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# Kinetic Study of SO5⁻ and HO2 Radicals Reactivity in Aqueous Phase Bisulfite Oxidation

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A continuous radiolysis has been used for the kinetic study of the radical driven bisulfite oxidation in oxygenated and $N_2O-O_2$ saturated solutions. The initiation rates and initial bisulfite concentrations were varied over the ranges $(3 \times 10^{-10})-(3 \times 10^{-4})$ M s⁻¹ and $10^{-4}-(3 \times 10^{-3})$ M, respectively. For oxygenated and $N_2O-O_2$ saturated solutions the long chain length bisulfite oxidation with the rate determining propagation reaction $SO_5^- + HSO_3^-$ $(k_6)$ was observed at low initiation rates. The measurement of the peroxydisulfate formation rates has shown that the main termination step in an $N_2O-O_2$ saturated solution is the reaction $SO_5^- + SO_5^-$ $\rightarrow S_2O_8^{2-} + O_2$ $(k_{7b})$ and in oxygenated solution is the reaction $SO_5^- + HO_2$ $(k_{10})$. The rate constants $k_6 = (3.6 \pm 0.5) \times 10^3$ and $k_{10} = (5 \pm 1) \times 10^7$ M⁻¹ s⁻¹ have been derived. The upper limit of the initiation reaction between of hydroperoxyl radical and bisulfite $HO_2 + HSO_3^-$ has been estimated as 20 M⁻¹ s⁻¹.

## Introduction

The free-radical mechanism of bisulfite autoxidation in acid solutions is important for an improved understanding of the acidification of atmospheric droplets[1–8] by the emission of $SO_2$ for an improved understanding of the chemistry of flue-gas scrubber's chemical processes[9] and so on. For the first time the chain autoxidation of sulfite ion has been observed by Backstrom.[10] Later the direct observations of oxysulfur radicals, $SO_3^-$, $SO_4^-$, and $SO_5^-$, involved in the chain mechanism of S(IV) oxidation, have been reported.[11–16] It was found that the rate constants of the propagation reactions of $SO_3^-$ with $O_2$ and $SO_4^-$ with $HSO_3^-$ are very high.[13,14] The peroxymonosulfate radical is considered as a chain carrier determining the oxidation rate of bisulfite ion, because the propagation reaction $SO_5^- + HSO_3^-$ is slow.[7,15] Therefore, the rate of chain oxidation of bisulfite critically depends on an absolute values of the rate constants of $SO_5^-$ radical termination reactions. The high concentration of hydroperoxyl radicals in the atmosphere and thereof high solubility require the determination of the termination reaction $(SO_5^- + HO_2)$ rate constant. In particular, the predominant role of the termination reaction $SO_5^- + O_2 - (HO_2)$ has been demonstrated for sulfite photooxidation[17] and for bisulfite oxidation under the action of ionizing radiation.[18] However, the rate constants of these reactions are unknown. The hydroperoxyl radicals may also play a role in the chain initiation by the reaction with bisulfite, $HO_2 + HSO_3^-$, but the available data are scanty and discrepant.[19–22]

Since the considered reactions of the oxysulfur and hydroperoxyl radicals are of such importance in the autoxidation of S(IV), we have determined the rate constants of the reactions: propagation reaction of $SO_5^-$ radicals with $HSO_3^-$, termination reaction $SO_5^- + HO_2$, and initiation reaction of $HO_2$ radicals with $HSO_3^-$. Both continuous electron beam irradiation and $\gamma$-irradiation of the bisulfite solutions have been employed for radical production and a kinetic study of bisulfite oxidation.
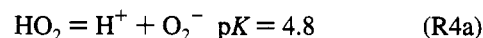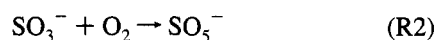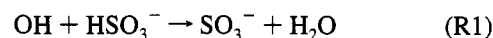
## Background

The peroxymonosulfate and hydroperoxyl radicals were generated in aqueous solution under action of ionizing radiation. The following primary species are produced in the irradiated water:

$$H_2O \rightarrow e_{aq}^-, H, OH$$
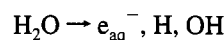
For the fast electron irradiation and $\gamma$-(Co⁶⁰) irradiation of the dilute solutions the primary radiation yields[23] (in species per 100 eV of absorbed energy) are $g(e_{aq}^-) = 2.6$, $g(H) = 0.6$, and $g(OH) = 2.8$. In bisulfite solutions with oxygen saturation these species are rapidly converted to the peroxymonosulfate and hydroperoxyl/superoxide radicals:

$$OH + HSO_3^- \rightarrow SO_3^- + H_2O \qquad (R1)$$

$$SO_3^- + O_2 \rightarrow SO_5^- \qquad (R2)$$

$$e_{aq}^- + H^+ \rightarrow H \qquad (R3)$$

$$e_{aq}^- + O_2 \rightarrow O_2^- \qquad (R3a)$$

$$H + O_2 \rightarrow HO_2 \qquad (R4)$$

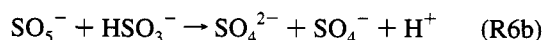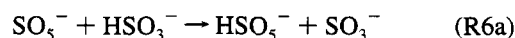$$HO_2 = H^+ + O_2^- \quad pK = 4.8 \qquad (R4a)$$

The available rate constants of reactions R1–R4 and other reactions involved in the chain oxidation of bisulfite are summarized in Table 1. Under the conditions of neglected initiation reaction $HO_2 + HSO_3^-$, the $G$-values of the radicals are as follows: $G(SO_5^-) = g(OH) = 2.8$; $G(HO_2) = g(e) + g(H) = 3.2$. In $N_2O-O_2$ (4:1) saturated bisulfite solution the reactions R3 and R3a are suppressed by reaction R5:

$$e_{aq}^- + N_2O \rightarrow N_2 + OH^- + OH \qquad (R5)$$
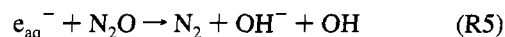
In this case $G$-values of the radicals are as follows: $G(SO_5^-) = g(e_{aq}^-) + g(OH) = 5.4$; $G(HO_2) = g(H) = 0.6$. The chain propagation reactions are[13–15]
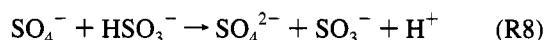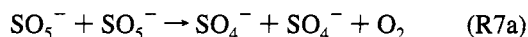
$$SO_5^- + HSO_3^- \rightarrow HSO_5^- + SO_3^- \qquad (R6a)$$

$$SO_5^- + HSO_3^- \rightarrow SO_4^{2-} + SO_4^- + H^+ \qquad (R6b)$$

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**TABLE 1: Rate Constants of the Reactions of the Bisulfite Oxidation Mechanism**

| reaction | k, M$^{-1}$ s$^{-1}$ | ref |
|----------|----------------------|-----|
| R1 | $4.5 \times 10^9$ | 15 |
| R2 | $1.1 \times 10^9$ | 13 |
| R3 | $2.3 \times 10^{10}$ | 24 |
| R3a | $2.0 \times 10^{10}$ | 25 |
| R4 | $2 \times 10^{10}$ | 25 |
| R5 | $9.1 \times 10^9$ | 24 |
| R6 | $3.6 \times 10^3$ | this work |
| R7 | $1 \times 10^8$ | 13 |
| R8 | $7.5 \times 10^8$ | 14 |
| R9 | $(5.6 \times 10^6)[\text{H}^+]$ | 26 |
| R10 | $5.5 \times 10^7$ | this work |
| R11 | $8.3 \times 10^5$ | 25 |
| R12 | $9.7 \times 10^7$ | 25 |
| R13 | $\leq 20$ | this work |

