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Temperature Dependence of the Branching Ratio of SO$_5^-$ Radicals Self-Reaction in Aqueous Solution

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Temperature dependence of chain oxidation of bisulfite occurring through the self-reaction of peroxomonosulfate radicals, SO$_5^-$ + SO$_5^-$ ⟹ SO$_4^-$ + SO$_4^-$ + O$_2$ (k_{1a}), SO$_5^-$ + SO$_5^-$ ⟹ S$_2$O$_8^{2-}$ + O$_2$ (k_{1b}), has been determined over the range 278−313 K. The activation energy of the branching ratio of SO$_5^-$ self-reaction, k_{1a}/k_{1b}, was derived, E_a = 7.4 ± 2.4 kcal mol^{-1}.

Introduction

The self-reaction of SO$_5^-$ radicals is of importance[1−11] in radical-driven S(1V) chain oxidation in aqueous solution. Although there are a number attempts of studying SO$_5^-$ self-reaction kinetics, including direct methods,[1,3−11] its mechanism and stoichiometry still remain uncertain. Of particular importanceis whether the SO$_5^-$ self-reaction is a nonterminating step. The concept of a radical's nonterminating processes goes back to the kinetic study of a number of self-reactions of tertiary organic peroxo radicals[12] (*tert*-butyl peroxo and cumylperoxo radicals and others). As applied to the interaction of SO$_5^-$ radicals, a nonterminating mechanism may be expressed as

$$SO_5^- + SO_5^- \Longrightarrow SO_4^- + SO_4^- + O_2 \qquad (R1a)$$

$$\Longrightarrow S_2O_8^{2-} + O_2 \qquad (R1b)$$
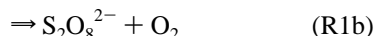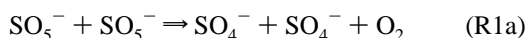
A number of experimental values of k_{1a}/k_{1b} are available. Most were extracted from a kinetic study of transition-metal-induced[13−16] decomposition of peroxomonosulfate at ambient temperatures; k_{1a}/k_{1b} = 7−10. These findings contrast with a recent value of k_{1a}/k_{1b} obtained from direct measurements[11] of SO$_4^-$ concentration arising from interaction of peroxomonosulfate radicals: $k_{1a}/k_{1b} \leq 4 \times 10^{-2}$.

A most suitable tool for determination of the branching ratio is steady-state radiolysis of S(IV) solutions saturated with N$_2$O/O$_2$. It has been derived that k_{1a}/k_{1b} is about 7 ± 1 at room temperature using this approach.[17] The aim of this work was to extend the prevoius kinetic study of SO$_5^-$ self-reaction performed at room temperature to other temperatures.
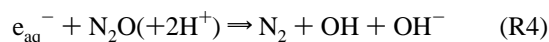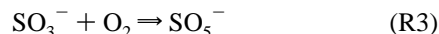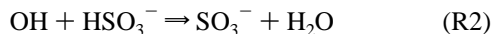
Experimental Section

A van de Graaff accelerator producing a beam of 1.8 MeV electrons served as a source of SO$_5^-$ radicals. Fast electrons were emitted sideways through a glass capillary filled with a bisulfite solution saturated with N$_2$O/O$_2$ (3/1). The irradiations were performed in flow conditions; the details of the experiment have been described elsewhere.[17−19] The vessel containing the initial bisulfite solution has a water jacket. The temperature of the solution was controlled by a thermostat. Additionally, the irradiated capillary was heated (cooled) outside by air stream with an appropriate temperature. The preliminary temperature was measured by a thermocouple located in the liquid stream immediately after the irradiation zone. During the experiments the temperature was maintained in the range ±1 K. Fricke

dosimetry was used to determine the dose rate. The solutions were prepared just before the experiments using triply distilled water; the resistivity of water ≅ 10^7 Ω cm^{-1}. The S(IV) content of the irradiated solutions was determined by spectrophotometry over the range 200−210 and 276.4 nm. Peroxodisulfate was determined by Fe(II) ⟹ Fe(III) oxidation in strong acid solution.[15] The pH was measured on a glass electrode pH-meter and calibrated with appropriate standard buffers. No buffers were used.

