

whose energy levels are reported in Table II. In view of the quartet state distortion⁴⁷ the thermally equilibrated ⁴T_{2g} state is expected at a lower level than can be deduced from the absorption maxima. For the analogous Cr(NH₃)₅NCS²⁺ ion, the ratio $\phi_{\text{NH}_3}/\phi_{\text{NCS}^-}$ is lower in the doublet than in the quartet region²⁸ and biacetyl sensitization increases this ratio greatly.⁷ It was deduced that only NH₃ photoaquation takes place from the thermally equilibrated quartet state, which photosensitization can populate with "purer" electronic energy.⁷ No data are available for the photolysis of Cr(NH₃)₅Cl²⁺ on irradiation of the doublet features, and the small amount of free Cl⁻ plus the analytical limitations make it impossible to determine the ratio of ammonia to chloride sensitized photoaquation with the desired precision. However, this is at least as high, if not even higher, than in direct photolysis. It is possible that in the present case, as inferred from the similarity of the quantum yields, a smaller difference exists between the direct

Table II: Excited-State Energies (kcal/mol)

Species	Triplet	⁴ T _{2g}	² E _g
Naphthalene	60.9 ^a		
Cr(NH ₃) ₆ ³⁺		61.7 ^b	43.5 ^b
Cr(NH ₃) ₅ Cl ²⁺		55.7 ^b	42.5 ^b

^a From ref 18b, p 182. ^b Absorption band maxima.

and the sensitized photoaquation, due to the energy matching between the naphthalene triplet and the quartet states of the complexes (as computed from the band maxima).

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Pulse Radiolysis of Aqueous Alkaline Sulfite Solutions

by Z. P. Zagorski, K. Sehested,^{*1} and S. O. Nielsen

Accelerator and Chemistry Departments, Danish Atomic Energy Commission, Research Establishment Risø, Roskilde, Denmark (Received February 16, 1971)

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$G(-\text{O}_2)$ was measured polarographically in 1 *N* sodium hydroxide solutions with different concentrations of sulfite and oxygen and at different dose rates. A mechanism for the chain oxidation of sulfite is proposed. The SO₃⁻ radical formed in the reaction $\text{O}^- + \text{SO}_3^{2-}$ reacts with oxygen and forms a radical SO₅⁻, which reacts with sulfite and yields sulfate and O⁻. The O⁻ radical is the chain carrier. The study showed that O₂⁻ does not react with sulfite, but O₃⁻ does, and the rate constant was determined to be $k(\text{SO}_3^{2-} + \text{O}_3^-) = (3.5 \pm 1.0) \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$. The spectrum of the SO₃⁻ radical was obtained in a N₂O-saturated solution giving a λ_{max} 260 nm and a molar absorptivity $\epsilon_{260} = 1300 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$. The rate constant of the O⁻ reaction with sulfite was determined from the competition with oxygen. On the basis of $k(\text{O}^- + \text{O}_2) = 3 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, we obtained $k(\text{O}^- + \text{SO}_3^{2-}) = (2.5 \pm 0.5) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$. Also in N₂O solutions a chain oxidation of sulfite took place yielding *G* values of several thousands. This means that SO₃⁻ reacts with N₂O, yielding O⁻, and the rate constant was found to be $k(\text{SO}_3^- + \text{N}_2\text{O}) = (3.5 \pm 1.0) \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$. The e_{aq}⁻ reacts with sulfite in Ar-saturated solutions with a rate constant $k(\text{e}_{\text{aq}}^- + \text{SO}_3^{2-}) \leq 1.5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$.

Introduction

In contradistinction to acid and neutral media, strongly alkaline solutions of sulfites react only slowly with oxygen and thus permit a study of these thermodynamically unstable systems. Zagorski reported in 1961 that γ irradiation causes the reaction $2\text{SO}_3^{2-} + \text{O}_2 \rightarrow 2\text{SO}_4^{2-}$ to proceed with *G* values reaching 1000.² When the reaction was followed polarographically in the radiation field, it was found to proceed stoichiometrically with the production of sulfate. For aerated as well as deaerated solutions hydrogen is produced at a constant yield of $G(\text{H}_2) = 0.44 \pm 0.02$.

The influence of CO₃²⁻, Cl⁻, or of varying concentrations of SO₃²⁻ was found to be negligible, but the presence of H₂O₂ and some organics shortened the chain. If organic substances are present in concentrations comparable to that of oxygen, the *G* value of oxygen consumption is reduced to a few units. The reaction mechanism proposed at that time is not adequate today.

