxygen on $G(Ce^{III})$ is to be expected, however, owing to the dependence of G_{H_2} on oxygen concentration.[18] We conducted some experiments in deoxygenated 4.0 M sulfuric acid solutions to evaluate the role of oxygen in the radiolysis of cerium(IV)-cerium(III)-formic acid mixtures.

In 0.0015 M cerium(III) solutions, the values for $G(Ce^{III})$ at all formic acid concentrations are slightly higher in initially air-saturated solutions than in initially deoxygenated solutions, as shown in Figure 3. This small effect of oxygen, an increase in $G(Ce^{III})$ of 0.22 ± 0.03 independent of formic acid concentration, is attributed to the reactions of oxygen in the spur that reportedly[18] cause G_{H_2} to decrease.

In 0.03 M cerium(III) solutions, we were surprised to observe net cerium(III) oxidation at low formic acid concentrations in initially deoxygenated solutions as shown in Figure 3. We have established[19,20] that net oxidation of cerium(III) results from reaction of H atom with hydrogen peroxide since reactions of cerium(IV) with both H atom and hydrogen peroxide are slow. Oxygen in air-saturated solutions inhibits reaction of H atom with hydrogen peroxide through intermediate formation of HO_2. For this reason, we used air-saturated solutions in this kinetic study. As indicated by the data in Figure 3, formic acid at high concentrations also inhibits reaction of H atom with hydrogen peroxide. This is attributed to reaction of formic acid with H atom,[21] presumably to yield an intermediate that reduces cerium(IV).

Discussion

The reaction mechanism for radiation-induced reduction of cerium(IV) in aqueous sulfuric acid solutions is well established. Allen[7] proposed that cerium(IV) is reduced by both H atom and hydrogen peroxide while cerium(III) is oxidized by OH radical and

$$G(Ce^{III}) = 2G_{H_2O_2} + G_H - G_{OH} \qquad (I)$$

His hypothesis was substantiated by Challenger and Masters[22] who observed concomitant oxidation of radioactive cerium(III) during net reduction of cerium(IV). Allen's hypothesis was further substantiated by studies of the enhancement of $G(Ce^{III})$ by formic acid,[23] thallium(I),[16] and 2-propanol[24] through their reaction with OH radical to yield intermediates that reduce cerium(IV).

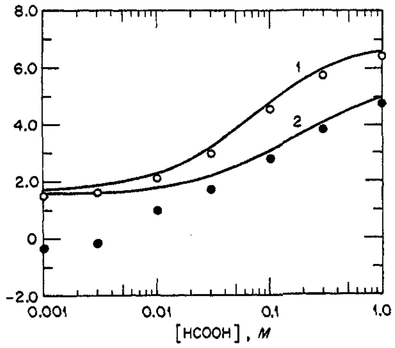

Figure 3. Dependence of $G(Ce^{III})$ on $[Ce^{III}]$ and [HCOOH] in the reduction of cerium(IV) in deoxygenated 4.0 M sulfuric acid solutions induced by ^{60}Co γ radiation. Initial $[Ce^{III}]$: (○) 1.5×10^{-3} M, (●) 3.0×10^{-2} M. The results for air-saturated solutions are indicated by curve 1 for $[Ce^{III}] = 1.5 \times 10^{-3}$ M and by curve 2 for $[Ce^{III}] = 3.0 \times 10^{-2}$ M.

We have considered reactions 1-9 of OH and SO_4^- radicals in order to explain the dependence of $G(Ce^{III})$ on cerium(III), formic acid, and 2-propanol concentrations.

$$OH + HSO_4^- \rightleftharpoons H_2O + SO_4^- \qquad (1)$$

$$OH + Ce^{III} \longrightarrow OH^- + Ce^{IV} \qquad (2)$$

$$SO_4^- + Ce^{III} \longrightarrow SO_4^{2-} + Ce^{IV} \qquad (3)$$

$$OH + HCOOH \longrightarrow H_2O + COOH \qquad (4)$$

$$SO_4^- + HCOOH \longrightarrow HSO_4^- + COOH \qquad (5)$$

$$COOH + Ce^{IV} \longrightarrow H^+ + CO_2 + Ce^{III} \qquad (6)$$

$$OH + CH_3CHOHCH_3 \longrightarrow H_2O + CH_3COHCH_3 \qquad (7)$$

$$SO_4^- + CH_3CHOHCH_3 \longrightarrow HSO_4^- + CH_3COHCH_3 \qquad (8)$$

$$CH_3COHCH_3 + Ce^{IV} \longrightarrow H^+ + CH_3COCH_3 + Ce^{III} \qquad (9)$$

One Primary oxidizing Radical Model: OH. In the radiolysis of cerium(IV)-cerium(III)-formic acid mixtures in air-saturated 0.4 M sulfuric acid solutions, Sworski[8] implicitly assumed that $G_{SO_4^-}$, $k_{-1}[H_2O]/(k_3[Ce^{III}])$, and $k_5[HCOOH]/(k_3[Ce^{III}])$ were negligibly small and obtained