$$\text{SO}_5^- + \text{SO}_5^- \rightarrow \text{SO}_4^- + \text{SO}_4^- + \text{O}_2 \qquad (\text{R7a})$$

$$\text{SO}_4^- + \text{HSO}_3^- \rightarrow \text{SO}_4^{2-} + \text{SO}_3^- + \text{H}^+ \qquad (\text{R8})$$
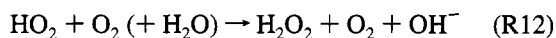
In accordance with the results,[26] peroxymonosulfate is assumed to react predominantly with bisulfite:

$$\text{HSO}_5^- + \text{HSO}_3^- + \text{H}^+ \rightarrow 2\text{HSO}_4^- + \text{H}^+ \qquad (\text{R9})$$
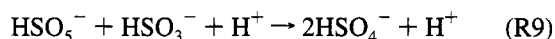
Since the chain propagation reactions R2 and R8 are very fast, the values of bisulfite oxidation chain length ($\nu$) depend on the competition of the chain propagation and the chain termination reactions involving the SO$_5^-$ radicals.[7]

The main termination steps is oxygenated and in N$_2$O−O$_2$ saturated solutions are

$$\text{SO}_5^- + \text{SO}_5^- \rightarrow \text{S}_2\text{O}_8^{2-} + \text{O}_2 \qquad (\text{R7b})$$

$$\text{SO}_5^- + \text{HO}_2 \rightarrow \text{HSO}_5^- + \text{O}_2 \qquad (\text{R10})$$

$$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \qquad (\text{R11})$$

$$\text{HO}_2 + \text{O}_2 (+ \text{H}_2\text{O}) \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{OH}^- \qquad (\text{R12})$$
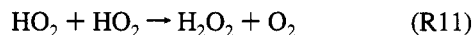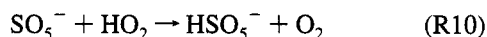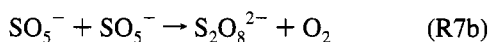
From a previously determined[18] peroxydisulfate $G$-value in oxygenated bisulfite solution ($G(\text{S}_2\text{O}_8^{2-}) \approx 0.2 \ll G(\text{SO}_5^-)$), it follows that reaction R10 is the main termination reaction. For bisulfite solutions saturated with N$_2$O−O$_2$ (4:1) it was found that the $G$-value of peroxydisulfate approximately equals half the $G$-value of the SO$_5^-$ radicals, $G(\text{S}_2\text{O}_8^{2-}) = 2.2$. This leaves the self-reaction of SO$_5^-$ radicals to provide a major termination reaction. Comparison of the radical's formation rates and the termination steps in both systems leads to the conclusion that under the same dose rates the SO$_5^-$ concentration in an N$_2$O−O$_2$ saturated bisulfite solution is higher than in of oxygenated bisulfite solutions.

The overall rate constant, $(k_{7a} + k_{7b}) = 10^8$ M$^{-1}$ s$^{-1}$, has been reported by Huie.[13] From the kinetic study of radiation-induced bisulfite oxidation we have recently determined[27] the branching ratio of the SO$_5^-$ radical self-reaction, $k_{7a}/k_{7b} = 7 \pm 1$. With known values of $(k_{7a} + k_{7b})$ and the branching ratio we find $k_{7b} = 1.3 \times 10^7$ M$^{-1}$ s$^{-1}$. This value and the well-known[25] values of the (R11) and (R12) rate constants were used as reference rate constants.

Under low initiation rates and high initial bisulfite concentrations both in oxygen and with an N$_2$O−O$_2$ saturated solutions the chain oxidation proceeds through the propagation reaction R6. By measurement the G-values of bisulfite oxidation, and peroxydisulfate formation, $G(\text{S}_2\text{O}_8^{2-})$, the value of the rate

constants ratio $k_6/k_{7b}^{0.5}$ can be obtained (see below). Since the chain propagation reactions (R2) and (R8) are very fast, this procedure is not sensitive to the branching ratio of reaction R6. It is applicable only to the determination of the overall rate constant $k_6$.

In oxygenated solution at high dose rates the G-values of peroxydisulfate formation and oxidation of bisulfite are determined by the competition of the termination reactions (R10)−(R12). Thus, the rate constant of reaction R10 can be derived from the G-values of peroxydisulfate formation and bisulfite loss at high dose rates. The well-known G-values of HO$_2$ and SO$_5^-$ radicals (see above) will be used in both approaches.

Our preliminary study[18] has shown that the initiation reaction

$$\text{HO}_2 + \text{HSO}_3^- \rightarrow \text{products} \qquad (\text{R13})$$
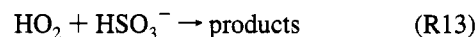
giving rise to OH or SO$_3^-$ radicals is sufficiently slow ($k_{13} < 10^3$ M$^{-1}$ s$^{-1}$). The existence of reaction R13 leads to the decrease of HO$_2$ radical concentration and simultaneous increase of SO$_5^-$ radical concentration. The competition of the reactions R9 and R13 should effect the $G$-value of peroxydisulfate formation in irradiated bisulfite solutions with oxygen saturation. The rate constant $k_{13}$ can be evaluated from dose rate and bisulfite concentration dependencies of $G$-values of peroxydisulfate at low dose rates and high bisulfite concentrations.

## Experimental Section

**Fast Electron Radiolysis.** For the continuous irradiation of the bisulfite solutions a Van de Graaff accelerator producing a beam of 1.8 MeV electrons was applied. An all-glass system was used. The solutions were flowed through a glass capillary tube, 0.8-mm internal diameter, 3.3 mm external, past the exit port of the accelerator. The tube dimensions were such that approximately ≤50% of the beam was stopped in the first glass surface and the solution. 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 gas (O$_2$ or an N$_2$O−O$_2$ mixture) into the tube. The 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 over the range $10^{-3}$−$10^{-1}$ mL s$^{-1}$. Normally the electron beam current was 0.02−1 $\mu$A. The dose was calibrated by the Fricke dosimeter. At the highest intensity used it was established that the ratio ferric yield/hydrogen yield[23] was 15.6:0.45.

**$\gamma$-Radiolysis.** Irradiations were performed by using a Co$^{60}$ $\gamma$-source at two dose rates, $7.5 \times 10^{15}$ and $2.2 \times 10^{17}$ eV L$^{-1}$ s$^{-1}$. The lower dose rate was obtained by using a lead chamber with a wall thickness of 4 cm. The irradiations were performed in the glass tubes with a volume 20 mL and a diameter of 1.5 cm. Dose rates were determined by Fricke dosimetry.