Schönherr, *et al.*,³ have reported a $G(\text{SO}_3) = 2.8$

(1) To whom correspondence should be addressed at Danish Atomic Energy Commission, Research Establishment Risø, DK-4000 Roskilde, Denmark.

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in liquid SO_2 saturated with O_2 , but with addition of water the G increases above 8, corresponding to a short-chain reaction. Chantry, *et al.*,⁴ have examined single crystals of dithionate and of salts containing the $-\text{SO}_3^-$ group after γ irradiation and have found a single esr line with an isotropic g factor of 2.004 and a corresponding ultraviolet absorption at 270 and 240 nm. The esr and uv spectra have been assigned to the SO_3^- radical. Adams and Boag⁵ have found a transient with maximum absorption about 720 nm in an oxygen-saturated solution of 0.5 M SO_3^{2-} . They have attributed this absorption to an electron adduct, HSO_3^{2-} . Dogliotti and Hayon⁶ have investigated sulfite and dithionate solutions at neutral pH using photochemical methods and have found the same transient, λ_{max} 720 nm decaying with first-order kinetics, both when oxygen was present and absent, but not in N_2O solutions. Furthermore they have found a transient absorption with λ_{max} 275 nm, which they attributed to the SO_3^- radical. The decay was second order with $2k/\epsilon = 2.0 \times 10^6 \text{ cm sec}^{-1}$ for sulfite and $2k/\epsilon = 3.5 \times 10^6 \text{ cm sec}^{-1}$ for dithionate solution. The existence of a chain reaction and a rapid thermal reaction between sulfite and oxygen have not been taken into account. Haber and Wansbrough-Jones⁷ have postulated from the photochemistry of sulfite in absence of oxygen the reaction $\text{SO}_3^- + \text{SO}_3^- \rightarrow \text{S}_2\text{O}_6^{2-}$, but because of the very low quantum yield (0.07) of dithionate, they suggested the possibility of the "back reaction" $\text{SO}_3^- + \text{H} \rightarrow \text{HSO}_3^-$. Anbar and Hart⁸ have measured the rate constant of the reaction between the hydrated electron and sulfite to be less than $1.3 \times 10^6 M^{-1} \text{ sec}^{-1}$. In the present work we describe an investigation of the sulfite oxidation in strongly alkaline solutions, 1 N NaOH. Sulfite is oxidized in a chain reaction, and the chain length was determined by the disappearance of oxygen measured polarographically. To determine the reaction mechanism, solutions with and without oxygen were studied by pulse radiolysis using spectrophotometric monitoring. Some of the important rate constants were determined, and a reaction mechanism is proposed.

Experimental Section

In the polarographic spectrum only O_2 and H_2O_2 can be followed. The polarographic activity of N_2O does not interfere with the determination of O_2 or H_2O_2 . The time resolution of the polarographic method is, however, at the present stage low and can only follow phenomena lasting longer than 0.1 sec (or down to 10 msec with oscillographic techniques).⁹ Therefore polarography was only used for determination of the O_2 concentration before and after the pulse, permitting a calculation of $G(-\text{O}_2)$.

Spectrophotometry has excellent time resolution but cannot be used for determination of the oxygen

concentration. The wavelength region available for measurement of intermediates in the uv is limited by OH^- absorption; if sulfite is present, the limitation is even greater. The sulfite ion does not show any absorption maximum, but the absorption curve increases steeply in uv. Absorption of HO_2^- appears from 350 nm and downward. The molar absorptivity of HO_2^- (Jortner and Stein¹⁰ and Landolt-Börnstein¹¹) is $180 M^{-1} \text{ cm}^{-1}$ at 260 nm.

Known methods for the determination of low SO_3^{2-} concentrations in strongly alkaline solutions are not very reliable. The concentrations were measured by determining the wavelength at which the absorption equals 1.00. A Cary 15 spectrophotometer was used, and the accuracy is comparable with that of other methods and even superior at concentrations of 1–10 mM SO_3^{2-} . SO_4^{2-} did not interfere with the determinations.

The results from the polarographic and the spectrophotometric measurements supplement each other. Application of pulsed spectroscopy and polarography simultaneously was not attempted in the present setup. Therefore parallel determinations were performed, the polarographic measurement giving the $G(-\text{O}_2)$ value and the spectrophotometric determinations giving the absorption of intermediates.

Polarographic Measurement. A PO4 polarograph (Radiometer, Copenhagen) was used, with a conventional dropping mercury electrode. Currents obtained with various electrode characteristics were normalized on the basis of a linear relationship of the O_2 diffusion current and the constant solubility of O_2 in solutions at fixed NaOH concentration and well-defined temperature and oxygen pressure.

