### Pulse Radiolysis Study of Concentrated Sulfuric Acid Solutions

Formation Mechanism, Yield and Reactivity of Sulfate Radicals

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In the pulse radiolysis of concentrated sulfuric acid solutions, the absorption spectrum and the molar absorption coefficient (1600 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) of the sulfate radical are unchanged up to 10 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, suggesting that the sulfate radical exists in the dissociated form (SO<sub>4</sub>). Two formation processes for the sulfate radical have been directly demonstrated in sulfuric acid and hydrogensulfate solutions: a fast one completed in the duration of the electron pulse, and a slow one occurring over a microsecond time range. For sulfate solutions only the fast formation process is observed. In sulfuric acid solutions the slow formation process is OH + HSO<sub>4</sub>  $\rightarrow$  H<sub>2</sub>O + SO<sub>4</sub> (4.7 × 10<sup>5</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) and OH + H<sub>2</sub>SO<sub>4</sub>  $\rightarrow$  HSO<sub>4</sub> + H<sub>2</sub>O  $\rightarrow$  SO<sub>4</sub> + H<sub>3</sub>O<sup>+</sup> (1.4 × 10<sup>7</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>), and the fast formation process is the direct action of radiation on sulfuric acid with a *G* value of (2.7  $\pm$  0.4) × 10<sup>-2</sup> molecule eV<sup>-1</sup>. The yields of (OH + SO<sub>4</sub>) and H can be quantified as: *G*(OH + SO<sub>4</sub>) = 2.9f<sub>w</sub> + 2.7f<sub>s</sub> and *G*(H) = 3.7f<sub>w</sub> + 2.7f<sub>s</sub>. The yields of SO<sub>4</sub> have also been evaluated and the decay kinetics and reactions of the sulfate radical studied.

Numerous investigations have been carried out on the radiolysis of concentrated aqueous solutions of sulfuric acid since they are widely used as reaction media in the radiation field.<sup>1-12</sup> The sulfate radical has been identified as one of the most important intermediates. Three formation processes have been postulated: (i) the reaction of OH radicals with hydrogensulfate anions  $(HSO_4^-)$ ,<sup>3-7</sup> (ii) the direct action of radiation on the solute molecules, 1,2,5-7 and (iii) the reaction of of the primary cation  $(H_2O^+)$  with the solute molecules.<sup>12,13</sup> However, the formation mechanism of the sulfate radical is still relatively obscure. Discrimination and confirmation of the various proposals are essential. Furthermore, knowledge of the formation kinetics and the yield of sulfate radical is also sparse. Though the reactivity of the sulfate radical has been studied extensively,  $^{14-21}$  there has been less work on its reactions with radiolytically generated radicals, which are important for understanding the radiolytic processes of sulfuric acid solutions.

For the radiolysis of concentrated aqueous solutions, the direct action of radiation on solutes and the reaction of the primary cation  $(H_2O^+)$  with solutes are of fundamental interest in radiation chemistry and have received much attention. Many investigations have been carried out, mainly on the production of the radical anion species  $(X_2^-)$  in the radiolysis of concentrated solutions of halide anions.<sup>13,22-24</sup> We have studied the production of NO<sub>3</sub> in the radiolysis of concentrated nitric acid and nitrate solutions.<sup>25</sup> The direct action of radiation on the solute molecules has been distinguished from the reaction of OH radicals with the solute molecules, and the reaction of  $H_2O^+$  with the solute molecules has been shown to be less probable. It is of considerable interest to extend these studies to concentrated solutions of sulfuric acid. hydrogensulfate and sulfate so as to understand these processes more fully.

The purposes of this study are: (i) to follow the formation and decay kinetics of the sulfate radical and (ii) to evaluate the yields of sulfate radical and other intermediates, so as to elucidate the formation and decay mechanisms of the sulfate radical and get a better understanding of the radiolytic processes.

#### Experimental

Electron pulses of 100 ns and 28 MeV from a linear accelerator at the Nuclear Engineering Research Laboratory, University of Tokyo, were used. Details of the pulse radiolysis system have already been described elsewhere.<sup>25,26</sup> For dosimetry, 10 mmol dm<sup>-3</sup> KSCN solutions saturated with N<sub>2</sub>O were used with  $G_{\mathcal{E}}(472 \text{ nm}) = 46400 \pm 600 (10^{-2} \text{ mol-}$  $ecule eV^{-1}) dm^3 \text{ mol}^{-1} \text{ cm}^{-1}$  for  $(\text{SCN})_2^{-.27}$  The unit of G values is  $10^{-2}$  molecule eV<sup>-1</sup>. The absorbed energy in concentrated solutions was corrected for the electron density of the solution. Chemicals were of the highest available purity and were used as received. All experiments were carried out at room temperature (*ca.* 20 °C) in aerated solutions if not otherwise stated.