Results

The steady-state radiolysis of S(IV) solutions saturated with N$_2$O/O$_2$ (3/1) yields mostly OH radicals with a ≅5% yield of H atom.[20] The fast processes leading to peroxomonosulfate radical are

$$OH + HSO_3^- \Longrightarrow SO_3^- + H_2O \qquad (R2)$$

$$SO_3^- + O_2 \Longrightarrow SO_5^- \qquad (R3)$$

$$e_{aq}^- + N_2O(+2H^+) \Longrightarrow N_2 + OH + OH^- \qquad (R4)$$

$$e_{aq}^- + H^+ \Longrightarrow H \qquad (R5)$$

$$e_{aq}^- + O_2 \Longrightarrow O_2^- \qquad (R6)$$

On the basis of the discussed mechanism of SO$_5^-$ self-reaction, one may expect that G values of peroxodisulfate should also be sufficiently high at any temperatures. The majority of our experiments were done at T = 278 and 313 K. The S(IV) contents were varied over the range [S(IV)] = 3 × 10^{-4} to 1.2 × 10^{-3} M. All experiments were performed at dose rate I = 7 × 10^{20} eV L^{-1} s^{-1}. It has been found that peroxodisulfate is formed as a product of S(IV) oxidation at both T = 278 and T = 313 K. Its concentration rose linearly with dose; see Figure 1. The average G value of peroxodisulfate, $G(S_2O_8^{2-})$ = 2.1 ± 0.2, is practically equal to $G(S_2O_8^{2-})$ = 2.2 obtained previously for the same solutions but at room temperature.[17] This fact indicates that reaction R6 and the hydrolysis of SO$_5^-$ radicals (or an intermediate tetraoxide, see below) are suppressed over the range of temperature. This finding, however, contrasts with McElroy's results[7] showing that only sulfate ion is formed as a product of SO$_5^-$ self-reaction. It is surprising because some contribution to S$_2$O$_8^{2-}$ formation should be expected through SO$_4^-$ self-reaction even assuming that reaction R1b does not proceed. Modeling calculations of the kinetics of peroxodisulfate formation from the self-reaction of sulfate radical with
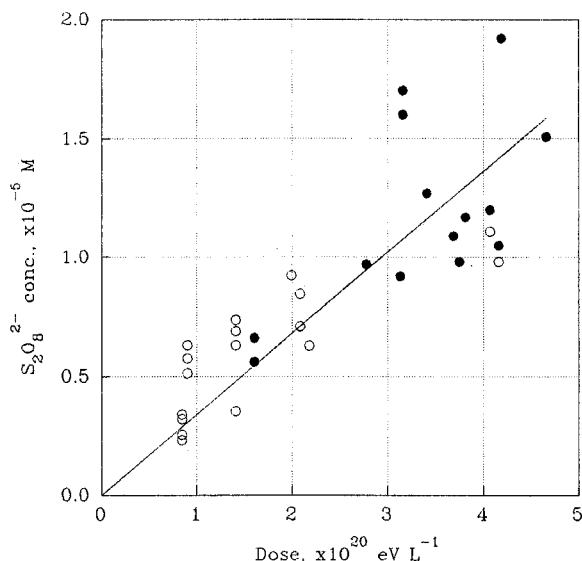
Figure 1. Dose dependence of $S_2O_8^{2-}$ concentration in irradiated bisulfite solutions. Dose rate $I = 7 \times 10^{20}$ eV L^{-1} s^{-1}, pH = 2.7–2.9, $[HSO_3^-]_0 = 3 \times 10^{-4}$ to 1.2×10^{-3} M, (●) $T = 278$ K, (○) $T = 313$ K.
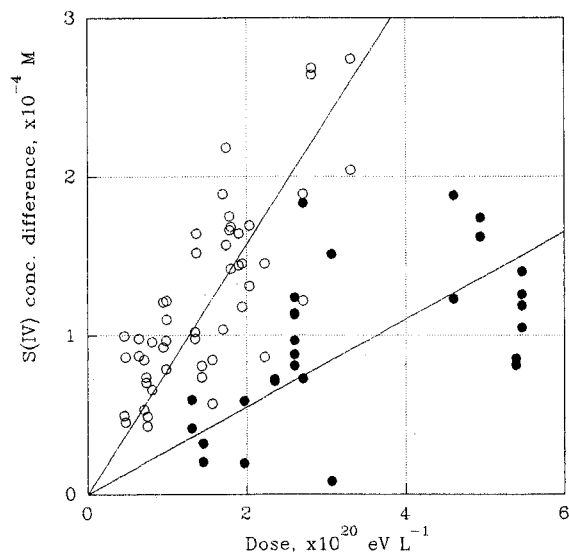
Figure 2. Dose dependence of S(IV) concentration decrease (●,○) and $[H^+]$ buildup for bisulfite solutions saturated with N_2O/O_2 (3/1). $[HSO_3^-]_0 = 3 \times 10^{-4}$ to 1.3×10^{-3} M, $I = 7 \times 10^{20}$ eV L^{-1} s^{-1}, (●) $T = 278$ K, (○) $T = 313$ K.

