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The Branching Ratio of SO_5^- Radicals Self-Reaction in Aqueous Solution

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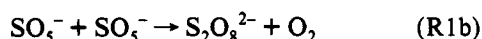
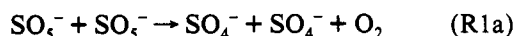
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The radiation-induced chain bisulfite oxidation is of short chain length and is independent of the dose rate (10^{20} – 5×10^{21} eV L^{-1} s^{-1}) and the initial concentration (5×10^{-4} – 2×10^{-3} M) of bisulfite. The mechanism of oxidation, including the propagation reaction $\text{SO}_5^- + \text{SO}_5^- \rightarrow \text{SO}_4^- + \text{SO}_4^- + \text{O}_2$ (k_{1a}) and the termination reaction $\text{SO}_5^- + \text{SO}_5^- \rightarrow \text{S}_2\text{O}_8^{2-} + \text{O}_2$ (k_{1b}), has been proposed. The branching ratio $k_{1a}/k_{1b} = 7 \pm 1$ has been derived at room temperature.

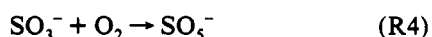
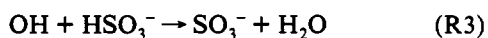
Introduction

Peroxy sulfate radical is a key intermediate in the chain autoxidation of aqueous SO_2^{1-5} and in the free-radical decomposition of peroxy monosulfate.⁶ For the self-reaction of SO_5^- radicals two parallel paths are under discussion:



As has been found⁷ in oxygen-18 tracer experiments both oxygen atoms in the O_2 are from the terminal peroxide oxygen in the peroxy sulfate radicals. The formation of sulfate radicals in the self-reaction of SO_5^- radicals, (R1a), has directly been observed in flash photolysis experiments.⁸ The unchanged perdisulfate concentration in the dual Ag^+ – $\text{S}_2\text{O}_8^{2-}$ catalytic decomposition of peroxy monosulfate led to the conclusion⁷ that $\text{S}_2\text{O}_8^{2-}$ was regenerated by (R1b). Quantitative rate data concerning (R1) are quite limited. The overall rate constant $k_{1a} + k_{1b}$ of self-reaction was recently determined⁸— $k_{1a} + k_{1b} = 10^8 \text{ M}^{-1} \text{ s}^{-1}$. However, the branching ratio, k_{1a}/k_{1b} , is still uncertain. From model calculations⁵ of SO_2 oxidation in atmospheric droplets the estimated value $k_{1a}/k_{1b} \approx 4$ although the calculations were performed with rate constants that were redetermined after the initial experiment.^{8,9} The experimental estimation of the branching ratio in a strong acid solution has been undertaken by Thompson;⁷ $k_{1a}/k_{1b} = 7$ – 10 . However, this value turned out to be quite sensitive to the rate constant of silver (I)-catalyzed perdisulfate decomposition.

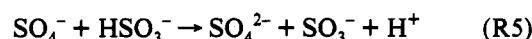
In this paper we determine the branching ratio, k_{1a}/k_{1b} , from a kinetic study of radiation-induced bisulfite oxidation. The SO_5^- radicals were generated^{5,8} in N_2O – O_2 (4:1) saturated bisulfite solutions (initial $[\text{HSO}_3^-]_0 \approx [\text{H}^+]_0 \approx 10^{-3} \text{ M}$):



Reactions R2–R4 are very fast, and using well-known primary radiation yields of active species ($g(\text{e}_{\text{aq}}^-) = 2.6$, $g(\text{OH}) = 2.8$) the radiation yield of SO_5^- radicals (molecules/100 eV) can be determined:

$$G(\text{SO}_5^-) = (g(\text{e}_{\text{aq}}^-) + g(\text{OH})) = 5.4 \quad (1)$$

At the same time the reaction



is also fast⁹ ($k_5 = 7.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and therefore at our dose rates and $[\text{HSO}_3^-]_0$ (see below) the rate of bisulfite oxidation is determined only by reactions of SO_5^- radicals (R1) and (R6):