The Ce<sup>IV</sup> molar absorption coefficients in sulfuric acid solutions were determined on the basis of the Ce<sup>IV</sup> molar absorption coefficient of 5610 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> (320 nm) in 0.4 mol dm<sup>-3</sup> sulfuric acid solution.<sup>1,8</sup> The measurement and the molar absorption coefficients of Ce<sup>IV</sup> are not affected by the presence of Ce<sup>III</sup> up to at least 10<sup>-2</sup> mol dm<sup>-3</sup> at wavelengths greater than 310 nm.

#### **Results and Discussion**

### Absorption Spectrum and Molar Absorption Coefficient (ɛ) of the Sulfate Radical

When sulfuric acid solutions were irradiated, a broad absorption band with a peak at 450 nm was observed, as shown in Fig. 1, which agrees well with the spectra of the sulfate radical observed in earlier studies.<sup>3,4,6,15,16,19,28</sup> For sulfate radical, several  $\varepsilon$  values of 450 (450 nm, recalculated as  $1100^{15}$ ),<sup>29,30</sup> 1100 (450 nm),<sup>3,31</sup> 1500 (440 nm),<sup>32</sup> > 1385 (443 nm),<sup>15</sup> and 1600 (450 nm)<sup>20,33</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> have been previously reported. The  $\varepsilon$  values of the sulfate radical in 5–11 mol dm<sup>-3</sup> sulfuric acid were measured as follows. In sulfuric acid solutions containing 0.1 mol dm<sup>-3</sup> HCl, OH and sulfate radicals give rise to formation of Cl<sub>2</sub>. The absorbance of Cl<sub>2</sub><sup>-</sup> may be observed at 340 nm. Since OH radicals are converted to sulfate radicals in the absence of



**Fig. 1** Absorption spectra of sulfate radical.  $\blacklozenge$ , 2.2;  $\blacktriangle$ , 5;  $\blacklozenge$ , 7.3;  $\blacksquare$ , 10.9 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>.  $\Box$ , neutral pH, McElroy and Waygood.<sup>19</sup>  $\bigcirc$ , pH = 1-5, Tang *et al.*<sup>15</sup>

additives, the  $\epsilon$ (450 nm) value of the sulfate radical was easily obtained by comparing the absorbance of the sulfate radical with that of Cl<sub>2</sub><sup>-</sup>. No significant change in the molar absorption coefficient of the sulfate radical was found in the concentration range (5–11 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>) investigated. A value of  $1700 \pm 150$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> was calculated based on  $\epsilon$ (Cl<sub>2</sub><sup>-</sup>, 340 nm) =  $8200 \pm 500$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>,† Similarly in Ar-saturated sulfuric acid solutions containing Ce<sup>III</sup> (10–30 mmol dm<sup>-3</sup>), OH and sulfate radicals convert it to Ce<sup>IV</sup>. The  $\epsilon$ (450 nm) values of sulfate radical were evaluated as  $1630 \pm 120$  (7.3 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>) and  $1570 \pm 130$  (10.9 mol dm<sup>-3</sup>) based on  $\epsilon$ (Ce<sup>IV</sup>, 370 nm) = 2820 (7.3 mol dm<sup>-3</sup>) and 3020 (10.9 mol dm<sup>-3</sup>) dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

Sulfate radical may exist in acid (HSO<sub>4</sub>) or base (SO<sub>4</sub><sup>-</sup>) form. The  $pK_a$  value is unknown. At neutral pH, it presumably exists in the base form  $(SO_4^-)$ . Since its absorption spectrum and molar absorption coefficient in sulfuric acid solutions are in close agreement with those in neutral or slightly acidic solutions,<sup>15,19,20,33</sup> it probably exists predominantly in the dissociated form  $(SO_4^-)$  even in up to 10 mol  $dm^{-3}$  H<sub>2</sub>SO<sub>4</sub>. In azeotropic sulfuric acid (98.3%, 18.4 mol  $dm^{-3}$ ), the absorption spectrum of the sulfate radical has a peak at 460 nm, slightly red shifted.<sup>10,11</sup> No such shift was observed in up to 10 mol dm<sup>-3</sup>  $H_2SO_4$ . It is appropriate to go further and attempt to give some opinion on the acid-base equilibrium of the sulfate radical by comparing it with the isoelectronic phosphate radical and some other structurally similar radicals, such as phosphorous and sulfurous radicals. These radicals (corresponding to their parent species with one electron removed),  $H_2PO_4$  (pK<sub>a</sub> 5.7),  $HPO_4^-$  (pK<sub>a</sub> 8.9),  $H_3PO_3^+$  (pK<sub>a</sub> -1.7),  $H_2PO_3$  (pK<sub>a</sub> 0),  $HPO_3^-$  (pK<sub>a</sub> 5.9) and HSO<sub>3</sub> (pK<sub>a</sub> ~ 0),<sup>34,35</sup> are much stronger acids than their parent species,  $H_2PO_4^-$  (pK<sub>a</sub> 7.2),  $HPO_4^{2-}$  (pK<sub>a</sub> 12.3),  $H_3PO_3$  $(pK_a 2.0), H_2PO_3^ (pK_a 6.6), HPO_3^{2-}$   $(pK_a unknown)$  and  $HSO_3^-$  (pK<sub>a</sub> 7.0). It is therefore predicted that the radical  $HSO_4$  is a much stronger acid than the parent anion  $HSO_4^ (pK_a 2)$ . Since HSO<sub>4</sub><sup>-</sup> dissociates appreciably in concentrated solutions of sulfuric acid (23% in 8 mol dm<sup>-3</sup>, 15% in 10 mol  $dm^{-3}$  H<sub>2</sub>SO<sub>4</sub> <sup>36</sup>), HSO<sub>4</sub> will dissociate to SO<sub>4</sub> to a much larger extent.