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$$G(\mathrm{Ce^{III}}) = G(\mathrm{Ce^{III}})^0 + 2G_{\mathrm{OH}}^*\Bigg/\left(1 + \frac{k_1[\mathrm{HSO_4^-}] + k_2[\mathrm{Ce^{III}}]}{k_aS}\right) \quad \text{(II)}$$

For cerium(IV)-cerium(III)-formic acid mixtures, k_aS denotes $k_4[\mathrm{HCOOH}]$. For cerium(IV)-cerium(III)-2-propanol mixtures, k_aS denotes $k_7[\mathrm{CH_3CHOHCH_3}]$. G_{OH}^*, a function of cerium(III) and sulfuric acid concentrations, denotes the value of G_{OH} that is obtained by the use of eq II. $G(\mathrm{Ce^{III}})^0$, also a function of cerium(III) and sulfuric acid concentrations, denotes the value of $G(\mathrm{Ce^{III}})$ in the absence of formic acid and 2-propanol.

All of our data adhered well to eq II. The experimental data were fit to eq II by the method of least squares, using the computer program of Lietzke.[25] The data were weighted by assuming that all $G(\mathrm{Ce^{III}})$ values had a constant percentage error. Values of $G(\mathrm{Ce^{III}})^0$, G_{OH}^*, and the kinetic parameter $(k_1[\mathrm{HSO_4^-}] + k_2[\mathrm{Ce^{III}}])/k_a$ were obtained as a function of cerium(III) and sulfuric acid concentrations.

Equation II seems to be a valid approximation for cerium(IV)-cerium(III)-formic acid mixtures in 0.04 and 0.4 M sulfuric acid solutions. As shown in Figure 4, the kinetic parameter $(k_1[\mathrm{HSO_4^-}] + k_2[\mathrm{Ce^{III}}])/k_4$ is approximately a linear function of cerium(III) concentration and has a finite positive value indicated for $[\mathrm{Ce^{III}}] = 0$. Figure 4 also shows that eq II is clearly not valid for cerium(IV)-cerium(III)-formic acid mixtures in 4.0 M sulfuric acid solutions.

Similarly, eq II seems to be a valid approximation for cerium(IV)-cerium(III)-2-propanol mixtures in 0.4 M sulfuric acid solutions. As shown in Figure 5, the kinetic parameter $(k_1[\mathrm{HSO_4^-}] + k_2[\mathrm{Ce^{III}}])/k_7$ is approximately a linear function of cerium(III) concentration and computer analysis yielded a finite positive value for $[\mathrm{Ce^{III}}] = 0$. Figure 5 also shows that eq II is again clearly not valid for 4.0 M sulfuric acid solutions.

G_{OH}^* increases with increase in cerium(III) concentration for cerium(IV)-cerium(III)-formic acid mixtures in 0.04 M sulfuric acid solutions, as shown in Figure 6, and for cerium(IV)-cerium(III)-2-propanol mixtures in 0.4 M sulfuric acid solutions, as shown in Figure 7. This is just what we anticipated for the dependence of G_{OH} on cerium(III) concentration, since $G_{\mathrm{H_2O_2}}$ decreases with increase in cerium(III) concentration.[16] It was clearly shown in the radiolysis of cerium(IV)-thallium(I) mixtures in 0.4 M sulfuric acid solutions that G_{OH} increases with increase in thallium(I) concentration by an amount equal to twice the concomitant decrease in $G_{\mathrm{H_2O_2}}$ causing $G(\mathrm{Ce^{III}})$ to be independent of thallium(I) concentration.[16]

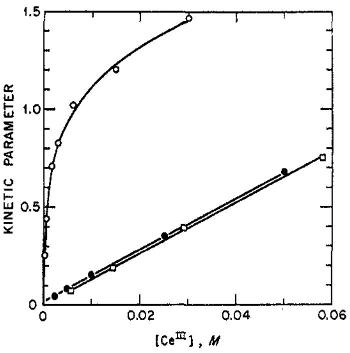

Figure 4. Dependence of the kinetic parameter $(k_1[\mathrm{HSO_4^-}] + k_2[\mathrm{Ce^{III}}])/k_4$ in eq II on $[\mathrm{Ce^{III}}]$. Sulfuric acid concentrations: (○) 4.0 M, (●) 0.4 M, (□) 0.04 M.