**Preparation and Analysis of Bisulfite Solutions.** The solutions were prepared just before the experiments by using triply distilled water. (The bidistilled water was subjected to a final distillation in an all-quartz system. The steam was purified for 10 s by heating at $T = 1000$ K.) The purity of the water was checked by the measurement of resistivity ($\approx 10^7$ $\Omega$ cm$^{-1}$). The oxygen was purified by heating at $T = 1000$ K and subsequent bubbling through alkali solution. The N$_2$O was used without further purification from standard steel vessels. The water saturation was carried out by bubbling O$_2$ or an N$_2$O-O$_2$ mixture for about 1 h. The N$_2$O content in the solution was checked before adding S(IV) by measuring of light absorption in the UV region, $\epsilon_{200} = 17$ M$^{-1}$ cm$^{-1}$. The initial bisulfite concentrations $[\text{HSO}_3^-]_0 = 10^{-4}$−$(3 \times 10^{-3})$ M were made by adding a concentrated deaerated S(IV) solution ($[\text{S(IV)}] =$

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$10^{-1}$–$10^{-2}$ M). This solution was prepared by bubbling reagent-grade helium through a 1 M $SO_2$ solution and subsequent saturation of triply distilled water by $SO_2$. No buffers were used.

The concentration of S(IV) has been measured by a UV–vis SPECORD MB-40 spectrophotometer over the wavelength range $\lambda = 200$–210 nm and at $\lambda = 276.9$ nm. The extinction coefficients of hydrated $SO_2$ and $HSO_3^-$ were determined by an iodometric method.[27] For bisulfite ion $\epsilon_{200} = 1840$, $\epsilon_{205} = 770$, and $\epsilon_{210} = 250$ $M^{-1}$ $cm^{-1}$. At $\lambda = 276.9$ nm the extinction coefficient of hydrated $SO_2$ equals 467 $M^{-1}$ $cm^{-1}$. Hydrated $SO_2$ also absorbs at $\lambda = 200$–210 nm ($\epsilon_{200} = 2490$, $\epsilon_{205} = 2050$, $\epsilon_{210} = 1490$ $M^{-1}$ $cm^{-1}$). The temperature of the absorption cells was maintained at $25 \pm 1$ °C.

Peroxydisulfate was determined by Fe(II) $\rightarrow$ Fe(III) oxidation.[28] Irradiated solutions were collected in the vessel containing 0.5 mL of $3 \times 10^{-3}$ M Fe(II). The oxidation of Fe(II) by $H_2O_2$ and Caro's acid produced under irradiation was negligible, since sufficiently fast reactions[22,29,26] ($HSO_3^- + H_2O_2$) and ($HSO_3^- + HSO_5^-$) were already completely finished in the capillary tube. In the parallel control run we have found that the reaction of Fe(III) with the bisulfite does not proceed. Thus Fe(II) was oxidized only by the peroxydisulfate.

The conversion of S(IV) under irradiation was obtained by subtraction of the absorptions at $\lambda = 200$–210 nm for the irradiated and nonirradiated solutions. This allowed the elimination of the contributions of the "dark" reaction occurring by parallel thermal reaction, $N_2O$ absorption, and also the loss of $SO_2$ by degassing from the solution.

The pH of the irradiated solutions was measured by using a glass electrode pH meter, calibrated with appropriate standard buffers. For our S(IV) concentrations the changes in $H^+$ concentration were approximately equal to changes in bisulfite concentrations and oxidation rates were also calculated from the acidity increase of the irradiated solutions.

All kinetic experiments were conducted at room temperature.

## Results

Under extremely low dose rates in $\gamma$-radiolysis, it is necessary to take into account the possible sinks of $SO_5^-$ and $HO_2$ radicals in the reactions with an impurities. As it follows from the Background, in bisulfite solution ($[HSO_3^-]_0 \sim 10^{-3}$ M) with $N_2O$–$O_2$ saturation, when the competition of reactions R3, R3a, and R5 is shifted to reaction R5, the $G$-value of the peroxymonosulfate radicals equals $G(SO_5^-) = 5.4$. The predicted $G$-value of peroxydisulfate under these conditions, $G(S_2O_8^{2-}) = (G(SO_5^-) - g(H))/2 = 2.4$, is expected. Figure 1 shows the dose dependence of peroxydisulfate formation under $\gamma$-irradiation. The experiments were performed over the initial bisulfite concentrations $[HSO_3^-]_0 = (5 \times 10^{-4})$–$(3.5 \times 10^{-3})$ M, dose rates $I = 7.5 \times 10^{15}$ and $2.2 \times 10^{17}$ eV $L^{-1}$ $s^{-1}$. It is seen that $G(S_2O_8^{2-})$ is dose independent, which indicates that the rate of $S_2O_8^{2-}$ decomposition in secondary reactions is negligible. The average $G$-value of the peroxydisulfate, $G(S_2O_8^{2-}) = 1.5 \pm 0.1$, is somewhat lower than $G(S_2O_8^{2-}) = 2.2$, obtained previously[27] for the same solutions but at a higher dose rates (fast electron irradiation). We do not attribute the observed lower $G$-value of the peroxydisulfate to the reactions of $SO_5^-$ radicals with impurities because the independence of $G(S_2O_8^{2-})$ on dose rate was observed; see Figure 1. The most probable explanation of the observed effect is the incomplete capture of electrons by $N_2O$ (reaction R5). This results in a decrease of $G$-value of the $SO_5^-$ radical and increase of $G$-value of the $HO_2$ radical. Apparently, some evaporation of $N_2O$ from the solutions might take place when filling the tubes. In a parallel control run, we
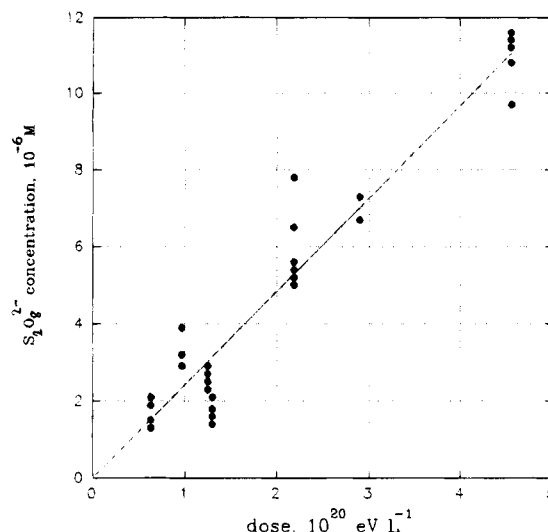


**Figure 1.** Dose dependence of the peroxydisulfate concentration in an $N_2O$–$O_2$ saturated bisulfite solution under $\gamma$-irradiation. The initial concentrations $[HSO_3^-]_0 = (5 \times 10^{-4})$–$(3.5 \times 10^{-3})$ M. Dose rates $7.5 \times 10^{15}$ and $2.2 \times 10^{17}$ eV $L^{-1}$ $s^{-1}$.
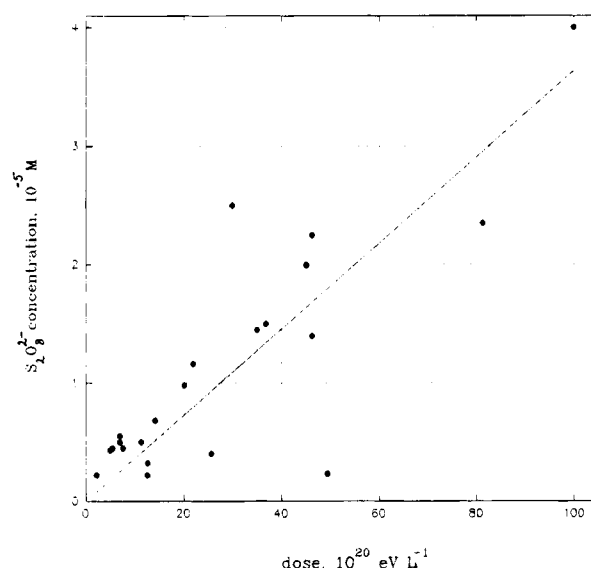