#### Formation Kinetics of the Sulfate Radical

In sulfuric acid solutions, following a 100 ns electron pulse, the formation of the sulfate radical could be easily observed.

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In less concentrated solutions, two formation processes for the sulfate radical were clearly observed on a microsecond time scale, as shown in Fig. 2 for 0.4 mol dm<sup>-3</sup> sulfuric acid solution. The fast formation process is completed in the duration of the electron pulse, whereas the slow formation process proceeds on a microsecond timescale. Addition of 5 mmol dm<sup>-3</sup> ethanol (as a radical scavenger) to 0.4 mol dm<sup>-3</sup> sulfuric acid solution completely suppressed the slow formation process, but had no measurable effect on the initial yield of the fast formation process (see Fig. 2). The rate of the slow formation process increased with increasing sulfuric acid concentration. In the presence of scavenger, the reduced extent of the slow formation process depends on both sulfuric acid and scavenger concentrations. Similarly, two formation processes for the sulfate radical were observed in sodium hydrogensulfate solutions as shown in Fig. 2 for 2 mol dm<sup>-3</sup> NaHSO<sub>4</sub> solutions in the absence and presence of ethanol. The rate of the slow formation process increased with increasing sodium hydrogensulfate concentration. Addition of ethanol depressed the slow formation process while it had no apparent influence on the initial yield of the fast formation process (see Fig. 2). The reduced extent of the slow formation process also depends on both sodium hydrogensulfate and scavenger concentrations. In contrast, only the fast formation process was observed in lithium sulfate solutions as shown in Fig. 2 for 2 mol dm<sup>-3</sup> Li<sub>2</sub>SO<sub>4</sub> solution with 0.01 mol dm<sup>-3</sup> sulfuric acid to suppress the absorption of hydrated electrons. It is evident from the foregoing results that the fast and slow formation processes have different precursors, indicating two different formation processes.



Fig. 2 Temporal profiles of the formation of sulfate radical. (a) 0.4 mol dm<sup>-3</sup>  $H_2SO_4$ ; (b) 0.4 mol dm<sup>-3</sup>  $H_2SO_4 + 5$  mmol dm<sup>-3</sup> ethanol; (c) 2 mol dm<sup>-3</sup> NaHSO<sub>4</sub>; (d) 2 mol dm<sup>-3</sup> NaHSO<sub>4</sub> + 5 mmol dm<sup>-3</sup> ethanol; (e) 2 mol dm<sup>-3</sup>  $Li_2SO_4 + 0.01$  mol dm<sup>-3</sup>  $H_2SO_4$ . The peak is the absorption of hydrated electrons

<sup>&</sup>lt;sup>†</sup> Evaluated in 0.4 mol dm<sup>-3</sup>  $H_2SO_4 + 0.1$  mol dm<sup>-3</sup> HCl.  $G(Cl_2^-) = G(OH + SO_4^-)$  was taken to be 2.9.

#### Mechanism of the Slow Formation Process of the Sulfate Radical

In the radiolysis of sulfuric acid and hydrogensulfate solutions, the OH radical has been proposed as the precursor of the sulfate radical.<sup>3-7</sup> In sulfuric acid solutions, sulfate anion, hydrogensulfate anion, and undissociated sulfuric acid coexist.<sup>37,38</sup> Since the slow formation process of the sulfate radical was not observed in lithium sulfate solutions in which only sulfate anion exists, reaction (1) is presumably very slow or does not occur at all.

$$OH + SO_4^{2-} \rightarrow SO_4^{-} + OH^{-}$$
(1)

It must therefore be  $HSO_4^-$  and  $H_2SO_4$  (undissociated) that react with OH radicals to form sulfate radicals. The formation kinetics of the sulfate radical were simulated on the basis of the reaction scheme shown in Table 1. The G values of the radiolytically generated species are as follows: G(OH) = $G_w f_w$ ,  $G(SO_4^-) = G_s f_s$ ,  $G(H_2O_2) = G^0(H_2O_2)f_w$ , where  $f_w$  and  $f_s$  are the electron fractions of water and sulfuric acid, respectively;  $G_w$  and  $G^0(H_2O_2)$ , the yields of OH radical and  $H_2O_2$ respectively in pure water, *i.e.* 2.9 and 0.8;  $G_s$ , the yield of sulfate radical from the direct action of radiation on sulfuric acid, *i.e.* 2.7 (see below). G(H) was evaluated as shown in Fig. 4. The concentrations of these species were calculated using eqn. (2),