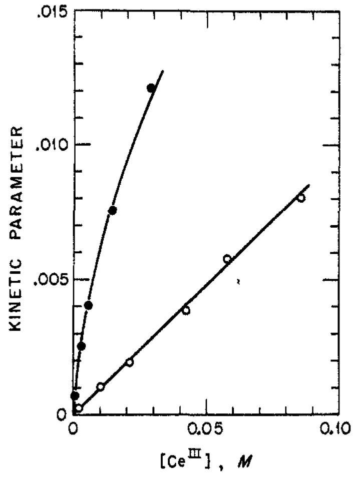

Figure 5. Dependence of the kinetic parameter $(k_1[\mathrm{HSO_4^-}] + k_2[\mathrm{Ce^{III}}])/k_7$ in eq II on $[\mathrm{Ce^{III}}]$. Sulfuric acid concentrations: (●) 4.0 M, (○) 0.4 M.

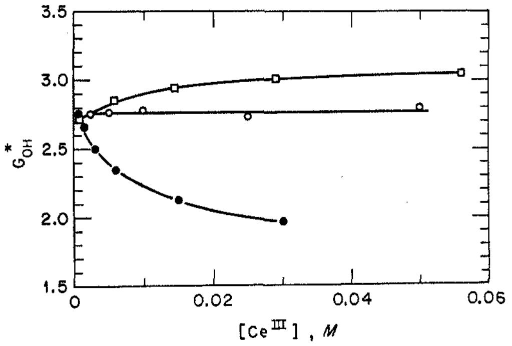

Figure 6. Dependence of G_{OH}^* in eq II on cerium(III) concentration for cerium(IV)-cerium(III)-formic acid mixtures. Sulfuric acid concentrations: (●) 4.0 M, (○) 0.4 M, (□) 0.04 M.

G_{OH}^* seems to be independent of changes in cerium(III) concentration for cerium(IV)-cerium(III)-formic acid mixtures in 0.4 M sulfuric acid solutions as shown in Figure 6. G_{OH}^* decreases markedly with increase in cerium(III) concentration in 4.0 M sulfuric acid solutions both for cerium(IV)-cerium(III)-formic acid mixtures, as shown in Figure 6 and for cerium(IV)-cerium(III)-2-propanol mixtures, as shown in Figure 7. These results were unexpected and indicate that eq II

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[25] M. H. Lietzke, ORNL-3259, Mar 21, 1962.

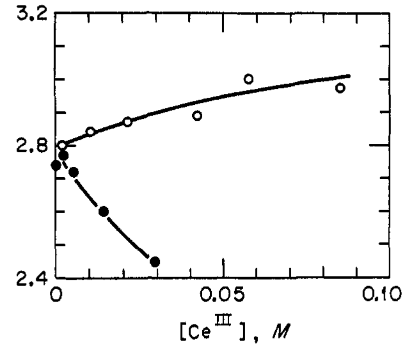

Figure 7. Dependence of G_{OH}^* in eq II on cerium(III) concentration for cerium(IV)-cerium(III)-2-propanol mixtures. Sulfuric acid concentrations: (●) 4.0 M, (○) 0.4 M.

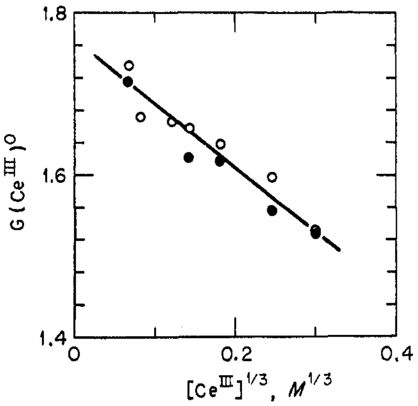

Figure 8. Dependence of $G(Ce^{III})^0$ in eq II on cerium(III) concentration in 4.0 M sulfuric acid solutions containing either (○) formic acid or (●) 2-propanol.

is a poor approximation for 0.4 M sulfuric acid solutions containing cerium(IV)-cerium(III)-formic acid mixtures and not valid for 4.0 M sulfuric acid solutions.