**Figure 2.** Dose dependence of the peroxydisulfate concentration in oxygen-saturated bisulfite solution. The initial $[HSO_3^-]_0 = (1$–3) $\times$ $10^{-3}$ M and dose rates $I = (7 \times 10^{19})$–$(7 \times 10^{21})$ eV $L^{-1}$ $s^{-1}$.

have estimated the $N_2O$ content in the tube's solutions as $\approx$-$(1.0$–1.5) $\times 10^{-2}$ M. Hence, at the lowest bisulfite concentration $[HSO_3^-]_0 = 5 \times 10^{-4}$ M and at $[N_2O] = 10^{-2}$ M, the competition of the reactions R3, R3a, and R5 provides an approximately 90% efficiency of $e_{aq}^-$ capture by $N_2O$. Under these conditions the expected $G$-values of the peroxymonosulfate and the hydroperoxyl radicals are as follows: $G(SO_5^-) = g(OH) + 0.9g(e_{aq}^-) \approx 5.1$, $G(HO_2) = g(H) + 0.1g(e_{aq}^-) = 0.9$, and consequently $G(S_2O_8^{2-}) \approx (G(SO_5^-) - G(HO_2))/2 = 2.1$. At $[HSO_3^-]_0 = 3 \times 10^{-3}$ M the $G$-value of the peroxydisulfate $G(S_2O_8^{2-}) = 1.3$ is expected. The dependence of $G(S_2O_8^{2-})$ on $[HSO_3^-]_0$ was not revealed experimentally. Nevertheless it is reasonable to expect that the considered competition of reactions R3, R3a, and R5 does take place. It results in decreasing the peroxydisulfate $G$-value. Thus, the fate of $SO_5^-$ radicals in $N_2O$–$O_2$ saturated bisulfite solutions is considered to be established.

The reaction between $HO_2$ and $SO_5^-$ radicals was studied in of oxygenated bisulfite solutions at high dose rates. Figure 2 shows the dose dependence of the peroxydisulfate formation at
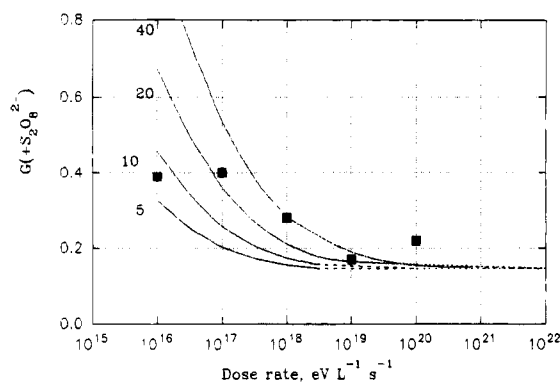
**Figure 3.** Dose rate dependence of $G(S_2O_8^{2-})$ in oxygen-saturated bisulfite solution. Experimental data are represented by squares. Values calculated by the kinetic model with the indicated value of $k_{13}$ (see text) appear as solid curves.

initial bisulfite concentration $[HSO_3^-]_0 \sim 10^{-3}$ M and $I = (7.1 \times 10^{19})-(7.1 \times 10^{21})$ eV $L^{-1}$ $s^{-1}$. As in solutions with $N_2O-O_2$ saturation, the $G$-value of peroxydisulfate is independent of dose; the decomposition of the $S_2O_8^{2-}$ in the secondary reactions is negligible. The standard routine procedure leads to $G(S_2O_8^{2-}) = 0.22 \pm 0.02$. Because this value is much lower than $G(SO_5^-)/2$, it follows that the main termination reaction of oxygenated bisulfite solutions is reaction R10, and the rate constant of reaction R10 can be derived on the basis of of the $G$-value of peroxydisulfate.

Figure 3 demonstrates the dose rate dependence of the peroxydisulfate $G$-value in oxygenated bisulfite solution. The $G$-values were calculated from the initial slopes of $S_2O_8^{2-}$ concentration dose dependencies. It is seen that dose rate has no pronounced influence on $G(S_2O_8^{2-})$. Only at the lowest dose rates ($\gamma$-irradiation) there may be a slight increase of $G(S_2O_8^{2-})$. However, the effect of bisulfite concentration $(10^{-3}-(3.5 \times 10^{-3})$ M) on $G(S_2O_8^{2-})$ at these dose rates was not revealed. This allows us to suggest that the initiation reaction R13 did not proceed at almost the entire range of dose rates and bisulfite concentrations. Therefore, only the upper limit of the reaction R13 rate constant can be estimated.

The rate constant of the reaction $SO_5^- + HSO_3^-$ has been determined from the kinetic study of the chain bisulfite oxidation. Figure 4 demonstrates the dose dependencies of $[HSO_3^-]$ concentration decrease and $[H^+]$ increase under $\gamma$-irradiation of bisulfite solutions with $N_2O-O_2$ saturation. The initial concentration of bisulfite $[HSO_3^-]_0 = 7 \times 10^{-4}$ and $1.5 \times 10^{-3}$ M; dose rate $I = 2.2 \times 10^{17}$ eV $L^{-1}$ $s^{-1}$. Figure 5 demonstrates the same dependencies for $\gamma$-irradiation of oxygenated bisulfite solutions. The initial bisulfite concentrations $[HSO_3^-]_0 = 8 \times 10^{-4}$ and $3.0 \times 10^{-3}$ M; the dose rates $I = 7.5 \times 10^{15}$ and $2.2 \times 10^{17}$ eV $L^{-1}$ $s^{-1}$.

It is seen that the stoichiometry of the oxidation is

$$HSO_3^- + 0.5O_2 = H^+ + SO_4^{2-}$$
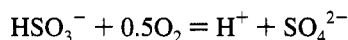
As a rule the conversion of bisulfite was not higher than 30% and represented data were approximated by the linear dependencies. The slopes of the lines correspond to the initial $G$-values of $HSO_3^-$ oxidation. Even for the lowest $[HSO_3^-]_0$ and the highest dose rate (curve 1 in Figure 5), $G(HSO_3^-) = 25 \pm 2$. Thus, the bisulfite oxidation proceeds in the chain regime in both systems. It is seen from comparison of curves 1 and 2 in Figures 4 and 5 that the oxidation rates for the $N_2O-O_2$ saturated solutions are higher than the oxidation rates in oxygenated solutions. This supports the key role of the propagation reaction (R6) since the concentration of $SO_5^-$ radicals in an $N_2O-O_2$ saturated solution is higher.
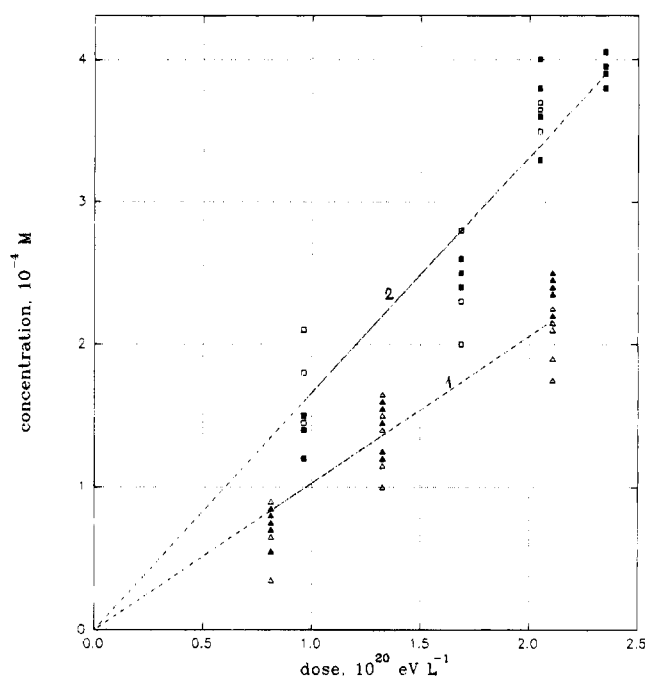


