# Pulse Radiolysis Study of the Direct Effect on Sulfuric Acid

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The radical  $SO_4^-$  (or HSO<sub>4</sub>) produced by the direct effect of radiation on sulfuric acid has been observed in aqueous 0.4, 2, and 4 M sulfuric acid in yields given by  $G(SO_4^-) = 4.3f(H_2SO_4)$ , where  $f(H_2SO_4)$  is the electron fraction of sulfuric acid present. A reaction scheme is proposed to explain the disappearance of  $SO_4^-$ .

**Experimental Section** 

## Introduction

It has long been recognized<sup>1,2</sup> that the free radicals  $SO_4^-$  and  $HSO_4$  play an important role in the radiolysis of sulfuric acid solutions. (For simplicity both forms of the radical are designated in the text as  $SO_4^{-}$ .) Their principal mode of formation is the action of OH on sulfuric acid

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

and the rate constant for this reaction has been measured by several competition methods<sup>3-8</sup> as  $3.5 \times 10^5 M^{-1}$  $sec^{-1}$ . The absorption spectrum of  $SO_4^-$  formed in this way has been determined<sup>9,10</sup> by pulse radiolysis and shows a maximum at 450 nm with  $\epsilon$  = 1.05  $\times$  10<sup>3</sup>  $M^{-1}$  $cm^{-1}$ . The same spectrum has been obtained by the flash photolysis of aqueous sulfate<sup>11</sup> and persulfate<sup>12</sup> solutions but in this case the value found for the extinction coefficient was  $\epsilon_{455} = 450 M^{-1} \text{ cm}^{-1}$ 

Boyle<sup>13</sup> has suggested another radiolytic mode of formation of the same radical, the direct action of radiation on sulfuric acid present in the solution

$$HSO_4^- \longrightarrow HSO_4 + e^-$$
 (2)

and has deduced the rate of appearance of the radical formed in this way from the yields of products accumulated after  $\gamma$  irradiation, in particular, the yields of monoand dipersulfuric acids. Mathews, Mahlman, and Sworski<sup>14,15</sup> reached an analogous conclusion also for  $\gamma$  radiolvsis, and from the rate of radiolytic reduction of Ce<sup>IV</sup> in sulfuric acid solutions containing Ce<sup>III</sup> and formic acid (or 2-propanol), estimated  $G(SO_4^-)$  for  $SO_4^-$  formed by direct action to be 0.2  $\pm$  0.04 in 0.4 M H<sub>2</sub>SO<sub>4</sub> and 0.94  $\pm$ 0.03 in  $4 M H_2 SO_4$ .

In agreement with these authors, we estimated  $G(SO_4^-)$  to be 0.18 ± 0.03 in 0.4 M H<sub>2</sub>SO<sub>4</sub> (taking  $\epsilon_{450}$  = 1000  $M^{-1}$  cm<sup>-1</sup>) from preliminary pulse radiolytic studies<sup>16</sup> which gave clear evidence of the presence of  $SO_4$ formed by a direct effect, immediately following a 12-nsec electron pulse.

The present paper deals with two further problems that seemed interesting to us, first to measure the immediate  $SO_4^-$  and OH yields as a function of sulfuric acid concentration to see whether a relationship characteristic of the direct effect was observed and then to establish the kinetics of the formation and disappearance of  $\mathrm{SO}_4{}^-$  and compare them with those of known reactions.

total pulse length to 12 nsec.<sup>17</sup> The Spectrosil quartz cell was mounted 150 mm from the stainless steel exit window (30 mm diameter, 12  $\mu$  thick) of the analyzing magnet to ensure uniform irradiation of the cell surface (6.25 cm<sup>2</sup>). Analyzing light from a pulsed 450-W xenon lamp, rendered parallel by a Cassegrain collimator, passed through a  $25 \times 3$  mm slit before passing through the (2.5-cm) cell in a direction perpendicular to the electron beam.