reference to McElroy's flash-laser photolysis of aerated dithionate solution experiments were performed. It was found using McElroy's sequence of elementary steps of SO_x^- ($x = 3-5$) transformation together with reported rate constants, $2SO_5^- \rightleftharpoons S_2O_{10}^{2-}$ ($k(\rightarrow) = 9.3 \times 10^7$ M^{-1} s^{-1}, $k(\leftarrow) = 6 \times 10^2$ s^{-1}), $S_2O_{10}^{2-} + 2H_2O \Rightarrow 2SO_4^{2-} + H_2O_2 + O_2 + 2H^+$ ($k = 6.9 \times 10^2$ s^{-1}), $SO_5^- + HSO_3^- \Rightarrow SO_4^- + SO_4^{2-} + H^+$ ($k = 4 \times 10^8$ M^{-1} s^{-1}), $SO_4^- + HSO_3^- \Rightarrow HSO_4^- + SO_3^-$ ($k = 3.3 \times 10^9$ M^{-1} s^{-1}), that formation of $S_2O_8^{2-}$ arising from $SO_4^- + SO_4^-$ reaction actually should take place.

Figure 2 shows dose dependencies for S(IV) decrease and H^+ concentration buildup for both mentioned temperatures; initial concentrations of S(IV) and dose rate are as described above. Curves 1 and 2 are linear and correspond to $T = 278$ and $T = 313$ K, respectively (conversion of S(IV) under these conditions did not exceed 30%). Within the margin of error the dose dependencies are the same for both $[H^+]$ and $[S(IV)]$, indicating that observed stoichiometry of HSO_3^- oxidation is $HSO_3^- + \frac{1}{2}O_2 \Rightarrow SO_4^- + H^+$. It is seen that the G value of
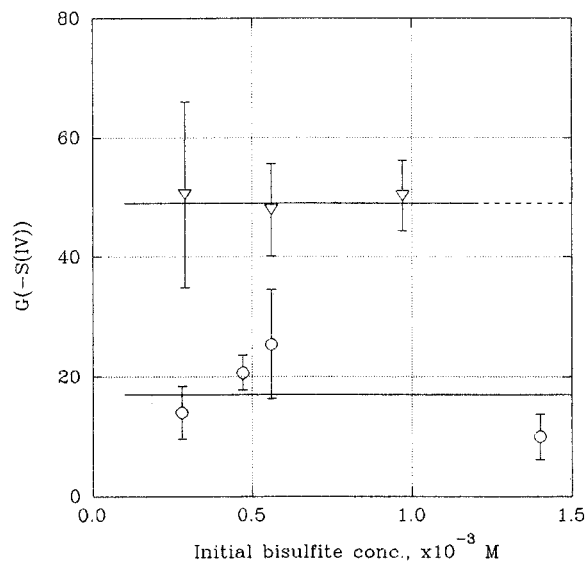
Figure 3. Correlation between experimental G values of S(1V) loss and initial bisulfite concentrations for solutions saturated with N_2O/O_2 (3/1). $I = 7 \times 10^{20}$ eV L^{-1} s^{-1}. (○) $T = 278$ K, (▽) $T = 313$ K.