$$C = 1.036 \times 10^{-7} \ rdDG \tag{2}$$

where r is the ratio of electron density of the solution studied to the solution used for dosimetry, d, the density (kg dm<sup>-3</sup>) of the solution studied, D, the dose (Gy) absorbed by the dosimetry solution measured under the same conditions as the solution studied; and G, the G values  $(10^{-2} \text{ molecule eV}^{-1})$ of the specific species. The concentrations of oxygen in sulfuric acid solutions were obtained from ref. 41. The rate constant of reaction (20) was assumed to be  $1 \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. For the reaction between OH and sulfate radicals, presumably, the value of the rate constant ( $k_{20}$ ) is between the values of the rate constants for recombination reactions of OH and sulfate radicals, *i.e.*  $k_{17}$  (7.6 × 10<sup>8</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) <  $k_{20} < k_5$  (5.5 × 10<sup>9</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>). Varying  $k_{20}$  in the given range has no significant effect on the formation and decay kinetics of the sulfate radical since this reaction is not a

 
 Table 1
 Formation and decay scheme for the sulfate radical<sup>a</sup>

		reaction			$k/dm^3 mol^{-1} s^{-1}$	ref.
он	+ HSO	→ SO <sub>4</sub>	+ H,O	(3)	k3	see text
ОН	$+ H_{3}SO_{2}$	$_{A} \rightarrow SO_{A}^{-}$	+ H,0*	· (4)	k <sub>a</sub>	see text
OH	+ OĤ	→ H,Õ,	2	(5)	$5.5 \times 10^{9}$	39
ОН	+ H	→ H,0		(6)	$7.0 \times 10^{9}$	39
он	$+ H_{2}O_{2}$	→ H,0	$+ HO_{2}$	(7)	$2.7 \times 10^{7}$	39
ОН	$+ HO_{3}^{+}$	→ H,O	$+0,^{1}$	(8)	$6 \times 10^{9}$	39
Н	+ H Î	→ H,	-	(9)	$7.8 \times 10^{9}$	39
Н	$+ H_{2}O_{2}$	→ H,0	+ OH	(10)	$9 \times 10^{7}$	39
Н	+ HÔ,	→ H,O,		àń	$1 \times 10^{10}$	39
н	+ 0,	→ HÔ,		(12)	$2.1 \times 10^{10}$	39
н	$+ S_{2}O_{0}^{2}$	→ SO	+ HSO2	- (13)	$2.5 \times 10^{7}$	39
н	+ HSO.	→ SO	$+ H_{2}O$	(14)	$2.2 \times 10^{8}$	39
н	+ SO,	→ HSOT	-	(15)	$1.0 \times 10^{10}$	see text
HO.	$+ HO_{2}$	→ H <sub>2</sub> O	$+ 0_{2}$	à6	$8.3 \times 10^{5}$	40
so⁼	$+ SO^{-1}$	$\rightarrow S_2 O_2^{2^-}$	2	$\dot{u}\dot{n}$	$7.6 \times 10^{8}$	see text
so	+ H.O.	→ HSO.	$+ HO_{2}$	(18)	$1.2 \times 10^{7}$	14
so	$+ HO_{2}^{2}$	→ HSO	$+0,^{2}$	(19)	$3.5 \times 10^{9}$	see text
so <sup>‡</sup>	$+ OH^{2}$	→ HSO	2	(20)	$1 \times 10^{9}$	see text
so	$+ S_2 O_2^{2-}$	$\rightarrow SO_{1}^{2}$	$+ S_2 O_2^{-}$	$\dot{(21)}$	$6.6 \times 10^{5}$	see text
so.	+ H,0	→ HSO_	+ OH	(22)	500 s <sup>-1</sup>	19

<sup>a</sup> Simulations based on this scheme were carried out by a numerical differentiation method. The time step was about one thousandth of the time range followed experimentally for the formation and/or decay curve of the sulfate radical, which was found to give good accuracy.

major one. The values of  $k_{15}$ ,  $k_{17}$ ,  $k_{19}$  and  $k_{21}$  were obtained as  $(1.0 \pm 0.3) \times 10^{10}$ ,  $(7.6 \pm 1.0) \times 10^8$ ,  $(3.5 \pm 1.0) \times 10^9$  and  $(6.6 \pm 2.7) \times 10^5$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> (see below). The pseudofirst-order formation rates of the sulfate radical, *R*, expressed by eqn. (23), were thus adjusted to fit the formation curves of the sulfate radical.

$$R = k_3[\text{HSO}_4^-] + k_4[\text{H}_2\text{SO}_4]$$
(23)