Two kinds of vessels were used. The conventional radiometer, Type E69, was used for purity test, O_2 current measurements, and for determination of the "dark" reaction between oxygen and sulfite. A special vessel was designed to obtain the same geometry and dimensions as those of the optical cell used in the spectrophotometric measurements. The polarographic cell was emptied by opening of a magnetic valve at the bottom of the vessel, thus draining the solution and the

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mercury, while at the same time the cell was filled with an appropriate gas.

Both polarographic cells were equipped with a sintered-glass diaphragm and a bridge connecting the solutions with the saturated calomel reference electrode. The sce had a large working area (approx. 30 cm²) making it possible to work for several hours with currents up to tens of microamperes without resulting in changes of potential.¹² The total electrical resistance of the cell was below 100 ohms; corrections for potential drop are then unnecessary at constant potential measurements.¹³ The electrode potential was kept at -0.65 V (sce) for O₂ measurements. At this potential the O₂ current is not affected by O₂ maximum, electrocapillary zero phenomena, or the second oxygen wave. At sulfite concentrations lower than 100 mM there is no influence of SO₃²⁻ on the polarographic wave.

Pulse Radiolysis. The equipment has been described by Christensen, *et al.*¹⁴ Throughout the work a two-pass cell (light path 5.2 cm) with the optical axis coinciding with the electron beam was used. As in the case of the polarographic measurements, the syringes were usually without gas phase. In systems showing rapid thermal reaction between SO₃²⁻ and O₂ (*i.e.*, at SO₃²⁻ concentrations of more than 20 mM) the solution in the syringe was continuously saturated with O₂.

Spectra and kinetic studies at longer wavelengths were recorded using a Jena filter WG7 which practically cut off all light below 300 nm. In the short-wave region we prepared a sulfite solution "filter" in a 5-mm quartz cell filled with a concentration of Na₂SO₃ at least ten times greater than that of the solution investigated. This filter gave complete protection against photolysis and had a very sharp cut-off in the region 230–270 nm.

The Varian linear accelerator¹⁵ gives an electron pulse with a rise and fall time of 0.2 μsec. The electron energy is 10 MeV. The peak current in the pulse is 250 mA, and the pulse length was usually 0.5 μsec except for some dose rate measurements in which it was varied from 0.25 to 4 μsec. The dose was 3–4 krad/pulse in a 0.5-μsec pulse.

The dosimetry in the polarographic experiments was performed with the "Super-Fricke" dosimeter.¹⁶ After irradiation the solution was transferred to a Cary 15 spectrophotometer; in some cases a direct polarographic measurement of the Fe^{III} current was used. In the pulse radiolysis measurements a solution of 10⁻³ M K₄Fe(CN)₆ saturated with N₂O and equilibrated with 5 ml of air per 100 ml of solution was used.¹⁷ A WG6 optical filter was applied, and ϵ of Fe(CN)₆³⁻ was taken to be 1000 at 420 nm and $G = 5.3$.

All solutions were prepared directly in the syringes. Transfer of a solution into another syringe was only done to achieve desired concentrations of two gases

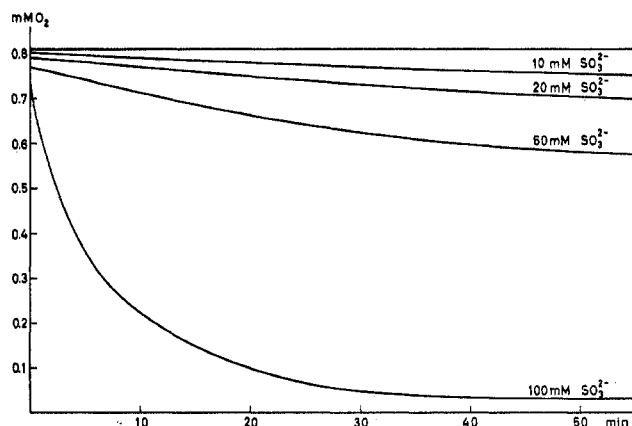


Figure 1. Disappearance (thermal reaction) of oxygen at different sulfite concentrations. All curves recalculated from continuous records on the polarograph of the O₂ current.

(*e.g.*, O₂ + N₂O). Different brands of sodium hydroxide were tested, and Merck (item 6498) was found to be the best for our purpose in spite of a 1% content of carbonate. Ba(OH)₂ could not be used because of the radiolytic production of sulfate. The following reagent grade chemicals (Merck) were used without further purification: Na₂SO₃, Na₂SO₄, and Na₂O₂. The N₂O was in some cases purified by bubbling through an alkaline pyrogallol solution, and no oxygen could be detected by polarography. The water was purified by conventional three-stage distillation, and all glassware was prebaked at 500°. A cleaning mixture of sodium hydroxide (1–5 M) and Na₂O₂ was used. The temperature during irradiation was kept at 25 ± 3°.