Irradiations were carried out using a Febetron 707 with

magnetic selection of 1.8-MeV electrons to reduce the

Absorbed dose was measured with aqueous potassium ferrocyanide solutions saturated with N<sub>2</sub>O taking  $\epsilon_{440}$  = 600  $M^{-1}$  cm<sup>-1</sup> for Fe(CN)<sub>6</sub><sup>3-</sup> and G(OH) + G(e<sup>-</sup>) =  $5.5.^{18}$  Details of the detection system have already been described in a preceding article.<sup>19</sup>

## Results

Spectra. In 4 M H<sub>2</sub>SO<sub>4</sub>, deaerated by bubbling with argon, measurement of the optical density immediately after the pulse (with a time scale of 50 nsec/oscilloscope division) gave the spectrum shown in Figure 1. Between 550 and 300 nm, this spectrum has the same form as that which we have already reported<sup>16</sup> for 0.4 M sulfuric acid solution and as that which was attributed<sup>9,11,12</sup> to the radical  $SO_4$ <sup>-</sup>. The increase in optical density from 300 to 250 nm corresponds to the longer wavelength of the OH radical absorption.20

Initial Optical Densities. For a dose of about 80 krads/ pulse and an optical path length of 2.5 cm, the initial optical densities at 450 and 250 nm are given in Table I.

Kinetic Curves. The change in optical density as a function of time after the pulse has been measured at 450 nm for  $4 M H_2 SO_4$  (Figure 2). The initial increase leads to a maximum after about 150 nsec and is followed by a slower decay. The same experiment was carried out with 4  $M H_2 SO_4$  containing  $4 \times 10^{-4} M H_2 O_2$  and the corresponding points were found to be situated close to the first curve (Figure 2).

### Discussion

Initial Yields of  $SO_4^-$  and OH Radicals. The spectra obtained allow the observed transient to be identified as SO<sub>4</sub>-. However, the initial formation is too fast to be attributed to reaction 1 and corresponds, therefore, to the



Figure 1. Absorption spectrum of transients in 4 M H<sub>2</sub>SO<sub>4</sub> 10 nsec after a 12-nsec electron pulse (l = 2.5 cm; dose = 5.99  $\times 10^{15}$  eV/cm<sup>3</sup>).

TABLE I: Optical Densities and H<sub>2</sub>SO<sub>4</sub> Concentration

H₂SO₄ concn, <i>M</i>	Optical densities		Dose per pulse	Gr
	450 nm	250 nm	× 10 <sup>-15</sup>	450 nm
0.4	0.038 ± 0.004	$0.240 \pm 0.03$	5.08	182
2	$0.147 \pm 0.02$	$0.210 \pm 0.02$	5.49	650
4	$0.344 \pm 0.04$	0.190 ± 0.02	5.99	1390

formation of  $SO_4^-$  by the direct effect (2). The kinetic treatment described below shows that the contribution of reaction 1 accounts for less than 2% of the initial optical densities.  $G_{\epsilon}$  values for  $SO_4^-$  10 nsec after the pulse are given in Table I; absorbed doses are corrected for the differing electron densities of the solutions.

Taking the value  $\epsilon_{450} \simeq 1000 \ M^{-1} \ {\rm cm^{-1}} \ {\rm proposed^{9,10}}$ for the molar extinction coefficient of  ${\rm SO_4^-}$  radicals formed by radiolysis, values for the yield of  ${\rm SO_4^-}$  are obtained which are shown in Figure 3 as a function of the electron fraction  $(f({\rm H_2SO_4}))$  of sulfuric acid. It is seen that, within the limits set by experimental error, the relationship is linear, conforming to that expected for a direct effect:  $G({\rm SO_4^-}) = 4.3 \ f({\rm H_2SO_4})$ . The yield of  ${\rm SO_4^-}$  (G =1.39) for 4 M sulfuric acid is greater than that (G = 0.94) estimated by Matthews, Mahlman, and Sworski.<sup>14</sup>