$G(Ce^{III})^0$ in 4.0 M sulfuric acid solutions decreases linearly with the cube root of the cerium(III) concentration as shown in Figure 8. The theoretical significance of this cube-root dependence is its implication that $G_{H_2O_2}$ decreases with increase in cerium(III) concentration, just as previously reported[16] for 0.4 M sulfuric acid solutions.

Two Primary Oxidizing Radicals Models. OH and SO_4^-. Our initial experiments were with cerium(IV)-cerium(III)-formic acid mixtures. The dependence of the kinetic parameter on cerium(III) concentration in 4.0 M sulfuric acid solutions as shown in Figure 4 was found to be quantitatively explicable by postulating that reaction (1) is sensibly reversible. The dependence of G_{OH}^* on cerium(III) concentration in 4.0 M sulfuric acid solutions as shown in Figure 6 was found to be quantitatively explicable by postulating two oxidizing radicals: the OH radical and an unidentified intermediate that either disappears by a first-order process to yield OH radical or reacts with cerium(III) but not with formic acid. The best fit of the experimental data to these postulates was obtained by assuming that the unidentified intermediate was not SO_4^-. This suggested the possibility that the unidentified intermediate may be either H_2O^+ or H_2O^*.

To test the validity of these two postulates, we extended our study to include the cerium(IV)-cerium(III)-2-propanol mixtures. Comparison of Figures 6 and 7 shows that G_{OH}^* in 4.0 M sulfuric acid solutions is not a function of cerium(III) concentration alone. We concluded, therefore, that the unidentified intermediate may also react with formic acid and 2-propanol.

The dependence of $G(Ce^{III})$ on cerium(III) and either formic acid or 2-propanol concentrations in 4.0 M sulfuric acid solutions is quantitatively explicable by the sequence of reactions 1-9 induced by primary yields of both OH and SO_4^-. This reaction mechanism and the stationary-state hypothesis for OH and SO_4^- concentrations require that

$$G(Ce^{III}) = G(Ce^{III})^0 + 2(aG_{OH} + bG_{SO_4^-})/c \quad \text{(III)}$$

in which

$$a = \frac{k_bS}{k_3C} + \frac{k_aS}{k_1A}\left(1 + \frac{k_bS + k_{-1}W}{k_3C}\right)$$

$$b = \frac{k_ak_{-1}SW}{k_3k_1CA} + \frac{k_bS}{k_3C}\left(1 + \frac{k_aS + k_2C}{k_1A}\right)$$

$$c = 1 + \frac{k_bS}{k_3C} + \left(1 + \frac{k_bS + k_{-1}W}{k_3C}\right)\left(\frac{k_aS + k_2C}{k_1A}\right)$$

$C = [Ce^{III}]$, $A = [HSO_4^-]$, and $W = [H_2O]$. For cerium(IV)-cerium(III)-formic acid mixtures, k_bS denotes $k_5[HCOOH]$. For cerium(IV)-cerium(III)-2-propanol mixtures, k_bS denotes $k_8[CH_3CHOHCH_3]$. Equation III was obtained with the assumption that G_{OH} and $G_{SO_4^-}$ are constants, independent of variations in concentrations of cerium(III), formic acid, and 2-propanol.

The experimental data were fit to eq III by the method of least squares. For cerium(IV)-cerium(III)-formic acid mixtures in 4.0 M sulfuric acid solutions, 13 unknowns were determined: the values of G_{OH}, $G_{SO_4^-}$, and four rate constant ratios listed in column 1 of Table I and seven values of $G(Ce^{III})^0$ for the seven different cerium(III) concentrations. For cerium(IV)-cerium(III)-2-propanol mixtures in 4.0 M sulfuric acid solutions, 11 unknowns were determined: the values of G_{OH}, $G_{SO_4^-}$, and four rate constant ratios listed in column 2 of Table I and five values of $G(Ce^{III})^0$ for the five different cerium(III) concentrations.

The experimental data adhere well to eq III, as indicated by the theoretical curves in Figures 1 and 2 that illustrate the least-squares fit of the data to eq III. The excellent agreement between the two sets of values for G_{OH} and $G_{SO_4^-}$ that are listed in columns 1 and 2 of Table I is evidence for the validity of eq III.