The competition of reactions R1 and R6 depends on the initiation rate and the bisulfite concentration. Only an upper limit of the R6 rate constant is available, $k_6 < 3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. At sufficiently high dose rates and low $[\text{HSO}_3^-]_0$ one may neglect chain propagation through (R6), and the chain length of bisulfite oxidation, $G(-\text{S(IV)})/G(\text{SO}_5^-)$, is to be independent of the initiation rate and the initial bisulfite concentration. Neglecting S(IV) oxidation produced under irradiation, hydrogen peroxide and peroxy monosulfate the radiation yield, $G(-\text{S(IV)})$, may be represented:

$$IG(-\text{S(IV)})/N \approx 2k_{1a}[\text{SO}_5^-]^2 + 2k_{1b}[\text{SO}_5^-]^2 \approx (1 + k_{1a}/k_{1b})IG(\text{SO}_5^-)/N \quad (2)$$

where I is dose rate (eV L^{-1} s^{-1}) and N is Avogadro's number. It depends only on the radiation yield of SO_5^- radicals and the branching ratio.

Experimental Section

For the continuous irradiation of bisulfite solutions a Van de Graaff accelerator producing a 100- μA beam of 1.8-MeV electrons was used. The solutions were flowed through a glass capillary tube, 0.8 mm internal diameter, 3.3 external, past the exit port of the accelerator. The tube dimensions were such that approximately $\leq 50\%$ of the beam was stopped in the first glass surface and the solution. Hence a fairly uniform irradiation of the solution was attained. A 100-mL glass vessel with the solution was attached to one end of the tube. The solutions were forced by a gas mixture N_2O – O_2 or N_2O – N_2 into the tube. A peristaltic pump was used for this procedure. The irradiated length of the tube was about 20 mm. The flow rate of the solution was varied in the range 10^{-3} – $10^{-1} \text{ mL s}^{-1}$. Normally the electron beam current was 0.02–1 μA . The dose was calibrated by the Fricke dosimeter. At the highest intensity used it was established that the ratio of ferric yield/hydrogen yield was 15.6:0.45. The experiments were carried out at room temperature.

The solutions were prepared just before the experiments by bubbling the appropriate gas mixtures (N_2O – O_2 or N_2O – N_2)

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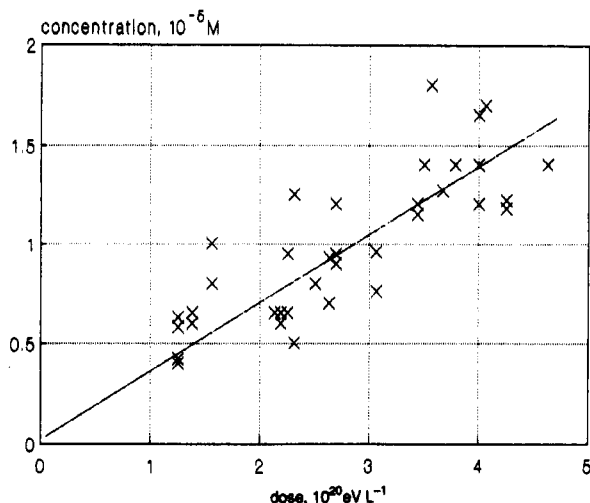


Figure 1. Dose dependence of the $\text{S}_2\text{O}_8^{2-}$ concentration in irradiated bisulfite solutions. Dose rate $I = 9.3 \times 10^{19}$ – $4.6 \times 10^{21} \text{ eV L}^{-1} \text{ s}^{-1}$, pH = 2.7–3.5, and $[\text{HSO}_3^-]_0 = 3 \times 10^{-4}$ – $2 \times 10^{-3} \text{ M}$.

through preliminary evacuated bidistilled water; the initial concentrations of $\text{HSO}_3^- = 5 \times 10^{-4}$ – $2 \times 10^{-3} \text{ M}$ were achieved by adding concentrated deaerated S(IV) solution. No buffers were used.