S(IV) loss is increased when temperature is increased. The standard procedure leads to $G(HSO_3^-) = 17 \pm 3$ and 47 ± 4, respectively, for $T = 278$ and $T = 313$ K. It is evident that S(IV) chain oxidation proceeds over this range of temperature. It has also been found that increase of temperature practically does not affect the oxidation rate of S(IV) in oxygen-free solutions. In those experiments O_2 is replaced by an equal amount of N_2O. This finding indicates that the competition of the R3 and the R7 reactions is strongly shifted to the R3 reaction also at elevated temperatures.

$$SO_3^- + N_2O + H^+ \Rightarrow SO_3 + N_2 + OH \qquad (R7)$$

Because the rate constant of the R8 reaction is sufficiently high[9,21] $(6.5-7.5) \times 10^8$ M^{-1} s^{-1}), it was assumed that its variation over the range of temperature does not influence the rate of S(IV) oxidation:

$$SO_4^- + HSO_3^- \Rightarrow HSO_4^- + SO_3^- \qquad (R8)$$

It is also unlikely that the observed S(IV) oxidation rate was complicated by occurrence of reaction R9:

$$SO_5^- + HSO_3^- \Rightarrow HSO_5^- + SO_3^- \qquad (R9a)$$

$$\Rightarrow HSO_4^- + SO_4^- \qquad (R9b)$$

Although the activation energy of reaction R9 is not available, on the basis of our[19] experimental value of the R9 rate constant 3.6×10^3 M^{-1} s^{-1} ($T = 288$ K) and assuming a preexponential factor $\simeq 10^9$ M^{-1} s^{-1}, one may estimate $E'_a \leq 8$ kcal mol^{-1} and k_9 ($T = 313$ K) $\leq 10^4$ M^{-1} s^{-1}. This leaves the self-reaction of SO_5^- radicals to provide a major contribution to the S(IV) oxidation rate under the considered conditions. These estimates are supported by the absence of correlation between experimental G values of S(1V) loss and its initial concentration over the range 3×10^{-4} to 1×10^{-3} M; see Figure 3. The dose rate in this case was the same as mentioned above. Thus, the observed temperature dependence of the G value of S(IV) loss may be related only to the competition of reactions R1a and R1b.

The temperature dependence of the branching ratio of SO_5^- radical self-reaction is plotted in an Arrhenius plot in Figure 4.
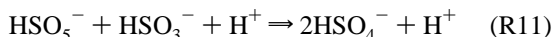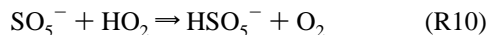
Branching Ratio of SO$_5^-$ Radical Self-Reaction

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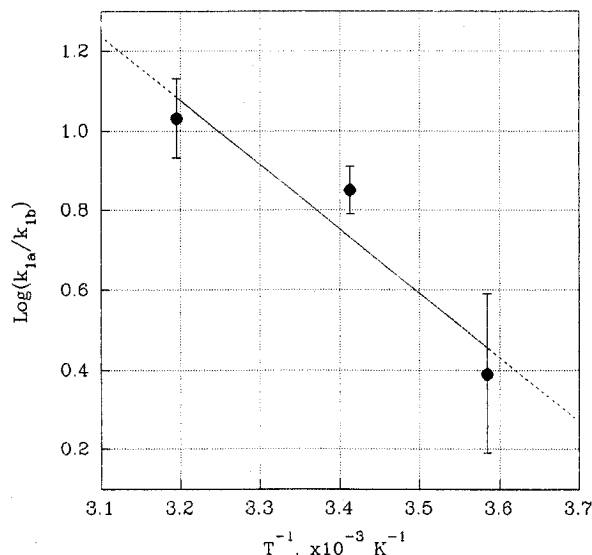
Figure 4. Temperature dependence of the branching ratio of SO$_5^-$ self-reaction plotted in an Arrhenius plot.