The calculations are in good agreement with the experimental results. The values of R thus obtained are shown in Table 2. On considering eqn. (23), a plot of  $R/[HSO_4^-]$  vs.  $[H_2SO_4]/[HSO_4^-]$  is shown in Fig. 3, giving  $k_3 = 4.7 \times 10^5$  and  $k_4 = 1.4 \times 10^7$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. The concentrations of HSO<sub>4</sub> and undissociated H<sub>2</sub>SO<sub>4</sub> (mol dm<sup>-3</sup>) were obtained by fitting the results of Librovich and Mairov<sup>37</sup> to polynomials as expressed by eqn. (24) and (25) (0–8 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>),

$$[HSO_{4}^{-}] = 0.07663 + 0.7716C$$
  
- 0.03052C<sup>2</sup> + 2.303 × 10<sup>-3</sup>C<sup>3</sup> (24)  
$$[H_{2}SO_{4}] = 5.549 \times 10^{-3} - 0.03389C$$

$$+ 0.02862C^2 + 4.984 \times 10^{-4}C^3 \quad (25)$$

where C (mol dm<sup>-3</sup>) is the concentration of sulfuric acid. The species designated as  $H_3O^+ \cdot HSO_4^-$  (ion pair) or  $H_2SO_4 \cdot H_2O$  (hydrated molecule) by Librovich and Mairov actually exists in neutral form (denoted as undissociated  $H_2SO_4$  in this study) as verified by Malinowski *et al.*<sup>38</sup> Since OH radicals do not react with  $SO_4^{2-}$  by an electron transfer reaction, they must react with  $HSO_4^-$  and  $H_2SO_4$ , presumably by H-abstraction reactions.

#### Yields of $SO_4^-$ , $OH + SO_4^-$ and H

The total yields of sulfate radical in sulfuric acid solutions and the yields of the fast formation processes in sulfuric acid

 Table 2
 Formation rate (R) of the sulfate radical

$[H_2SO_4]/mol \ dm^{-3}$	$R/10^6  \mathrm{s}^{-1}$	$[H_2SO_4]/mol \ dm^{-3}$	$R/10^6  { m s}^{-1}$
0.4	$0.12 \pm 0.02^{a}$	3.0	$3.7 \pm 0.10$
1.0	$0.39 \pm 0.02$	4.0	$6.5 \pm 0.5$
1.5	$0.78 \pm 0.15$	5.0	$11.0 \pm 1.0$
2.0	$1.70 \pm 0.03$	7.4	$23.0 \pm 1.5$

<sup>a</sup> Precision only.



Fig. 3  $R/[HSO_4^-]$  vs.  $[H_2SO_4]/[HSO_4^-]$  for sulfuric acid solutions



**Fig. 4** *G* value as a function of electron fraction of solute,  $f_s$ ,  $\dagger$  Total yields of sulfate radical in  $H_2SO_4$ :  $\bigcirc$ , 5 cm cell (optical path 10 cm), 17.6 Gy per pulse;  $\square$ , 4 cm cell (optical path 4 cm), 30 Gy/pulse. Yields of sulfate radical from the fast formation process:  $\blacksquare$ ,  $H_2SO_4$ , this work;  $\blacklozenge$ ,  $H_2SO_4$ , Lesigne *et al.*;<sup>7</sup>  $\blacktriangle$ ,  $Li_2SO_4$ .  $\triangle$ ,  $G(Cl_2^-)$  in  $H_2SO_4$  + 0.1 mol dm<sup>-3</sup> HCl.  $\diamond$ ,  $G(1Ce^{IV})$  in  $H_2SO_4$  + Ce<sup>III</sup>, aerated.  $\blacklozenge$ ,  $G(H) = [G2(Ce^{IV}) - G1(Ce^{IV})]/\eta$ . Straight lines:  $(---) 2.7f_s$ ;  $(----) 2.7f_s + 2.9(1 - f_s)$ ;  $(---) 2.7f_s + 3.7(1 - f_s)$ . The values of Gy/pulse are all for the dosimetry solution

and lithium sulfate solutions were evaluated on the basis of  $\epsilon(SO_4^-, 450 \text{ nm}) = 1600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  as shown in Fig. 4. In lithium sulfate solutions, the slow formation process does not occur to any observable extent. The yields of the fast formation process, G(fast), were evaluated directly with addition of 0.01 mol dm<sup>-3</sup> sulfuric acid to all solutions to suppress the absorption of hydrated electrons. For sulfuric acid solutions, G(fast) was evaluated by various methods, according to the concentrations employed. At lower concentration (0.4 mol dm<sup>-3</sup>), G(fast) was directly separated from the formation curves. At medium concentration, G(fast) was evaluated by addition of ethanol to suppress completely the slow formation process. At higher concentration, G(fast) was evaluated by a competition method described previously.<sup>25</sup> For 5 mol dm<sup>-3</sup> sulfuric acid solution with ethanol as scavenger,  $G(SO_4^-, \text{ total}) = 2.58 \pm 0.15$ ,  $G(SO_4^-, \text{ fast}) = 1.1 \pm 0.1$ and  $R = 1.0 \times 10^7$  s<sup>-1</sup> based on k(OH + ethanol) = $1.9 \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. <sup>39</sup> The total yield of sulfate radical in sulfuric acid solutions increases rapidly with sulfuric acid concentration in the lower concentration range, indicating that the reactions of OH radicals with other reactive species are in competition with reactions (3) and (4). In this concentration range, the yields of sulfate radical depend on the absorbed dose per pulse. The yields of the fast formation process, however, are independent of the absorbed dose per pulse for both sulfuric acid and lithium sulfate solutions.