We have also tried to estimate G(OH) from the optical densities at 250 nm. At this wavelength,  $\epsilon(OH) = 420$  $M^{-1}$  cm<sup>-120</sup> and, assuming that SO<sub>4</sub><sup>-</sup> does not absorb at 250 nm, it is possible to calculate that G(OH) = 1.83 for 4 M H<sub>2</sub>SO<sub>4</sub>, 2.20 for 2 M H<sub>2</sub>SO<sub>4</sub>, and 2.7 for 0.4 M H<sub>2</sub>SO<sub>4</sub>. These values are in good agreement with the estimate made by Matthews, Mahlman, and Sworski<sup>14</sup> and they are also proportional to the electron fractions of water, which are 0.7, 0.84, and 0.94, respectively. This proportionality, which leads to about G(OH) = 2.75 for pure water, confirms that SO<sub>4</sub><sup>-</sup> is formed at the expense of the radiolysis of water by a direct effect on H<sub>2</sub>SO<sub>4</sub>.

Kinetics of  $SO_4^-$  Formation and Decay. Figure 2 shows that the concentration of  $SO_4^-$  increases after the pulse. The growth is attributed to reaction 1, although the concentration of  $SO_4^-$  does not reach the maximum calculated from the yield of OH radicals because a large proportion of these react according to the two-radical reaction scheme

$$OH + OH \longrightarrow H_2O_2$$
 (3)

$$OH + H \longrightarrow H_2O$$
 (4)



**Figure 2.** Kinetics of disappearance of SO<sub>4</sub><sup>-</sup> in 4 M H<sub>2</sub>SO<sub>4</sub>: \_\_\_\_\_, theoretical curve; × or +, experiments without adding H<sub>2</sub>O<sub>2</sub>; O, in presence of H<sub>2</sub>O<sub>2</sub> (4 × 10<sup>-4</sup> M).



Figure 3. Yield of direct effect as a function of the electronic fraction of sulfuric acid.

$$H + H \longrightarrow H_2$$
 (5)

However, examination of the initial rate of formation of  $SO_4^-$ , corrected for decay by measurements based on the second part of the curve, shows that the rate of formation is much greater than the value calculated using the value of  $k_1$  currently accepted for other media ( $3.5 \times 10^5 M^{-1} sec^{-1}$  for  $0.4 M H_2 SO_4^{3-8}$ ).

The data of Figure 2 are shown in the form of a "second-order plot" in Figure 4 in order to compare the decay of SO<sub>4</sub><sup>-</sup> with photolytic experiments at pH 5.5,<sup>11,12</sup> which gave a value of  $2k_6 = 8 \times 10^8 M^{-1} \sec^{-1} at \mu = 0$  for

$$SO_4^- + SO_4^- \xrightarrow{\sim} S_2O_8^{2^-}$$
(6)

It can be seen that the line, which, on the average, best represents the experimental results, has a slope of about  $2k/\epsilon l = 1.44 \times 10^6 \text{ sec}^{-1}$ , leading to  $2k = 3.6 \times 10^9 M^{-1} \text{ sec}^{-1}$ , a value which is much higher than  $2k_6$ . The difference can be accounted for by the different acidities and ionic strengths in the two cases. A rough estimate from extended Debye theory of ionic solutions leads to an increase of  $2k_6$  by a factor of about 4.5 if we admit that  $SO_4^-$  is the predominant form. It is also possible that in the radiolysis experiments the rate of disappearance of  $SO_4^-$  is increased on account of its reduction by the radiolytic products present at the end of each pulse

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Figure 4. Second-order decay of  $SO_4^-$  in 4 M H<sub>2</sub>SO<sub>4</sub> (dose = =  $1.88 \times 10^{15} \text{ eV/cm}^3$ ): ----, second-order law with  $2k/\ell$ =  $1.88 \times 10^{6} \text{ sec}^{-1}$ ; -----, theoretical curve;  $\times \text{ or } +$ , experiments without adding H<sub>2</sub>O<sub>2</sub>; O, in presence of H<sub>2</sub>O<sub>2</sub> (4  $\times$  10<sup>-4</sup> M

$$SO_4^- + H_2O_2 \longrightarrow HSO_4^- + HO_2$$
$$SO_4^- + H \longrightarrow HSO_4^-$$
(7)

$$SO_4^- + OH \longrightarrow HSO_5^-$$
 (8)