**Figure 4.** Dose dependencies of $[HSO_3^-]$ decrease (▲, ■) and $[H^+]$ increase (△, □) under $\gamma$-irradiation of $N_2O-O_2$-saturated solutions. The initial $[HSO_3^-]_0 = 7 \times 10^{-4}$ (curve 1) and $1.5 \times 10^{-3}$ M (curve 2). Dose rate $I = 2.2 \times 10^{17}$ eV $L^{-1}$ $s^{-1}$.
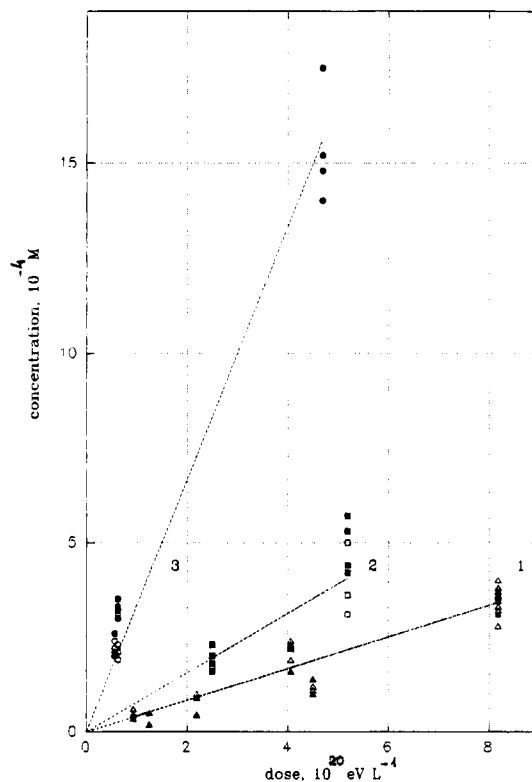


**Figure 5.** Dose dependencies of $[HSO_3^-]$ decrease (▲, ■, ●) and $[H^+]$ increase (△, □, ○) under $\gamma$-irradiation of $O_2$-saturated solutions. $[HSO_3^-]_0 = 8 \times 10^{-4}$ M, $I = 2.2 \times 10^{17}$ eV $L^{-1}$ $s^{-1}$ (curve 1); $[HSO_3^-]_0 = 3.0 \times 10^{-3}$ M, $I = 2.2 \times 10^{17}$ eV $L^{-1}$ $s^{-1}$ (curve 2); $[HSO_3^-]_0 = 3.0 \times 10^{-3}$ M, $I = 7.5 \times 10^{15}$ eV $L^{-1}$ $s^{-1}$ (curve 3).

Figures 6 and 7 show the initial $G$-value of bisulfite oxidation in bisulfite solutions saturated with oxygen and $N_2O-O_2$ as a function of the initial bisulfite concentration. Initial $G$-values at various bisulfite concentrations were calculated from the initial slopes of the curves, giving $[HSO_3^-]$ as a function of dose. The experiments were performed using $\gamma$-irradiation and
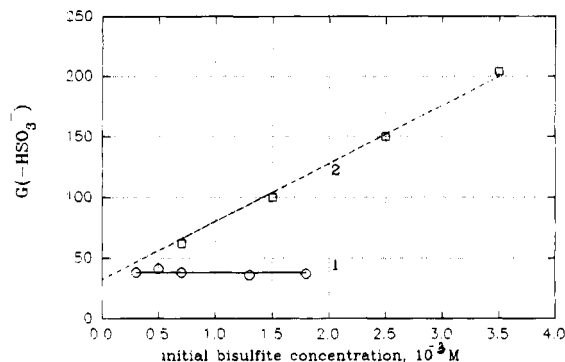
**Figure 6.** $G(-HSO_3^-)$ as a function of initial bisulfite concentration for $N_2O-O_2$-saturated bisulfite solutions. Curve 1, dose rates $I = (7 \times 10^{19})-(7 \times 10^{21})$ eV $L^{-1}$ $s^{-1}$; curve 2, $I = 2.2 \times 10^{17}$ eV $L^{-1}$ $s^{-1}$.
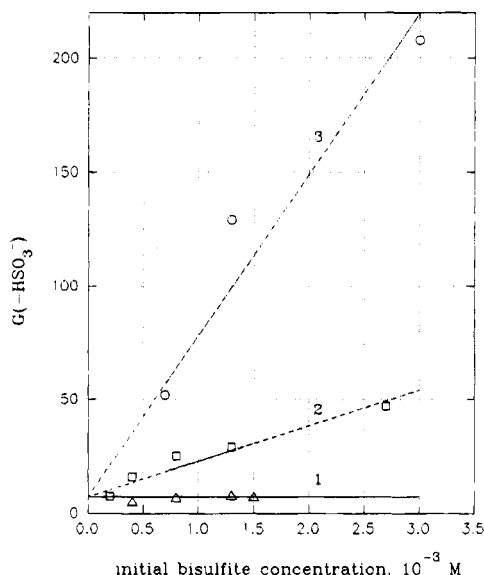


**Figure 7.** $G(-HSO_3^-)$ as a function on initial bisulfite concentration for oxygen-saturated bisulfite solutions. Curve 1, dose rates $I = (7 \times 10^{19})-(7 \times 10^{21})$ eV $L^{-1}$ $s^{-1}$; curve 2, $I = 2.2 \times 10^{17}$ eV $L^{-1}$ $s^{-1}$; curve 3, $I - 7.5 \times 10^{15}$ eV $L^{-1}$ $s^{-1}$.

fast electron irradiation. At high dose rates $G(-HSO_3^-)$ remains constant with the increase of bisulfite concentration (lines 1 in Figure 6 and 7). For $N_2O-O_2$ saturated solutions $G(-HSO_3^-)$ = 38 ± 7. Under these conditions the chain oxidation occurs through reaction R7a. This oxidation regime is chacterized by the independence of $G(-HSO_3^-)$ from the dose rate and has been studied previously.[27] For oxygenated solutions $G(-HSO_3^-)$ ≅ 8.3 ± 0.4 and is independent of the dose rate (see Figure 8). This means that the rate of reaction R6 is much less than that of reaction R10 and no chain bisulfite oxidation takes place.