The computations were carried out on the Risø GIER computer with a fifth-order Runge-Kutta method for solving of the differential equations representing the course of the radiolytic reactions in aqueous solutions.¹⁸

Results

The thermal ("dark") reaction, SO₃²⁻ + O₂, was measured by constant potential polarography at -0.65 V (sce) after saturation with oxygen, air, O₂-Ar, or O₂-N₂O. We did not study the nature of this reaction; the measurements were only performed to find the limits of concentrations that could be used.

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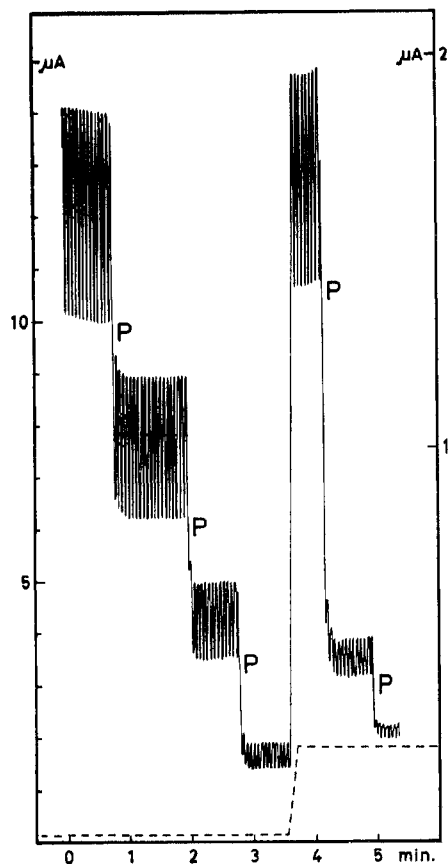


Figure 2. Polarographic record of the O_2 current in pulsed irradiation. System: 1 *N* NaOH, 10 *mM* SO_3^{2-} , oxygen-saturated, 4.3 krad/pulse. After the third pulse the sensitivity was increased 7.5 times.

Figure 1 shows the rate of O_2 disappearance at different SO_3^{2-} concentrations. The results did not differ appreciably from what had been obtained previously.² We are not able to offer an explanation of the results in 100 *mM* solutions, because the mechanism of the reaction is not known in detail.¹⁹ Lower concentrations of OH^- increased the rate, whereas lower concentrations of oxygen and lower temperature decreased the rate. The O_2 consumption was enhanced by uv light and initiated by intermediate products of the electrode O_2 reactions. This took place only at -1.0 to -1.5 V (sce) potentials and high SO_3^{2-} concentrations. Neither this effect nor the presence of the mercury electrode changed the measured radiation yields. This was proved by an indirect determination of the chain length. The appearance of the electron absorption in spectrophotometric measurements after a few pulses showed O_2 disappearance with G values corresponding to those measured by polarography.

In the polarographic measurements the O_2 current was continuously recorded before every pulse. The pulse caused a very sharp drop of the O_2 current, Figure 2. The current is recalculated into O_2 concentration and $G(-O_2)$. The measured G values

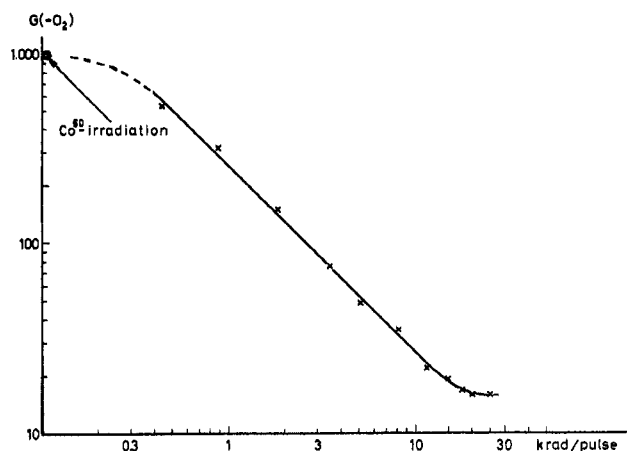


Figure 3. $G(-O_2)$ in the first pulse as function of dose per pulse. System: 1 *N* NaOH, 20 *mM* SO_3^{2-} , 0.5 *mM* O_2 as initial concentration. Pulse length 0.5–4 μ sec.

were between 10 and 1000 with a precision of $\pm 10\%$. The O_2 disappearance depended on the SO_3^{2-} and O_2 concentrations. Decreasing of the concentrations decreased the G value. Increased dose per pulse also caused a decrease in $G(-O_2)$, but the change in pulse length from 0.4 to 4.0 had no influence if the dose was kept constant. The $G(-O_2)$ in Figure 3 is plotted vs. the dose/pulse. At low doses the yield approaches the G value obtained in ^{60}Co γ irradiation for the same concentrations of SO_3^{2-} and O_2 . At doses higher than 20 krad/pulse the curve seemed to level out with a G value of about 16.