With addition of 0.1 mol dm<sup>-3</sup> HCl to sulfuric acid solutions, OH and SO<sub>4</sub><sup>-</sup> radicals gave rise to  $Cl_2^-$  via reactions

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(26)-(28). The absorbance of  $Cl_2^-$  was followed at 340 nm.  $G(OH + SO_4^-)$  was obtained on the basis of  $\varepsilon(Cl_2^-, 340 \text{ nm}) = 8200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  as shown in Fig. 4.

$$OH + Cl^- + H^+ \rightarrow Cl + H_2O$$
 (26)

$$\mathrm{SO}_4^- + \mathrm{Cl}^- \longrightarrow \mathrm{Cl} + \mathrm{SO}_4^{2-}$$
 (27)

$$\operatorname{Cl} + \operatorname{Cl}^{-} \rightarrow \operatorname{Cl}_{2}^{-}$$
 (28)

$$G(Cl_2^-) = G(OH + SO_4^-)$$
 (29)

In Ar-saturated sulfuric acid solutions containing Ce<sup>III</sup> (10–30 mmol dm<sup>-3</sup>), only OH and SO<sub>4</sub><sup>-</sup> radicals gave rise to Ce<sup>IV</sup>. The absorbance of Ce<sup>IV</sup> was followed at 370 nm. G(OH + SO<sub>4</sub><sup>-</sup>) was evaluated on the basis of  $\varepsilon$ (Ce<sup>IV</sup>, 370 nm) = 2550 (1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>), 2720 (3 mol dm<sup>-3</sup>), 2740 (5 mol dm<sup>-3</sup>), 2820 (7.3 mol dm<sup>-3</sup>) and 3020 (10.9 mol dm<sup>-3</sup>) dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>. The results are shown in Fig. 4, in agreement with those evaluated from formation of Cl<sub>2</sub><sup>-</sup>.

$$OH + Ce^{III} \rightarrow OH^- + Ce^{IV}$$
(30)

$$SO_4^- + Ce^{III} \rightarrow SO_4^{2-} + Ce^{IV}$$
 (31)

$$G1(Ce^{IV}) = G(OH + SO_4^{-})$$
(32)

In aerated sulfuric acid solutions containing Ce<sup>III</sup>, H radical was converted to HO<sub>2</sub> via reaction (12). HO<sub>2</sub> then oxidized Ce<sup>III</sup> to Ce<sup>IV</sup>, which proceeded completely, since [Ce<sup>III</sup>] (10–30 mmol dm<sup>-3</sup>) was much higher than [Ce<sup>IV</sup>] (<10<sup>-5</sup> mol dm<sup>-3</sup>). Because of the limited solubility of oxygen in concentrated sulfuric acid solutions, the conversion of H to HO<sub>2</sub> is incomplete. The conversion ratios ( $\eta$ ) of H to Ce<sup>IV</sup> were estimated as 95% (1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>), 94.2% (3 mol dm<sup>-3</sup>), 93.9% (5 mol dm<sup>-3</sup>), 83% (7.3 mol dm<sup>-3</sup>) and 81.8% (10.9 mol dm<sup>-3</sup>) by simulation based on the reaction scheme shown in Table 1 with addition of reactions (30), (31) and (33). G(H) was obtained by eqn. (35) as shown in Fig. 4.

$$HO_2 + Ce^{III} \rightarrow HO_2^- + Ce^{IV}$$
(33)

$$G2(Ce^{IV}) = G(OH + SO_4^-) + \eta G(H)$$
 (34)

$$G(H) = [G2(Ce^{IV} - G1(Ce^{IV})]/\eta$$
 (35)

The rate constant of reaction (33) depends on sulfuric acid concentration. The results are shown in Table 3.

## Mechanism of the Fast Formation Process of the Sulfate Radical

In concentrated solutions, the observed yield of a given species can be expressed by eqn. (36),

$$G = f_{s}G_{s} + (1 - f_{s})G_{w}$$
(36)

where  $f_s$  is the ratio of the energy directly absorbed by the solute S to the total energy absorbed by the solution. To a first approximation,  $f_s$  is the electron fraction of the solute.  $G_s$  and  $G_w$  are the yields of the considered species or the yields of the species which then form the considered species from the direct and indirect effects respectively.

A plot of G value vs.  $f_s$  is shown in Fig. 4 for sulfuric acid and lithium sulfate solutions. Assuming  $G_s$  and  $G_w$  do not change significantly with concentration, the data were fitted to eqn. (36). For sulfate radical formed by the fast processes,  $G_s = 2.8$  and  $G_w = 0.1$  (this work),  $G_s = 2.8$  and  $G_w = 0$ (Lesigne *et al.*<sup>7</sup>) for sulfuric acid;  $G_s = 3.0$  and  $G_w = 0.17$  for lithium sulfate. The reason and the meaning of the small  $G_w$ values are not clear. In any case,  $G_w$  is less than 0.2. For  $G(OH + SO_4^-)$  in sulfuric acid solutions,  $G_s = 2.2$  and  $G_w =$ 2.9. Though  $G_s$  values obtained in several cases are somewhat scattered, an averaged value of  $G_s = 2.7 \pm 0.4$  was obtained.