Table I: Results from Least-Squares Fit of Experimental Data to Eq III–V

	1^a	2^b	3^c	4^d
G_{OH}	1.78 ± 0.03	1.76 ± 0.19	1.76 ± 0.03	2.60 ± 0.04
$G_{SO_4^-}$	0.94 ± 0.03	0.95 ± 0.18	0.94 ± 0.03	0.20 ± 0.04
$k_2/(k_1[HSO_4^-])$	30 ± 3	84 ± 17	30 ± 3	$(9.3 \pm 1.1) \times 10^2$
$k_{-1}[H_2O]/k_3$	$(1.7 \pm 0.5) \times 10^{-4}$	$(2.7 \pm 3.9) \times 10^{-4}$	$(1.2 \pm 0.5) \times 10^{-4}$	$(1.1 \pm 0.6) \times 10^{-4}$
$k_4/(k_1[HSO_4^-])$	14.4 ± 0.5		14.7 ± 0.6	$(6.9 \pm 0.8) \times 10^2$
k_5/k_3	$(6.0 \pm 0.5) \times 10^{-3}$		$(6.5 \pm 0.5) \times 10^{-3}$	$(7.2 \pm 6.7) \times 10^{-3}$
$k_7/(k_1[HSO_4^-])$		360 ± 34	202 ± 12	$(1.1 \pm 0.2) \times 10^4$
k_8/k_3		0.61 ± 0.11	0.64 ± 0.03	0.71 ± 0.30
$k_{12}[H^+]/k_{11}$			0.35 ± 0.04	
k_{10}/k_7			1.4 ± 0.3	

[a] Cerium(IV)–cerium(III)–formic acid mixtures in 4.0 *M* sulfuric acid; eq III. [b] Cerium(IV)–cerium(III)–2-propanol mixtures in 4.0 *M* sulfuric acid; eq III. [c] All data in 4.0 *M* sulfuric acid; eq IV. [d] All data in 0.4 *M* sulfuric acid; eq V.

Absolute rate constants for reactions of SO_4^- with cerium(III), formic acid, and 2-propanol have been reported:[26] $k_3 = 1.43 \times 10^8\ M^{-1}\ \text{sec}^{-1}$, $k_5 = 1.35 \times 10^6\ M^{-1}\ \text{sec}^{-1}$, and $k_8 = 4.60 \times 10^7\ M^{-1}\ \text{sec}^{-1}$. These values yield $k_5/k_3 = 9.4 \times 10^{-3}$ and $k_8/k_3 = 0.32$, in fair agreement with our determinations listed in Table I.

The large standard errors listed in Table I for $k_{-1}\cdot[H_2O]/k_3$ suggest that $k_{-1}[H_2O]/k_3$ is almost negligibly small for most of our solutions, hydrolysis of SO_4^- being significant only for a few of the more dilute cerium(III) solutions. We previously assumed[2] that $k_{-1}[H_2O]/k_3 = 0$ and obtained G_{OH} values of 1.70 ± 0.02 and 1.64 ± 0.08 and $G_{SO_4^-}$ values of 0.97 ± 0.03 and 1.06 ± 0.09 for formic acid and 2-propanol solutions in 4.0 *M* sulfuric acid, respectively. These two sets of values for G_{OH} and $G_{SO_4^-}$ are in agreement within standard errors, but the agreement is not as good as for the values obtained by use of eq III.

The poor agreement between the two values for $k_2/(k_1[HSO_4])$ listed in columns 1 and 2 of Table I is disappointing in view of the excellent agreement between the two sets of values for G_{OH} and $G_{SO_4^-}$. We have speculated on the cause of this poor agreement and suggest that it may be due to reactions 10–12. The net

$$OH + CH_3CHOHCH_3 \longrightarrow H_2O + CH_3CHOCH_3 \quad (10)$$

$$CH_3CHOCH_3 + CH_3CHOHCH_3 \longrightarrow CH_3CHOHCH_3 + CH_3COHCH_3 \quad (11)$$

$$H^+ + CH_3CHOCH_3 + Ce^{III} \longrightarrow CH_3CHOHCH_3 + Ce^{IV} \quad (12)$$

effect for the sequence of reactions (10) and (12) is the oxidation of cerium(III) by OH, thus causing a higher value of $k_2/(k_1[HSO_4^-])$ for 2-propanol solutions.