The values of the branching ratio at various temperatures were calculated using eq 1:

$$0.01 IG(HSO_3^-)/N_a = 2k_{1a}[SO_5^-]^2 + 2k_{1b}[SO_5^-]^2 =$$
$$2 \times 0.01 IG(S_2O_8^{2-})(1 + k_{1a}/k_{1b}) + \Delta \quad (1)$$

where $0.01I$ is the dose rate in units 100 eV L^{-1} s^{-1}, N_a is Avogadro's number. The contribution of reactions R10–R12 to S(IV) oxidation under the considered conditions is denoted as Δ.

$$SO_5^- + HO_2 \Rightarrow HSO_5^- + O_2 \quad (R10)$$

$$HSO_5^- + HSO_3^- + H^+ \Rightarrow 2HSO_4^- + H^+ \quad (R11)$$

$$H_2O_2 + HSO_3^- \Rightarrow HSO_4^- + H_2O \quad (R12)$$

The G value of S(IV) oxidation through these reactions is[20] $2g(H) + g(H_2O_2) \geq 2$. From routine procedure it was calculated that the activation energy of the branching ratio of SO$_5^-$ self-reaction is 7.4 kcal mol^{-1}. On the basis of Thompson's results one may estimate $E_a \cong 2$ kcal mol^{-1}. At "high" temperatures ($T \geq 290$ K) our approach and Thompson's[13] approach to k_{1a}/k_{1b} determination are in close agreement. At low temperatures our values of the branching ratio of SO$_5^-$ self-reaction are somewhat lower. It must be noticed that Thompson's study was carried out in a narrow range of temperature (283–298 K) and at high ionic strengths (≥ 0.5 M).

Discussion
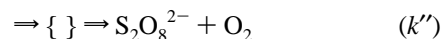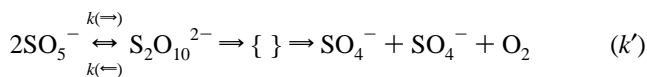
The first hint that SO$_5^-$ self-reaction is a nonterminating step came from the study of two-cocatalyst (Ag$^+$ peroxodisulfate) HSO$_5^-$ decomposition kinetics.[13] HSO$_5^-$ decomposition was observed to proceed by a chain reaction of short chain length ($\nu \cong 7$–10). A number of other fine kinetic studies of peroxomonosulfate decomposition under the action of transition metals (Ce(IV), Co(II), Fe(III), Mn(II))[14–16] or ionizing radiation[22] also implicate a chain mechanism for HSO$_5^-$ decomposition ($\nu \geq 1$). Following Mariano's and other authors' suggestions of S$_2$O$_8^{2-}$ formation upon catalytic decomposition of HSO$_5^-$, an investigation of the amount of peroxodisulfate formed and peroxomonosulfate and Ce(IV) lost was made by Marsh and Edwards.[16] It was found that the increase in