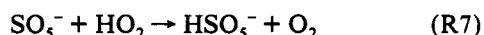
The concentration of S(IV) has been measured spectrophotometrically in the range 200–210 nm and at 276.4 nm (UV-vis spectrophotometer SPECORD M-40). The extinction coefficients of hydrated SO_2 and HSO_3^- were determined by the iodometric method. Sulfur(IV) oxides were oxidized by I_3^- , and the excess of I_3^- was measured spectrophotometrically at 350 nm. The extinction coefficient of I_3^- , $\epsilon = 25\,700 \text{ M}^{-1} \text{ cm}^{-1}$, was found to be close to literature data.¹⁰ At $\lambda = 276.4 \text{ nm}$ the extinction coefficient of hydrated SO_2 equals $467 \text{ M}^{-1} \text{ cm}^{-1}$. The similar value— $498 \text{ M}^{-1} \text{ cm}^{-1}$ has been obtained by Huss and Eckert.¹¹ At the same time the lower value— $367 \text{ M}^{-1} \text{ cm}^{-1}$ at 280 nm was also reported.¹² The highest $\epsilon = 600 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 276 \text{ nm}$ was obtained by Eriksen.¹³ It was found that hydrated SO_2 also absorbs at $\lambda = 200$ – 210 nm ($\epsilon_{200} = 2490$, $\epsilon_{205} = 2050$, and $\epsilon_{210} = 1490 \text{ M}^{-1} \text{ cm}^{-1}$). For the bisulfite ion, $\epsilon_{200} = 1840$, $\epsilon_{205} = 770$, and $\epsilon_{210} = 250 \text{ M}^{-1} \text{ cm}^{-1}$. The temperature of the absorption cells was maintained at $25 \pm 1^\circ \text{C}$.

The conversions of S(IV) under irradiation were obtained by subtraction of absorptions at 200–210 nm for irradiated and nonirradiated solutions. It allowed us to eliminate the contribution of the dark reaction, N_2O absorption, and also the loss of SO_2 by degassing from solution.

The pH was measured on a glass electrode pH meter, calibrated with appropriate standard buffers. For our S(IV) concentrations the changes in H^+ concentration were approximately equal to the changes in bisulfite concentrations and oxidation rates were also calculated from acidity growth of solutions. The details of the experiment have been described elsewhere.¹⁴

Results and Discussion

In the frame of reactions R1–R6 the expected radiation yield $G(\text{S}_2\text{O}_8^{2-}) = G(\text{SO}_5^-)/2 = 2.7$. Making a correlation for SO_5^- radicals lost in a reaction with hydroperoxyl radicals⁴



one obtains $G(\text{S}_2\text{O}_8^{2-}) \approx 2.4$ ($G(\text{HO}_2) = g(\text{H}) = 0.6$). Perodisulfate was determined by $\text{Fe(II)} \rightarrow \text{Fe(III)}$ oxidation.¹⁵ Irradiated solutions were collected in the vessel containing 0.5 mL of $3 \times 10^{-3} \text{ M Fe(II)}$. The oxidation of Fe(II) produced under irradiation of H_2O_2 and Caro's acid was neglected, since sufficiently fast reactions⁴ ($\text{HSO}_3^- + \text{H}_2\text{O}_2$) and ($\text{HSO}_3^- + \text{HSO}_5^-$) were already completely finished in the capillary tube. Thus Fe(II) was oxidized

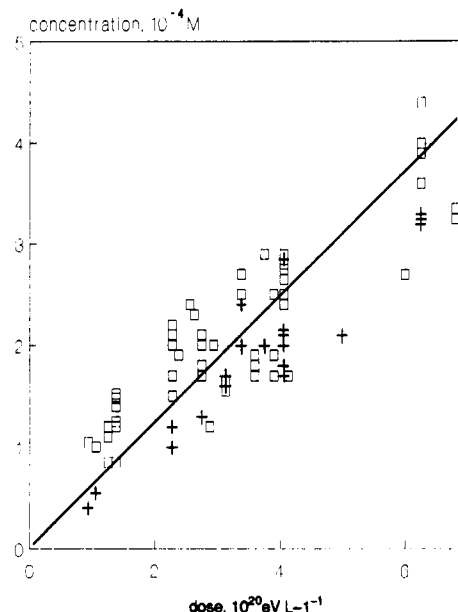


Figure 2. Dose dependence of the decrease in the S(IV) concentration (\square) and the build up of the $[\text{H}^+]$ (+) for bisulfite solutions saturated with $\text{N}_2\text{O}-\text{O}_2$. $[\text{HSO}_3^-]_0 = 3 \times 10^{-4}$ – $2 \times 10^{-3} \text{ M}$ and $I = 4.6 \times 10^{20}$ and $4.6 \times 10^{21} \text{ eV L}^{-1} \text{ s}^{-1}$.