<sup>&</sup>lt;sup>†</sup> The total electron fraction was used. Use of valence-electron fraction has been suggested, A. J. Swallow and M. Inokuti, *Radiat. Phys. Chem.*, 1988, **32**, 185. Numerically, however, the difference is small for sulfuric acid solutions (<10%). The direct action of radiation on  $H_2SO_4$ ,  $HSO_4^-$  and  $SO_4^{2-}$  were assumed to be the same.

 Table 3
 Reaction rate constants evaluated in this work

	k/dm³ mo	$k/dm^3 mol^{-1} s^{-1}$		
reaction	this work	reported		
$ \begin{array}{c} \hline OH + HSO_4^- \rightarrow H_2O + SO_4^- \\ OH + H_2SO_4 \rightarrow H_3O^+ + SO_4^- \\ \hline SO_4^- + HSO_4 \rightarrow H_3O^- + SO_4^- \\ \hline \end{array} $	$4.7 \times 10^{5}$ $1.4 \times 10^{7}$ $(1.6 + 0.2) \times 10^{8}$	$3.5 \times 10^{5} - 10^{6}$ <sup>16.39</sup>		
$SO_{4}^{+} + HO_{2}^{-} \rightarrow HSO_{4}^{-} + HO_{2}^{-}$ $SO_{4}^{-} + Ce^{3+} \rightarrow SO_{4}^{2-} + Ce^{4+}$ $SO_{4}^{-} + TI^{+} \rightarrow SO_{4}^{2-} + TI^{2+}$ $SO_{4}^{-} + HO_{2}^{-} \rightarrow HSO_{4}^{-} + O_{2}^{-}$	$(1.6 \pm 0.3) \times 10^{7}$ $(5.0 \pm 0.8) \times 10^{7}$ $(1.6 \pm 0.2) \times 10^{9}$ $(3.5 \pm 1.0) \times 10^{9}$	$ 5.0 \times 10^{7} - 1.6 \times 10^{8} {}^{14} \\ (1.7 \pm 0.2) \times 10^{9} {}^{14} $		
$SO_4^- + H \longrightarrow HSO_4^-$ $SO_4^- + SO_4^- \longrightarrow S_2O_8^{2-}$ $SO_4^- + S_2O_8^{2-} \longrightarrow SO_4^{2-} + S_2O_8^-$ $OH + HNO_2 \longrightarrow H_2O + NO_2$	$(1.0 \pm 0.3) \times 10^{10}$ $(7.6 \pm 1.0) \times 10^{8}$ $(6.6 \pm 2.7) \times 10^{5}$ $2 \times 10^{9}$	$\begin{array}{c} 3\times10^{8}3\times10^{9} ^{15,19} \\ 0.61.2\times10^{6} ^{19,42} \end{array}$		
$HO_2 + Ce^{HI}^2 \rightarrow Ce^{IV} + HO_2^2$	$\begin{array}{l} 7.3 \times 10^5 \ (1 \ \text{mol} \ \text{dm}^{-3} \ \text{H}_2 \text{SO}_4) \\ 1.9 \times 10^6 \ (3 \ \text{mol} \ \text{dm}^{-3}) \\ 2.5 \times 10^6 \ (5 \ \text{mol} \ \text{dm}^{-3}) \\ 3.0 \times 10^6 \ (7.3 \ \text{mol} \ \text{dm}^{-3}) \\ 3.0 \times 10^6 \ (10.9 \ \text{mol} \ \text{dm}^{-3}) \end{array}$	$2.1 \times 10^{5}$ <sup>43</sup> (0.4 mol dm <sup>-3</sup> H <sub>2</sub> SO <sub>4</sub> )		

As shown in Fig. 4, though deviating slightly,  $G(OH + SO_4^-)$ and  $G(SO_4^-)$  (in the concentration range where OH is totally converted to  $SO_4^-$ ) can be expressed as  $2.7f_s + 2.9(1 - f_s)$ , indicating that G(OH) and  $G(SO_4^-)$  are proportional to the electron fractions of water and sulfuric acid. This is strong evidence that the fast formation process is the direct action of radiation on sulfuric acid. The above results cannot exclude the reaction of  $H_2O^+$  with the solute molecules, but they do suggest that its contribution to the production of  $SO_4^-$  is negligible. Since no secondary formation reactions were observed for the fast process, it probably occurs by the direct dissociation reactions:

$$SO_4^{2-} \rightarrow 1SO_4^{-} + e^{-} \xrightarrow{H^+} SO_4^{-} + H$$
 (37)

$$HSO_4^- \rightarrow HSO_4 + e^- \xrightarrow{H^+} SO_4^- + H$$
 (38)

$$H_2SO_4 \rightarrow H_2SO_4^+ + e^- \xrightarrow{H^+} SO_4^- + H$$
 (39)

As shown in Fig. 4, G(H) can also be explained by eqn. (36) with  $G_w(H) = 3.7$  (which is equal to the yield of H in acidic water) and  $G_s(H) = 2.7$  (which is equal to the yield of sulfate radical from the direct action of radiation on sulfuric acid). This supports reactions (37)-(39).