This suggestion was substantiated by a least-squares fit of the combined data from formic acid and 2-propanol solutions in 4.0 *M* sulfuric acid to

$$G(Ce^{III}) = G(Ce^{III})^0 + 2(aG_{OH} + bG_{SO_4^-})/c + 2(dG_{OH} + eG_{SO_4^-})/f \quad (IV)$$

in which

$$d = \frac{k_8P}{k_3C} + \frac{k_7P}{k_1A}\left[1 + \frac{k_{10}}{k_7}\Big/\left(1 + \frac{k_{12}[H^+]C}{k_{11}P}\right)\right]\left(1 + \frac{k_8P + k_{-1}W}{k_3C}\right)$$

$$e = \frac{k_7k_{-1}PW}{k_3k_1CA}\left[1 + \frac{k_{10}}{k_7}\Big/\left(1 + \frac{k_{12}[H^+]C}{k_{11}P}\right)\right] + \frac{k_8P}{k_3C}\left(1 + \frac{k_7P + k_{10}P + k_2C}{k_1A}\right)$$

$$f = 1 + \frac{k_8P}{k_3C} + \left(1 + \frac{k_8P + k_{-1}W}{k_3C}\right) \times \left(\frac{k_7P + k_{10}P + k_2C}{k_1A}\right)$$

P denotes $[CH_3CHOHCH_3]$ so that *d*, *e*, and *f* are used for cerium(IV)–cerium(III)–2-propanol mixtures. In eq IV, k_aS and k_bS only denote $k_4[HCOOH]$ and $k_5[HCOOH]$ so that *a*, *b*, and *c*, are used for cerium(IV)–cerium(III)–formic acid mixtures.

Twenty-two unknowns were determined: the values of G_{OH}, $G_{SO_4^-}$, and 8 rate constant ratios listed in column 3 of Table I and 12 values of $G(Ce^{III})^0$ for the 12 different cerium(III) concentrations. There are two major effects of assuming the sequence of reactions 10–12 and using eq IV: the value for $k_2/(k_1[HSO_4^-])$ becomes identical with that listed in column 1 of Table I for formic acid solutions and $k_7/(k_1[HSO_4^-])$ decreases significantly.

The difference in the dependence of G_{OH}^* on cerium(III) concentration between formic acid and 2-propanol solutions in 0.4 *M* sulfuric acid, shown in Figures 4 and 5, may be evidence for a significant value of $G_{SO_4^-}$. Therefore, a least-squares analysis of the combined data from formic acid and 2-propanol solutions in 0.4 *M* sulfuric acid was made with the constraint that the dependence of G_{OH} on cerium(III) concentration be iden-

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(26) L. Dogliotti and E. Hayon, *J. Phys. Chem.*, 71, 3802 (1967).

tical for formic acid and 2-propanol solutions. G_{OH} was assumed to increase linearly with increase in the cube root of the cerium(III) concentration.

The experimental data were fit by the method of least squares to

$$G(\mathrm{Ce^{III}}) = G(\mathrm{Ce^{III}})^0 + 2[a(G_{\mathrm{OH}} + A[\mathrm{Ce^{III}}]^{1/3}) + bG_{\mathrm{SO_4^-}}]/c \qquad (\mathrm{V})$$

Twenty-one unknowns were determined: the values of G_{OH}, $G_{\mathrm{SO_4^-}}$, and 6 rate constant ratios listed in column 4 of Table I, 12 values of $G(\mathrm{Ce^{III}})^0$ for the 12 different cerium(III) concentrations, and $A = 0.57 \pm 0.08$.

The agreement between the values of $k_{-1}[\mathrm{H_2O}]/k_3$, k_5/k_3, and k_8/k_3 for 4.0 and 0.4 M sulfuric acid solutions listed in columns 3 and 4 of Table I is surprisingly excellent and is further evidence for the validity of our two primary oxidizing radicals model. The larger standard errors indicated in the values for 0.4 M sulfuric acid solutions listed in column 4 of Table I are attributable to the role of $\mathrm{SO_4^-}$ in 0.4 M sulfuric acid solutions being less important than in 4.0 M sulfuric acid solutions, though still significant. The present determination of $k_2:k_4:k_1[\mathrm{HSO_4^-}] = 930:690:1$ for 0.4 M sulfuric acid solutions supersedes the previous determination of $k_2:k_4:k_1[\mathrm{HSO_4^-}] = 1600:950:1$ that was obtained by approximation.[8]

In view of the low electron fraction sulfuric acid in 0.04 M sulfuric acid solutions, no attempt was made to determine $G_{\mathrm{SO_4^-}}$. The experimental data for cerium(IV)-cerium(III)-formic acid mixtures in 0.04 M sulfuric acid solutions were fit by the method of least squares to eq V with the previous approximations that $G_{\mathrm{SO_4^-}}$, $k_{-1}[\mathrm{H_2O}]/(k_3[\mathrm{Ce^{III}}])$, and $k_5[\mathrm{HCOOH}]/(k_3[\mathrm{Ce^{III}}])$ were negligibly small. Ten unknowns were determined: $G_{\mathrm{OH}} = 2.67 \pm 0.04$, $A = 1.05 \pm 0.13$, $k_2/(k_1[\mathrm{HSO_4^-}]) = (1.2 \pm 0.2) \times 10^4$, $k_4/(k_1[\mathrm{HSO_4^-}]) = (9.2 \pm 0.9) \times 10^3$, and six values of $G(\mathrm{Ce^{III}})^0$ for the six different cerium(III) concentrations.