It must be noticed that in our preliminary study of oxygenated bisulfite solution radiolysis[18] at high dose rate, I ≅ 5 × 10^19 eV $L^{-1}$ $s^{-1}$, we have reported that $G$-value loss of bisulfite is increased with increase of $[HSO_3^-]_0$. This discordance can be assigned to the possible influence of impurities in bidistilled water, which was used in our previous work. Besides that, we use here a more correct procedure of S(IV) determination from UV absorption spectra.

Under low dose rates ($\gamma$-irradiation) the linear dependencies of $G$-value loss of bisulfite on $[HSO_3^-]_0$ were observed in both systems. The ratio of the line 2 and 3 slopes (Figure 7) approximately corresponds to the ratio of dose rates to a power of 0.5. This confirms that the chain propagation proceeds through reaction R6 and the chain termination occurs only in the reactions of the radicals, in the case of oxygenated solutions,
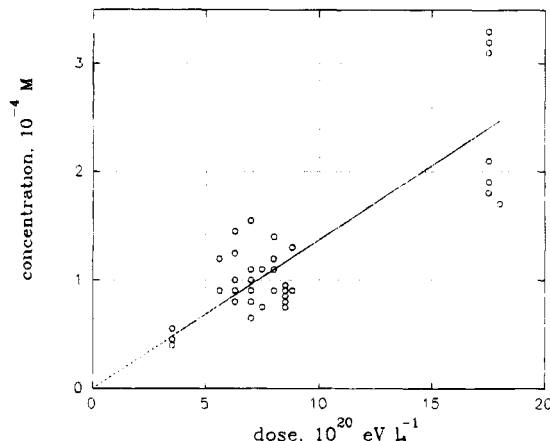


**Figure 8.** Dose dependence of $[HSO_3^-]$ concentration decrease under fast electron irradiation of $O_2$-saturated bisulfite solutions. Dose rates: $(1.4 \times 10^{20})-(7 \times 10^{21})$ eV $L^{-1}$ $s^{-1}$. Initial bisulfite concentration: $(5 \times 10^{-4})-(1.5 \times 10^{-3})$ M.

mainly through reaction R10, in case of $N_2O-O_2$ saturated solutions, mainly through reaction R7b. The decrease of the initial bisulfite concentration leads to reaction R6 rate diminution; the oxidation process turns into the no chain regime for oxygen-saturated solutions and to short-chain oxidation for $N_2O-O_2$ saturated solutions. The intercepts of the lines 2 and 3 (Figures 6 and 7) with the ordinate represent the $G$-values of oxidation processes without the contribution of reaction R6. The intercept values approximately correspond to the experimental $G$-values of bisulfite oxidation obtained at high dose rates in oxygenated and $N_2O-O_2$ saturated solutions (line 1 in Figures 6 and 7).

## Discussion

**$SO_5^- + HO_2$.** Let us consider the kinetics of radiation-induced bisulfite oxidation and peroxydisulfate formation in oxygenated bisulfite solutions at high dose rates. In the frame of kinetic scheme (R1)−(R13) describing the free-radical driven bisulfite oxidation, the steady-state concentrations of $SO_5^-$ and $HO_2$ radicals may be obtained from eqs 1 and 2:

$$0.01IG(SO_5^-)/N_a = 2k_{7b}[SO_5^-]^2 + k_{10}[SO_5^-][HO_2] \quad (1)$$

$$0.01IG(HO_2)/N_a = 2k_{11}[HO_2]^2 + 2k_{12}[HO_2][O_2^-] + k_{10}[SO_5^-][HO_2] \quad (2)$$

where $N_a$ is Avogadro's number and $0.01I$ the dose rate in units of 100 eV $L^{-1}$ $s^{-1}$. The equations do not include the possible termination reaction[17] $SO_5^- + O_2^-$. For our solutions (pH ≤ 3.3) $[HO_2]/[O_2^-]$ is higher than 30. Thus, if the reactivity of peroxymonosulfate radicals toward superoxide radicals is not higher by 1 order of magnitude than the reactivity of peroxymonosulfate radicals toward hydroperoxyl radical, then reaction R10 is the main sink of $SO_5^-$ radicals in oxygen-saturated solutions.

There is only one available value of the reaction $SO_5^- + O_2^-$ rate constant, $1.9 \times 10^7$ $M^{-1}$ $s^{-1}$, which was derived by Warneck from a kinetic study of chain sulfite photooxidation.[17] The propagation reaction $SO_5^- + SO_3^{2-}$ ($1.3 \times 10^7$ $M^{-1}$ $s^{-1}$) and the termination one $SO_5^- + SO_5^-$ ($1.4 \times 10^8$ $M^{-1}$ $s^{-1}$) were used as reference reactions.[15] However, the correct value of the termination rate constant $k_{7b}$ is much less—$1.3 \times 10^7$ $M^{-1}$ $s^{-1}$. This value follows from the redetermined[13] rate constant of the $SO_5^-$ radical self-reaction ($1 \times 10^8$ $M^{-1}$ $s^{-1}$)

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and recently determined[27] the branching ratio of SO$_5^-$ radical self-reaction. Substituting into the founded[17] boundary conditions the correct values of $k_{7b}$ and the effective rate constant for the loss of O$_2^-$ radicals at pH = 9, $k_{eff}$ = 6.1 × 10$^3$ M$^{-1}$ s$^{-1}$ ($k_{eff}$[O$_2^-$]$^2$ = $k_{12}$[HO$_2$][O$_2^-$]) for the rate constant of the reaction SO$_5^-$ + O$_2^-$, we find the value which equals to 2.6 × 10$^7$ M$^{-1}$ s$^{-1}$. The last value should be considered an upper limit because the propagation reaction rate constant has been obtained by Huie[13] at high ionic strength (≈0.5 M) and some correction for experimental[17] ionic strength is necessary.

The steady-state treatment leads to an expression for the peroxydisulfate production in irradiated oxygenated bisulfite solutions:

$$0.01 IG(S_2O_8^{2-})/N_a = k_{7b}[SO_5^-]^2 \qquad (3)$$

From eqs 1–3 one may obtain

$$k_{10}/(2k_{7b}k'_{11})^{0.5} =$$

$$\frac{G(SO_5^-) - 2G(S_2O_8^{2-})}{((G(HO_2) + 2G(S_2O_8^{2-}) - G(SO_5^-))G(S_2O_8^{2-}))^{0.5}} \qquad (4)$$

where $k'_{11}$ = $k_{11}$ + $k_{12}K$/[H$^+$] is the effective rate constant of HO$_2$ radical loss and $K$ is the dissociation constant of HO$_2$. The rate constants $k_{11}$ and $k_{12}$ are well-known:[25] $k_{11}$ = 8.3 × 10$^5$ M$^{-1}$ s$^{-1}$; $k_{12}$ = 9.7 × 10$^7$ M$^{-1}$ s$^{-1}$. The rate constant $k_{7b}$ is 1.3 × 10$^7$ M$^{-1}$ s$^{-1}$ (see Background). As follows from the eq 4, the $k_{10}$ value depends not only on the $G$-value of peroxydisulfate but also on [H$^+$]. The decrease of [H$^+$] in the experimental range from pH = 2.5 to 3.3 leads to a $k'_{11}$ increase from 1.3 × 10$^6$ to 3.9 × 10$^6$ M$^{-1}$ s$^{-1}$. Under these conditions the $G$-value of peroxydisulfate should increase from 0.16 to 0.28. However, the acidity influence on the $G$-value of peroxydisulfate was not revealed because of unsufficient experimental accuracy. With the experimental $G$-values of the peroxydisulfate, $G(S_2O_8^{2-})$ = 0.22 (Figure 2), $G(SO_5^-)$, and $G(HO_2)$, we find the ratio $k_{10}$/$(2k_{7b}k_{11})^{0.5}$ = 5.5. At the average experimental pH = 3 ($k'_{11}$ = 2.4 × 10$^6$ M$^{-1}$ s$^{-1}$) the rate constant of reaction R10 is equal to $k_{10}$ = 4 × 10$^7$ M$^{-1}$ s$^{-1}$.