#### Decay and Reaction of the Sulfate Radical

In Ar-saturated sulfuric acid solutions containing  $K_2S_2O_8$ (10-20 mmol dm<sup>-3</sup>). H radicals were converted to sulfate radicals *via* reaction (13). The decay of sulfate radical is determined by reactions (17) and (21), obeying mixed first- and second-order kinetics. The temporal profiles of sulfate radical at 450 nm (only sulfate radical absorbs at this wavelength) were fitted to eqn. (40) (derived for mixed first- and secondorder decay kinetics<sup>19</sup>) by a non-linear least-square method with  $2k_{17}/(k\epsilon l)$ ,  $2k_{17}/(k\epsilon l) + 1/A(0)$ , and k as parameters in the calculation.

$$1/A(t) = -2k_{17}/(k\epsilon l) + [2k_{17}/(k\epsilon l) + 1/A(0)]\exp(kt) \quad (40)$$

In eqn. (40), A(t) is the absorbance at time t(s), A(0), the absorbance at t = 0,  $\varepsilon$ , the molar absorption coefficient of the sulfate radical (1600 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), l, the optical path (cm), and k, the first-order decay rate constant. Under the experimental conditions,  $k = k_{21}[S_2O_8^{3-7}]$  (s<sup>-1</sup>). It was found that  $k_{17}$  and  $k_{21}$  do not change significantly with sulfuric acid concentration (1-7 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>). Values of  $k_{17} = (7.6$ 

 $\pm 1.0$  × 10<sup>8</sup> and  $k_{21} = (6.6 \pm 2.7) \times 10^5$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> were obtained.

In Ar-saturated solutions, the decay of the sulfate radical is determined mainly by reactions (9), (15) and (17). For 5 mol dm<sup>-3</sup> sulfuric acid, simulation was carried out on the basis of the reaction scheme shown in Table 1. The value of  $k_{15}$  was adjusted to fit the decay curves of the sulfate radical, giving  $k_{15} = (1.0 \pm 0.3) \times 10^{10}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> based on  $k_{17} = 7.6 \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. In aerated solutions the decay of the sulfate radical is mainly determined by reactions (17) and (19). By a similar simulation, it was found that  $k_{19}$  does not change significantly with sulfuric acid concentration (0.4–10 mol dm<sup>-3</sup>).  $k_{19} = (3.5 \pm 1.0) \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> was obtained. Fig. 5 shows the result for 7 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>.

The reactions of sulfate radical with HNO<sub>2</sub>,  $Ce^{3+}$  and Tl<sup>+</sup> were studied in 4 mol dm<sup>-3</sup> sulfuric acid solutions with addition of NaNO<sub>2</sub>(1.0, 2.5 and 5.0 mmol dm<sup>-3</sup>),  $Ce^{3+}(2.5, 5.0 \text{ and } 10.0 \text{ mmol dm}^{-3})$ , and Tl<sup>+</sup>(0.25, 0.5 and 1.0 mmol dm<sup>-3</sup>). Since HNO<sub>2</sub> is volatile, a small amount of alkane was added to the surface of the solution in the cell and then NaNO<sub>2</sub> solution was injected into the solution so as to minimize the loss of HNO<sub>2</sub> during the experiment.

For HNO<sub>2</sub>, reactions (41)-(43) were added to the scheme shown in Table 1. The value of  $k_{41}$  was adjusted to fit the yield of sulfate radical, giving  $k_{41} \approx 2 \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, and  $k_{42}$  was adjusted to fit the decay curve, giving  $k_{42} = (1.6 \pm 0.3) \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. The effect of reaction (43) on



Fig. 5 Decay curve of sulfate radical in 7 mol dm<sup>-3</sup>  $H_2SO_4$  (aerated): (····), experimental data, 2 cm cell, 99.7 Gy per pulse for dosimetry solution; (----), simulation

 $k_{42}$  is not significant.

$$OH + HNO_2 \rightarrow H_2O + NO_2$$
(41)  
$$SO_4^- + HNO_2 \rightarrow HSO_4^- + NO_2$$
(42)

$$HO_2 + NO_2 \rightarrow HO_2NO_2$$
  
 $k = 4.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} {}^{40}$  (43)

For Ce<sup>3+</sup> and Tl<sup>+</sup>, reactions (30), (31) and (44), (45), respectively, were added, to the scheme shown in Table 1. The values of  $k_{31}$  and  $k_{45}$  were adjusted to fit the decay curves of the sulfate radical, giving  $k_{31} = (5.0 \pm 0.8) \times 10^7$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> and  $k_{45} = (1.6 \pm 0.2) \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.

OH + 
$$TI^+ \rightarrow OH^- + TI^{2+}$$
  
 $k = 1.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1-39}$  (44)

$$SO_4^- + Tl^+ \to SO_4^{2-} + Tl^{2+}$$
 (45)

In Table 3 the rate constants obtained in this study are compared with those reported previously. They are in reasonable agreement.

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