G_{OH} increases with increase in cerium(III) concentration in both 0.04 M and 0.4 M sulfuric acid solutions. As stated above, this is just what we expected. Our assumption that both G_{OH} and $G_{\mathrm{SO_4^-}}$ are constants, independent of variations in cerium(III) concentration, in 4.0 M sulfuric acid solutions may be unjustified. Therefore, we determined the effects of assuming that both G_{OH} and $G_{\mathrm{SO_4^-}}$ in eq IV vary linearly with the cube root of the cerium(III) concentration. We also determined, at the same time, the effect of assuming that $G(\mathrm{Ce^{III}})^0$ in eq IV and V varies linearly with the cube root of the cerium(III) concentration. The dependence of G_{OH} on cerium(III) concentration is given in Table II. The dependence of $G(\mathrm{Ce^{III}})^0$ on cerium(III) concentration is given in Table III. $G_{\mathrm{SO_4^-}}$ in 4.0 M sulfuric acid solutions was found to be $(0.95 \pm 0.14) - (0.35 \pm 0.45)[\mathrm{Ce^{III}}]^{1/3}$.

Table II: Dependence of G_{OH} on Cerium(III) Concentration

$[\mathrm{H_2SO_4}]$, M	G_{OH}
4.0	$(1.78 \pm 0.14) + (0.02 \pm 0.42)[\mathrm{Ce^{III}}]^{1/3}$
0.4	$(2.57 \pm 0.05) + (0.60 \pm 0.09)[\mathrm{Ce^{III}}]^{1/3}$
0.04	$(2.60 \pm 0.04) + (1.29 \pm 0.14)[\mathrm{Ce^{III}}]^{1/3}$

Table III: Dependence of $G(\mathrm{Ce^{III}})^0$ on Cerium(III) Concentration

$[\mathrm{H_2SO_4}]$, M	$G(\mathrm{Ce^{III}})^0$
4.0	$(1.76 \pm 0.01) - (0.72 \pm 0.04)[\mathrm{Ce^{III}}]^{1/3}$
0.4	$(2.40 \pm 0.02) - (0.74 \pm 0.06)[\mathrm{Ce^{III}}]^{1/3}$
0.04	$(2.48 \pm 0.02) - (1.30 \pm 0.09)[\mathrm{Ce^{III}}]^{1/3}$

The assumption that G_{OH} and $G(\mathrm{Ce^{III}})^0$ vary linearly with the cube root of the cerium(III) concentration is a good approximation, except for the dependence of G_{OH} on cerium(III) concentration in 4.0 M sulfuric acid solutions, as evidenced by the low standard errors for the coefficients of $[\mathrm{Ce^{III}}]^{1/3}$. In 4.0 M sulfuric acid solutions, it is apparently a gross oversimplification to assume that G_{OH} would vary linearly with $[\mathrm{Ce^{III}}]^{1/3}$. The value of 30 ± 3 for $k_2/(k_1[\mathrm{HSO_4^-}])$ indicates that the sulfuric acid anions are as reactive with OH radical as 0.033 M cerium(III). We assume, therefore, that sulfuric acid anions in 4.0 M sulfuric acid solutions inhibit significantly the formation of hydrogen peroxide in the spur and enhance the formation of peroxosulfuric and peroxodisulfuric acids. The negligibly small dependence of G_{OH} on $[\mathrm{Ce^{III}}]^{1/3}$ in 4.0 M sulfuric acid solutions is attributed to inhibition of reactions of OH with cerium(III) in the spur by sulfuric acid anions.

If the only effect of cerium(III) on reactions of OH radical in the spur were to inhibit the formation of hydrogen peroxide, then the decrease in $G(\mathrm{Ce^{III}})^0$ by any particular concentration of cerium(III) should be equal to twice the concomitant increase in G_{OH}. Tables II and III show that $2\Delta G_{\mathrm{OH}}$ is much larger than $-\Delta G(\mathrm{Ce^{III}})^0$ for 0.04 M and 0.4 M sulfuric acid solutions and suggest that cerium(III) is also inhibiting re-formation of water in the spur.