In the frame of the described mechanism of the bisulfite oxidation, the $G$-values of bisulfite loss and peroxydisulfate formation are connected by the equation

$$G(-HSO_3^-) = 2G(S_2O_8^{2-})(1 + k_{7a}/k_{7b}) + 2(G(SO_5^-) -$$

$$2G(S_2O_8^{2-})) + (G(HO_2) - G(SO_5^-)) +$$

$$2G(S_2O_8^{2-}))/2 + g(H_2O_2) \qquad (5)$$

The first term represents oxidation through reaction R7 and the second term describes sulfate production by reactions R9 and R10. The third and fourth terms correspond to bisulfite oxidation by hydrogen peroxide produced in reactions R11 and R12 and also in the primary action of the radiation[23] ($g(H_2O_2)$ = 0.7). With the $G$-value of SO$_5^-$ radicals, $G(SO_5^-)$ = 2.8, and the experimental $G$-value of the peroxydisulfate, $G(S_2O_8^{2-})$ = 0.22, we find $G(-HSO_3^-)$ = 9.3. At the same time the value $G(-HSO_3^-)$ = 8.3 ± 0.4 has been obtained experimentally at high dose rates (fast electron irradiation); see Figure 8. The calculated value of the peroxydisulfate radiation yield is $G(S_2O_8^{2-})$ = 0.15 when the experimental value of $G(-HSO_3^-)$ is substituted in eq 5. This gives $k_{10}$ = 6 × 10$^7$ M$^{-1}$ s$^{-1}$. Taking into account also the $k_{10}$ value derived from measurements of the peroxydisulfate $G$-value, we obtain for the rate constant $k_{10}$ = (5 ± 1) × 10$^7$ M$^{-1}$ s$^{-1}$. It is seen that the $k_{10}$ is sufficiently close to the $k_7$ and $k_{12}$.

**HO$_2$ + HSO$_3^-$.** Evaluation of the initiation reaction (R13) rate constant has been performed on the basis of dose rate dependence of peroxydisulfate radiation yield in oxygenated bisulfite solutions (Figure 3). Assuming that the G-value of peroxydisulfate formation is independent of the dose rate down to 7.5 × 10$^{15}$ eV L$^{-1}$ s$^{-1}$ and of [HSO$_3^-$]$_0$ up to 3.5 × 10$^{-3}$ M, the (R13) rate constant upper limit can be estimated from consideration of the competition of reactions R10 and R13. Equation 6 shows that reaction R10 is the main sink of HO$_2$ radicals:
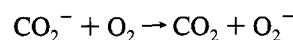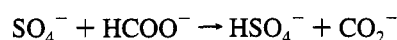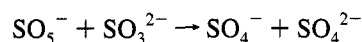
$$k_{13}[HO_2][HSO_3^-]_0 < k_{10}[HO_2][SO_5^-] \qquad (6)$$

From eqs 3 and 6 it follows that

$$k_{13} < k_{10}(0.01 IG(S_2O_8^{2-})/N_a k_{7b})^{0.5}/[HSO_3^-]_0 \qquad (7)$$

Using $k_{7b}$ = 1.3 × 10$^7$, $k_{10}$ = 5 × 10$^7$ M$^{-1}$ s$^{-1}$ and $G(S_2O_8^{2-})$ = 0.22 at $I$ = 7.5 × 10$^{15}$ eV L$^{-1}$ s$^{-1}$ and [HSO$_3^-$]$_0$ = 3.5 × 10$^{-3}$ M, one obtains $k_{13}$ < 20 M$^{-1}$ s$^{-1}$. The computer fitting of the dose rate dependence of the $G$-value of peroxydisulfate formation in oxygenated bisulfite solution has been performed at [HSO$_3^-$]$_0$ = 2 × 10$^{-3}$ M. The solid curves in Figure 3 shows the calculated dependencies for different values of the (R13) rate constants. It is seen that the upper limit of $k_{13}$ is 20 M$^{-1}$ s$^{-1}$ indeed.

There are no direct kinetic data on the initiation reaction (R13). The available data concern only the reaction between superoxide radicals and sulfite ion, O$_2^-$ + SO$_3^{2-}$. It has been shown in the pulse radiolysis experiments[19] that O$_2^-$ does not react with sulfite. Later[20] the rate constant 82 M$^{-1}$ s$^{-1}$ has been obtained from the evolution at 245 nm of the optical density of O$_2^-$ radicals, produced by an electron pulse, in aerated 3 × 10$^{-3}$ M sulfite solution in the presence of 0.3 M formate ions at pH = 9.8. The observed increase of the O$_2^-$ decay rate in sulfite solution in comparison with sulfite-free solutions was attributed to the reaction O$_2^-$ + SO$_3^{2-}$. However, the regeneration of superoxide radicals by reaction R2 and consequent fast reactions[30]

$$SO_5^- + SO_3^{2-} \rightarrow SO_4^- + SO_4^{2-}$$

$$SO_4^- + HCOO^- \rightarrow HSO_4^- + CO_2^-$$

$$CO_2^- + O_2 \rightarrow CO_2 + O_2^-$$

was not taken into account. This allowed us to consider the obtained value of 82 M$^{-1}$ s$^{-1}$ as a lower limit of the rate constant.