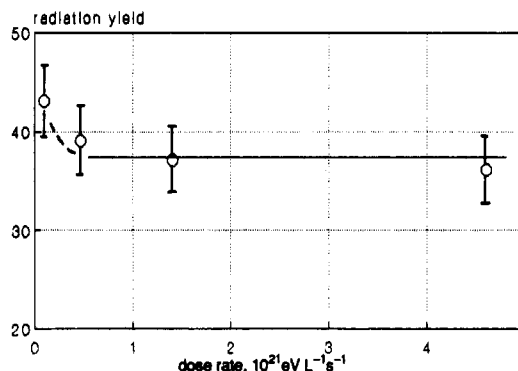
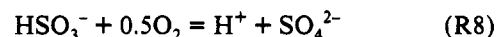


Figure 3. Dose rate dependence of the radiation yield of S(IV) oxidation. $[\text{HSO}_3^-]_0 = 5 \times 10^{-4} \text{ M}$.

only by perdisulfate. Figure 1 demonstrates the dose dependence of $\text{S}_2\text{O}_8^{2-}$ formation at $I = 9.3 \times 10^{19}$ – $4.6 \times 10^{21} \text{ eV L}^{-1} \text{ s}^{-1}$, pH = 2.7–3.5, and initial bisulfite concentrations $[\text{HSO}_3^-]_0 = 3 \times 10^{-4}$ – $2 \times 10^{-3} \text{ M}$. From the approximation of the $\text{S}_2\text{O}_8^{2-}$ dose dependence by a linear function $G(\text{S}_2\text{O}_8^{2-}) = 2.2$ has been obtained. The experimental and predicted values are in a satisfactory agreement, and the balance for SO_5^- radicals can be considered as established. It indicates also that perdisulfate is the single product of the termination reaction (R1b).

Figure 2 demonstrates the dose dependence for S(IV) concentration decrease and $[\text{H}^+]$ increase for $[\text{HSO}_3^-]_0 = 3 \times 10^{-4}$ – $2 \times 10^{-3} \text{ M}$ and dose rates $I = 4.6 \times 10^{20}$ and $4.6 \times 10^{21} \text{ eV L}^{-1} \text{ s}^{-1}$. It can be seen that within experimental error dose dependence is linear and is the same for both H^+ and S(IV). It leads to the conclusion that the stoichiometry of the oxidation is as follows:



The radiation yield of the oxidation $G(-\text{S(IV)}) = 38 \pm 4$; the chain oxidation was realized. It should be noticed that without N_2O at $I \geq 4.6 \times 10^{20} \text{ eV L}^{-1} \text{ s}^{-1}$ and the same $[\text{HSO}_3^-]_0$ bisulfite oxidation $G(-\text{HSO}_3^-) \leq 10$ has been observed.¹⁴

The variations of dose rate in the range 4.6×10^{20} – $4.6 \times 10^{21} \text{ eV L}^{-1} \text{ s}^{-1}$ (see Figure 3) had no essential influence on $G(-\text{S(IV)})$ at $[\text{HSO}_3^-]_0 = 5 \times 10^{-4} \text{ M}$. Only at the lowest $I = 9.3 \times 10^{19} \text{ eV L}^{-1} \text{ s}^{-1}$ has some enhancement of $G(-\text{S(IV)})$ been observed. Figure 4 demonstrates that $G(-\text{S(IV)})$ is independent of bisulfite

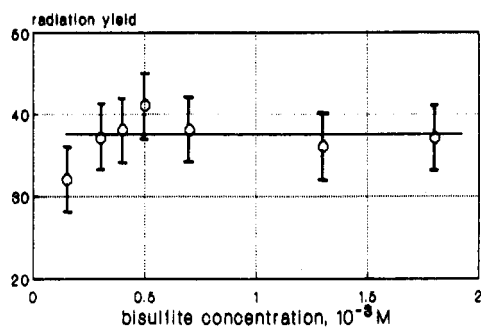


Figure 4. Dependence of the radiation yield of S(IV) oxidation on the initial bisulfite concentration. $I = 4.6 \times 10^{20}$ – 4.6×10^{21} eV L⁻¹ s⁻¹.