We previously reported that $G(\mathrm{Ce^{III}})^0 = 1.66 \pm 0.03$[15] in air-saturated 4.0 M sulfuric acid solutions containing 3.0×10^{-3} M cerium(III) and $G(\mathrm{Ce^{III}})^0 = 2.39$[16] in air-saturated 0.4 M sulfuric acid solutions containing no initial cerium(III). These values are in agreement with the results listed in Table III.

Let E_{W} denote electron fraction water and $G_{\mathrm{OH}}{}^0$ denote the G value for OH production that results from energy absorption by water. Then $G_{\mathrm{OH}}{}^0 = G_{\mathrm{OH}}/E_{\mathrm{W}}$, provided that energy absorption by water is proportional to electron fraction water, neither ionization transfer nor excitation transfer occurs between water and sulfuric acid anions, and the fraction of OH radicals escaping from the spur by diffusion into the bulk of the solution is independent of sulfuric acid concentration. The dependence of G_{OH}, E_W, and G_{OH}^0 on sulfuric acid concentration is given in Table IV.

Table IV: Dependence of G_{OH} on Electron Fraction Water

$[H_2SO_4]$, M	G_{OH}	E_W	G_{OH}^0
4.0	1.76 ± 0.03	0.700	2.51 ± 0.05
0.4	2.60 ± 0.04	0.963	2.70 ± 0.04
0.04	2.67 ± 0.04	0.997	2.68 ± 0.04
0	2.59 ± 0.09[a]	1.000	2.59 ± 0.09

[a] From ref 27.

The values of G_{OH}^0 for 0.04, 0.4, and 4.0 M sulfuric acid solutions are all equal within standard errors to $G_{OH} = 2.59 \pm 0.09$, the most recent value of G_{OH} for pure water that has been determined in our laboratory.[27] These results substantiate the proposal of Boyle[6] that G_{OH} is proportional to electron fraction water in the radiolysis of aqueous sulfuric acid solutions. They refute the suggestion of Allen[7] that SO_4^- may result from reaction of HSO_4^- with H_2O^+, a commonly assumed precursor of the OH radical.

Evidence has been reported[28] for the dry charge pair[11] in the radiolysis of water: a decrease in $G(H_2O_2)$ by chloride ion in neutral aqueous solutions containing oxygen has been attributed to trapping of the dry hole, H_2O^+, by chloride ion at high concentrations. Our evidence that G_{OH} is proportional to electron fraction water in 4.0 M sulfuric acid solutions and in 4.0 M nitric acid solutions[12] indicates that hole trapping by anions, if it occurs at all, is not a general phenomenon. Definitive evidence for hole trapping would be a dependence of G_{OH} on both electron fraction water and anion concentration.

Under our experimental conditions, equilibrium between OH and SO_4^- is not established. If equilibrium were established, it can be easily shown that a one oxidizing radical model would be applicable even though there were primary yields of both OH and SO_4^-. We can, however, evaluate $[SO_4^-]/[OH]$ for equilibrium conditions by noting that $[SO_4^-]/[OH] = k_1[HSO_4^-]/(k_1[H_2O])$ at equilibrium. Using the reported values of $1.43 \times 10^8\ M^{-1}\ sec^{-1}$ for k_3[26] and $2.2 \times 10^8\ M^{-1}\ sec^{-1}$ for k_2,[29] our values for $k_2/(k_1[HSO_4^-])$ of 30 and 930 and for $k_{-1}[H_2O]/k_3$ of 1.7×10^{-4} and 1.1×10^{-4} yield values for $[SO_4^-]/[OH]$ of 302 and 15.0 for 4.0 and 0.4 M sulfuric acid solutions, respectively. At these sulfuric acid concentrations, $[HSO_4^-]$ is approximately equal[30] to seven-tenths of the sulfuric acid molarity, and the equilibrium concentration quotient $[SO_4^-]/([OH][HSO_4^-])$ for reaction 1 is approximately equal to 100 and 50 for 4.0 and 0.4 M sulfuric acid solutions, respectively. The high concentrations of sulfuric acid in our solutions preclude the calculations of equilibrium values for $[SO_4^-]/[OH]$ using the equilibrium constant evaluated by Wilmarth and Haim.[31]

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