Some evidence of the significance of the reaction of S(IV) with HO$_2$/O$_2^-$ radicals at pH = 4.96 occurring with effective rate constant (3 ± 2) × 10$^4$ M$^{-1}$ s$^{-1}$ has been obtained[21] from the indirect method. It consisted of the subtraction from the experimental value of H$_2$O$_2$ concentration produced by γ-irradiation of synthetic cloud water the contribution of a parallel thermal reaction between hydrogen peroxide and S(IV). The contribution of the thermal reaction H$_2$O$_2$ + S(IV) was calculated by using a previously determined[31] rate constant of the reaction, (9.6 × 10$^7$)[H$^+$] M$^{-1}$ s$^{-1}$. This procedure is very sensitive to the absolute value of the thermal reaction rate constant. The effective rate constant estimated by Schwartz[21] of the reaction between S(IV) and HO$_2$/O$_2^-$ radicals could not be derived by using other available published values for the reaction H$_2$O$_2$ + S(IV) rate constant (for example,[29] (4.4 × 10$^7$)-[H$^+$]).
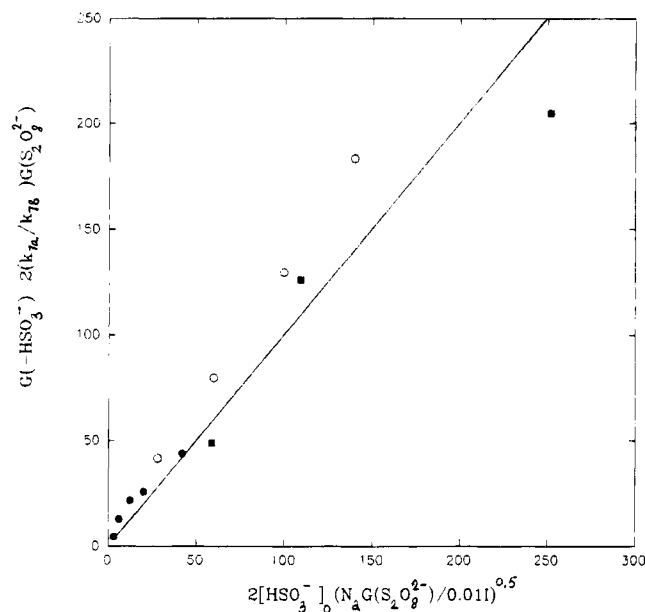
**Figure 9.** $G(-HSO_3^-) - 2(k_{7a}/k_{7b})G(S_2O_8^{2-})$ is plotted versus $2[HSO_3^-]_0$-$(N_aG(S_2O_8^{2-})/0.01I)^{0.5}$ (see eq 9). The experimental data of bisulfite oxidation in $N_2O-O_2$ (O) and $O_2$ (●, ■) saturated bisulfite solutions under dose rates $2.2 \times 10^{17}$ eV $L^{-1}$ $s^{-1}$ (O, ●) and $7.5 \times 10^{15}$ eV $L^{-1}$ $s^{-1}$ (■).

**$SO_5^- + HSO_3^-$.** In the frame of the described mechanism of bisulfite oxidation, the rate loss of bisulfite in the chain regime of oxidation for $N_2O-O_2$ and $O_2$ saturated solutions may be represented by the equation

$$0.01IG(-HSO_3^-)/N_a = 2k_{7a}[SO_5^-]^2 +$$
$$2k_6[SO_5^-][HSO_3^-] \quad (8)$$

The first term describes oxidation through reaction R7a and the oxidation rate is independent of the bisulfite concentration. The second term represents sulfate production by reaction R6 and the oxidation rate depends on $[HSO_3^-]_0$. The $G$-value of bisulfite oxidation can be expressed from eqs 3 and 8 as

$$G(-HSO_3^-) = 2(k_{7a}/k_{7b})G(S_2O_8^{2-}) +$$
$$2(k_6/k_{7b}^{0.5})[HSO_3^-](G(S_2O_8^{2-})N_a/0.01I)^{0.5} \quad (9)$$

The rate constant $k_6$ is determined from eq 9 by using the experimental $G$-values of bisulfite loss and peroxydisulfate formation and also the rate constants of reactions R7a and R7b, Figure 9 shows the experimental data of Figures 6 and 7 plotted in the form $G(-HSO_3^-) - 2(k_{7a}/k_{7b})G(S_2O_8^{2-})$ versus $2[HSO_3^-]_0$-$(N_aG(S_2O_8^{2-})/0.01I)^{0.5}$. The data are seen to fall on a straight line (correlation coefficient 0.475), indicating that eq 9 is applicable. From a routine linear approximation, $k_6/k_{7b}^{0.5} = 1.0$ is found. Using $k_{7b} = 1.3 \times 10^7$ $M^{-1}$ $s^{-1}$ for the rate constant of reaction R6, we have found $k_6 = (3.6 \pm 0.5) \times 10^3$ $M^{-1}$ $s^{-1}$.

The reaction between of the peroxymonosulfate radical and bisulfite is so slow that the rate constant of the reaction could not be extracted from the pulse radiolysis experiments with S(IV) solution containing ascorbate.[15] At the used pH = 4.9 and at the ionic strength of the solution (0.5 M) reported in the experiments,[15] the concentration of sulfite ions is sufficient to suppress slow reaction R6. For this reason extremely high value of the rate constant of reaction R6, $k_6 = 7 \times 10^6$ $M^{-1}$ $s^{-1}$, recently derived from a kinetic study[32] of bisulfite oxidation under stationary conditions and at pH $\approx$ 6, cannot be attributed
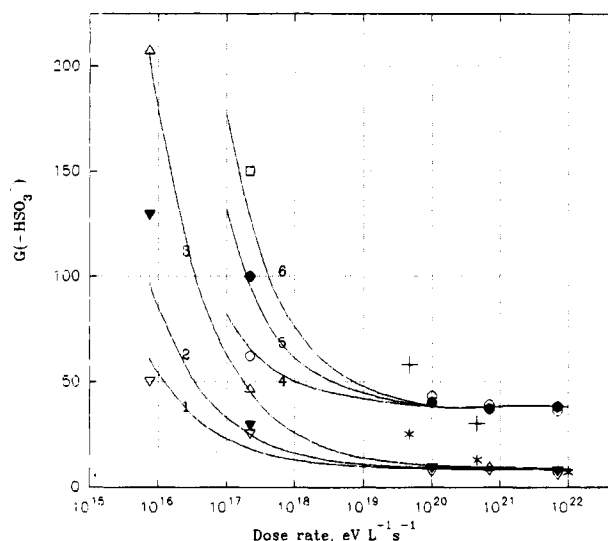


**Figure 10.** Experimental (symbols) and calculated (curves) dose rate dependencies of $G(-HSO_3^-)$ for $O_2$ (curves 1−3) and $N_2O-O_2$ (curves 4−6) saturated solutions at various bisulfite concentrations. 1,4 ($\nabla$, O), $[HSO_3^-]_0 = 7 \times 10^{-4}$ M; 2, 5 ($\blacktriangledown$, ●), (1.3−1.5) $\times$ $10^{-3}$ M; 3, 6 ($\triangle$, □), (2.5−3.0) $\times$ $10^{-3}$ M; (*, +), from our previous study[18] at $[HSO_3^-]_0 = 2 \times 10^{-3}$ M.

to the reaction between the peroxymonosulfate radicals and bisulfite but rather is due to that between $SO_5^-$ radicals and sulfite.

Figure 10 shows experimental and calculated dose rate dependencies of $G$-values of bisulfite oxidation for oxygenated and $N_2O-O_2$ saturated bisulfite solutions. Some experimental data were taken from our previous study.[18] The calculated curves were obtained by using rate constants for Table 1. Good agreement between the experimental and the calculated data is observed for both systems in a wide range of dose rate (from $7.5 \times 10^{15}$ up to $7 \times 10^{21}$ eV $L^{-1}$ $s^{-1}$) and initial bisulfite concentration (($7 \times 10^{-4}$) − ($3.5 \times 10^{-3}$) M). This is an indication of the correctness of the determination of the key rate constants of the free-radical bisulfite oxidation.

It should be noticed in the conclusion that $pK$ of $HSO_5$ radicals is unknown. The reference rate constant $k_7$ has been obtained[13] at pH $\approx$ 6 and was attributed to $SO_5^-$ radicals. In our experiments, pH $\leq$ 4. Therefore, the determined early[27] branching ratio and rate constants of reactions R6 and R10 obtained here cannot be strictly attributed to $SO_5^-$ radicals.

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