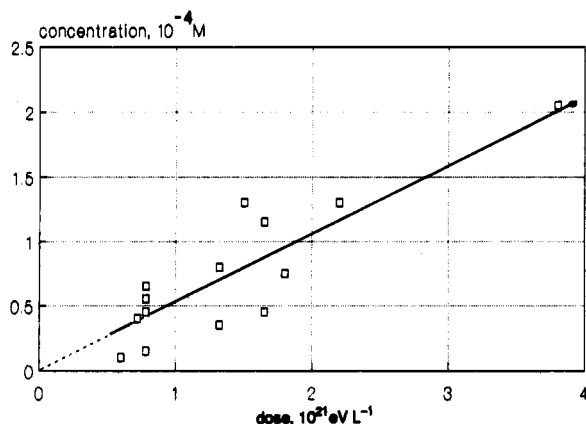


Figure 5. Dose dependence of the decrease in the S(IV) concentration for bisulfite solutions saturated with N₂O–N₂. $[\text{HSO}_3^-]_0 = 3 \times 10^{-4}$ – 2×10^{-3} M and $I = 4.6 \times 10^{20}$ and 4.6×10^{21} eV L⁻¹ s⁻¹.

concentration in the range 3×10^{-4} – 2×10^{-3} M (dose rates of 4.6×10^{20} – 4.6×10^{21} eV L⁻¹ s⁻¹). Thus a chain bisulfite oxidation irrespective of dose rate and $[\text{HSO}_3^-]_0$ is observed. It allows us to exclude chain propagation through (R6) for $I \geq 4.6 \times 10^{20}$ eV L⁻¹ s⁻¹ and $[\text{HSO}_3^-]_0 \leq 2 \times 10^{-3}$ M, and eq 2 may be used for the branching ratio determination.

The correct estimation of the branching ratio also demands the evaluation of the oxidation rate through the reaction



The rate data on the production of OH from (R9) are discrepant: $k_9 = 3.5 \times 10^7$ M⁻¹ s⁻¹ and $k_9 < 10^6$ M⁻¹ s⁻¹ have been reported.^{16,17} Figure 5 demonstrates the dose dependence for the S(IV) concentration decrease obtained for N₂O–N₂ saturated bisulfite

solutions. These data correspond to the same dose rates and $[\text{HSO}_3^-]_0$ as in N₂O–O₂ saturated solutions (see Figure 2). As follows from the experiments with oxygen-free solutions, oxidation proceeds in the nonchain regime with $G(-\text{S(IV)}) \approx 3$. The low radiation yield led us to the use of doses higher than those for oxygen-containing solutions; the dotted line extrapolates the linear dependence to the range of doses shown in Figure 2. In conditions used in Figure 5 the rates of termination reactions dominate over that of (R9). The main termination reaction is $(\text{SO}_3^- + \text{SO}_3^-)$ with a rate constant⁸ equal to 5.7×10^8 M⁻¹ s⁻¹. The termination reaction $(\text{H} + \text{SO}_3^-)$ is not considered because of its low $g(\text{H}) = 0.6$. The consideration of the competitive reactions (R9) and $(\text{SO}_3^- + \text{SO}_3^-)$ allows us to assume that k_9 is less than 10^4 M⁻¹ s⁻¹ and to completely exclude (R9) for oxygen-containing solutions.

Thus, at the bisulfite concentrations and dose rates mentioned above, the oxidation rate is dependent only on the branching ratio k_{1a}/k_{1b} . Substituting the average experimental value of $G(-\text{S(IV)}) = 38$ (see Figure 2) in eq 2 one may obtain the branching ratio $k_{1a}/k_{1b} = 6$. Actually there is a certain sink of SO_3^- radicals in reaction (R7). Making allowance for this sink and taking into account the experimental accuracy, the branching ratio is equal to 7 ± 1 . This value mainly depends on the accuracy of the $G(-\text{S(IV)})$ determination. With the assumption that all HO_2 radicals disappear in (R7) and neglecting bisulfite oxidation by H_2O_2 ($g(\text{H}_2\text{O}_2) = 0.7$) the variation in k_{1a}/k_{1b} is insignificant because of low radiation yields of these species.

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