peroxodisulfate occurred only up to the point where all Ce(IV) reacted; the ratio of Ce(IV) consumed to HSO$_5^-$ consumed (ν(HSO$_3^-$)) was 7.5 ± 0.2. This value, related by authors to the branching ratio of SO$_5^-$ self-reaction, is in satisfactory agreement with estimates of the ν which were found by Willson[14] and Thompson[13] and also with the branching ratio extracted from S(IV) oxidation rate measurements using ionizing radiation as a source of SO$_5^-$ radicals.[17] These results contrast with $k_{1a}/k_{1b} \leq 4 \times 10^{-2}$ derived from measurements of SO$_4^-$ concentrations in flash-laser photolysis of aerated dithionate solution using time-resolved multichannel spectroscopy.[11] Because reaction R1a is a single source of the sulfate radicals under the considered conditions, the last value of k_{1a}/k_{1b} does not explain the initial rate formation of the radicals ($\leq 10^{-2}$ M s^{-1}) observed by Huie[4] and McElroy[7] in similar experiments. It is probably difficult to isolate reaction R1a from others occurring in photolyzed aerated dithionate solution: SO$_4^-$ + HSO$_3^-$, k_8 = 6.5 × 10^8 M^{-1} s^{-1}, SO$_4^-$ + H$_2$O, $k = 16$ M^{-1} s^{-1}, and others. The existence of the SO$_4^-$ + HSO$_3^-$ reaction in this case is explained by the results of McElroy's experiments[24] showing that dithionate is not a clean source of sulfite radicals; in a parallel channel equal amounts of SO$_2$ and SO$_4^{2-}$ are produced when dithionate is photolyzed.

An analysis of the existing data on the self-reaction of the SO$_5^-$ radical led Marsh and Edwards[16] to recommend that SO$_5^-$ self-reaction is common propagation and termination steps for all cases of radical-induced chain decomposition of peroxomonosulfate initiated by transition metal, light, and ionizing radiation. This recommendation is beyond question in the case of HSO$_5^-$ decomposition initiated by transition metal or γ-rays of Co.^{60} Photoinduced chain decomposition of HSO$_5^-$ is, however, practically suppressed. For example in accord with Maruthamathu's[25] results ($\lambda = 254$ nm) the quantum yield of HSO$_5^-$ decomposition - ϕ_{max}(HSO$_5^-$) is about 1.2, even for the highest employed concentrations of peroxomonosulfate ($\cong 5 \times 10^{-2}$ M). No attempts were made to detect S$_2$O$_8^{2-}$ during photolysis of HSO$_5^-$, although according to Marsh and Edwards,[16] up to 20% of HSO$_5^-$ undergoing photolysis is converted to peroxodisulfate. Because the decay of HSO$_5^-$ was determined using an iodometric method, sensitive also to peroxodisulfate, some corrections leading to an increase of ϕ(HSO$_5^-$) are needed. It seems reasonable to say that photoinduced chain reaction is totally restricted by low reactivity of the sulfate radical toward peroxomonosulfate ($k \leq 10^5$ M^{-1} s^{-1}).[22] When coupled with the fact that the SO$_4^-$ radicals are formed by scission of the O–O bond in peroxomonosulfate (rate of the sulfate radical production is proportional to [HSO$_5^-$]), both facts lead to suppression of the chain process in the case of the photoinduced process even for the highest concentrations investigated.

On the basis of the mechanism of a nonterminating self-reaction accepted for reactions of tertiary organic peroxoradicals, Marsh and Edwards proposed the following mechanism of SO$_5^-$ self-reaction:

$$2SO_5^- \overset{k(\rightarrow)}{\underset{k(\leftarrow)}{\rightleftharpoons}} S_2O_{10}^{2-} \Rightarrow \{\ \} \Rightarrow SO_4^- + SO_4^- + O_2 \quad (k')$$

$$\Rightarrow \{\ \} \Rightarrow S_2O_8^{2-} + O_2 \quad (k'')$$

Here $k(\rightarrow)$ and $k(\leftarrow)$ constitute the rate constants of forward and back reactions of an equilibrium stage formation of an intermediate (tetraoxide). The tetraoxide decomposes to form a cage complex shown as { } which was presumed to contain two sulfate radicals and molecular oxygen; k' and k'' are rate