provided that H<sub>2</sub>O<sub>2</sub>, H, and OH disappear at a rate parallel to that of  $\mathrm{SO}_4^-$  in order to preserve the second-order decay of SO<sub>4</sub><sup>-</sup>. However, these possibilities must be discarded, the first since the addition of  $4 \times 10^{-4} M$  hydrogen peroxide does not seriously alter the decay curve of  $SO_4^-$  (see Figures 3 and 4), the second and the third because they are only possible in the short time interval before the H atoms and OH radicals have disappeared by reactions 1, 3, 4, and 5. Effectively, it appears from Figure 4 that the disappearance of  $SO_4^-$  is most rapid at about 1  $\mu$ sec after the pulse, the curve subsequently becoming asymptotic to a line of slope  $1.44 \times 10^{6} \text{ sec}^{-1}$ .

A kinetic calculation based on the following mechanism has been programmed in a Wang 500 calculator.

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

OH + OH 
$$\longrightarrow$$
 H<sub>2</sub>O<sub>2</sub> (2k<sub>3</sub> = 10<sup>10</sup>  $M^{-1} \sec^{-1})^{20}$   
(3)

$$OH + H \longrightarrow H_2O$$
  $(k_4 = 3.2 \times 10^{10} M^{-1} \text{ sec}^{-1})^{21}$  (4)

$$H + H \longrightarrow H_2 (2k_5 = 1.3 \times 10^{10} M^{-1} \text{ sec}^{-1})^{22}$$
(5)

$$SO_{4}^{-} + SO_{4}^{-} \longrightarrow S_{2}O_{2}^{2-}$$
 (6)

$$SO_{-}^{-} + H \longrightarrow HSO_{-}^{-}$$
 (7)

$$SO_4^- + OH \longrightarrow HSO_5^-$$
 (8)

As seen above, these two last reactions are necessary in order to describe accurately the beginning of the kinetic curves.

In the calculation, the initial concentrations of  $SO_4$ and OH were those found experimentally immediately after a pulse of  $5.99 \times 10^{15} \text{ eV/cm}^3$ , that is to say about 1.32 and  $1.7410^{-4}$  M, respectively, and the concentration of H was determined by proportion taking  $G(SO_4^{-}) =$ 

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1.39 and assuming G(H) = 3.7. The rate constants quoted for reactions 3, 4, and 5 were taken from the literature.

The other rate constants were chosen so that the results of the calculation would agree quantitatively with the experimental results if

$$k_1 = 1.5 \times 10^6 M^{-1} \text{ sec}^{-1}$$
  
 $2k_6 = 3.6 \times 10^9 M^{-1} \text{ sec}^{-1}$ 

$$k_7 + 0.4k_8 = 3.3 \times 10^9 M^{-1} \text{ sec}^{-1} \quad (k_8 \leq k_7)$$

It can be seen from Figures 3 and 4 that, under these conditions, the agreement between the experimental results and the theoretical curves is quite good.

The relationship found between  $k_7$  and  $k_8$  shows that reaction 8 is relatively unimportant given the high concentration of OH radicals at the end of the pulse, which favors other OH reactions. For the same reason the reactions

$$H + S_2 O_8^{2-} \longrightarrow HSO_4^- + SO_4^-$$
(9)

$$H + HSO_5^{-} \longrightarrow H_2O + SO_4^{-}$$
(10)

which involve species formed at a relatively long time after the pulse, make a negligible contribution under our conditions, although they may be significant in steadystate radiolysis.13

It should be noted that use of slightly different values for the rate constants  $k_3$ ,  $k_4$ , and  $k_5$  does not require any significant changes in the values taken for  $k_1$  and  $k_6$ , changing only  $k_7$  and  $k_8$ . For example, taking  $k_4 = 1.5 \times$  $10^{10} M^{-1} \sec^{-1} 2^{3,24}$  the best fit is obtained if

$$k_7 + 0.4k_8 = 5.8 \times 10^9 M^{-1} \text{ sec}^{-1} \qquad (k_8 \leq k_7)$$

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