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constants of { } decomposition to sulfate radicals and peroxodisulfate, respectively. Competing steps from the cage complex are a chain propagation (to release the two radicals and dioxygen) and a chain termination (to give peroxodisulfate and dioxygen). On the basis of Benson's thermodynamic analysis,[26] one may expect that $S_2O_{10}{}^{2-}$ would undergo an exothermic reaction ($\Delta H°_{r,298} = -2 \pm 10$ kcal mol^{-1}) to produce two sulfate radicals and O_2, as alkyl tetraoxides RO_4R (R = *tert*-butyl, cumyl, and others) decay to produce two alkoxoradicals and O_2. Bartlett and Guaraldi[27] were the first to demonstrate the existence of an equilibrium between *tert*-butylperoxo radical and di-*tert*-butyl tetraoxide by the ESR technique at low temperature ($T \leq 180$ K). The only reported evidence of tetraoxide formation as an intermediate product of $SO_5{}^-$ self-reaction is based on a direct method. An intermediate product absorbing at about $\lambda = 245$ nm and stable on the millisecond time scale was observed by Huie[4] using flash-laser photolysis of oxygenated dithionate solution. The observed time decay of an intermediate does not, however, explain the rapid buildup of $SO_4{}^-$ radical concentration (≤ 100 μs) under the considered conditions. Formation of the tetraoxide as an intermediate of $SO_5{}^-$ radical interaction was also deduced by McElroy.[7] On the basis of the results of kinetics of $SO_5{}^-$ and SO_4- radicals produced in oxygenated dithionate solutions, it was found that the best agreement between experimental and calculated temporal profiles of the radicals is only achieved assuming that the self-reaction is a reversible process: $k(\rightarrow) = 9.3 \times 10^7$ M^{-1} s^{-1}, $k(\leftarrow) = 6.0 \times 10^2$ s^{-1}. The extracted k is in satisfactory agreement with other values[4-6,11] obtained from the decay of $SO_5{}^-$ radicals $(7-1.3) \times 10^7$ M^{-1} s^{-1}. The strongest evidence supporting the concept of intermediate tetraoxide formation as a result of head-to-head interaction of $SO_5{}^-$ radicals has been obtained by Thompson[13] and Lunenok-Burmakina.[28] The isotopic composition of O_2 evolved during the self-reaction of $SO_3O^{18}O^-$ or $SO_3{}^{18}O^{18}O^-$ has been studied. The conclusion that both oxygen atoms in the O_2 are from terminal peroxide oxygens in the peroxomonosulfate radicals was made. Because a good balance between G values of peroxodisulfate and $SO_5{}^-$ radicals was established over the range of temperatures, we conclude that $S_2O_8{}^{2-}$ is a single product of $SO_5{}^-$ self-termination reaction and the role of $SO_5{}^-$ radical (or tetraoxide $S_2O_{10}{}^{2-}$) hydrolysis is negligible. Thus, it is safe to assume that the mechanism of $SO_5{}^-$ self-reaction is actually described by the mechanism proposed to describe the interaction of tertiary peroxo radicals. Within the framework of the discussed mechanism of $SO_5{}^-$ radical self-reaction under conditions where quasi-steady-state is valid the extracted value k_{1a}/k_{1b} in fact is a ratio k'/k''. The obtained result that the R1a channel is preferable over the R1b one, however, contrasts with available thermochemistry data[29] showing that the R1a channel is accompanied by a lower Gibbs energy change ($\Delta G°_{r,298}(\text{R1a}) \leq 0$, $\Delta G°_{r,298}(\text{R1b}) \cong -25$ kcal mol^{-1}). This indicates probably that the competition of R1a and R1b channels is governed not only by driving force but also by spin conservation. For example the energetics of peroxodisulfate production makes the formation of $^1O_2$ ($^1\Delta_g$) possible if the peroxide is produced directly from reactants via a concerted mechanism. Under the discussed mechanism the driving forces of both channels become practically equal: $\Delta G°_{r,298}(\text{R1a}) \cong \Delta G°_{r,298}(\text{R1b})$ (we assume that $\Delta G°_{f,298}(^1O_2\,(^1\Delta_g)) \cong \Delta H°_{f,298}(^1O_2\,(^1\Delta_g))$).

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