The influence of N_2O on the $G(-O_2)$ in alkaline solutions was a drastic increase in the disappearance of O_2 . At equal amounts of O_2 and N_2O the O_2 was practically consumed after the first pulse. Even different concentrations (2–20 *mM*) of sulfite, oxygen, and N_2O , and different doses exhibited almost the same result. Without oxygen, N_2O produced a chain oxidation of sulfite with G values exceeding several thousand. The hydrogen peroxide caused a decrease in the O_2 consumption, which has previously been shown in γ -irradiation experiments. Equal amounts of HO_2^- and O_2 lowered the $G(-O_2)$ by half, and 10 *mM* HO_2^- and 1 *mM* O_2 almost quenched the chain oxidation of sulfite. H_2 added to the solution before irradiation had a slight effect on the chain length. At 0.5 atm H_2 there was a small decrease in $G(-O_2)$.

In oxygen-saturated solutions there were two peaks in the ultraviolet region: one at 430 nm and one at 250–260 nm. The one at 430 nm was attributed to the O_3^- .²⁰ The extinction coefficient was about the same as that found by Czapski²⁰ ($\epsilon \approx 1900 M^{-1} cm^{-1}$). The half-width was slightly smaller (105 nm). The

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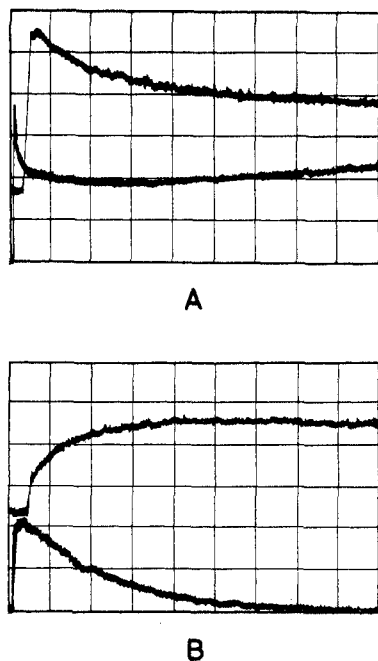


Figure 4. Optical traces at A, 285 nm; B, 430 nm. Upper traces in both pictures 20 $\mu\text{sec}/\text{div}$, lower 500 $\mu\text{sec}/\text{div}$. Absorption 2.5%/div. System: 1 N NaOH, 20 mM SO_3^{2-} , oxygen-saturated, first pulse.

peak at 260 nm was the same as Dogliotti and Hayon⁶ found at 275 nm and assigned to SO_3^- . The initial optical densities at both peaks depended on the sulfite concentration. At 260 nm the initial optical density was increased, whereas at 430 nm the optical density decreased by increasing of the sulfite concentration. The absorption at 260 nm decayed in 0.1–1 msec (depending on the sulfite concentration) and it reached a minimum, after which it increased very slowly (Figure 4). At 430 nm the absorption increased with time until it reached a maximum after 50–100 μsec . It then decayed in the millisecond range. The build-up kinetics at 430 nm were similar to the fast-decay kinetics at 260 nm. The kinetics were neither first nor second order. The absorption at the maximum at 430 nm depended on the sulfite concentration, *i.e.*, high SO_3^{2-} concentration, low absorption. The decay of O_3^- became pseudo first order with respect to sulfite concentration. There was no absorption in the visible range at 720 nm where Adams⁵ and Dogliotti⁶ had found an absorption in the neutral O_2^- and air-saturated solution. In N_2O -saturated solutions only the peak at 260 nm was observed. This peak was sulfite concentration dependent, and the maximum was shifted from shorter wavelength to 260 nm when the SO_3^{2-} concentration was increased (Figure 5). The absorption built up in a few microseconds. The half-time in 2 mM SO_3^{2-} was 1.5 μsec . The decay kinetics were of mixed order like the kinetics in O_2 solutions, but in N_2O solutions the species decayed to zero within 100–500 μsec , depending on sulfite concentration.

The absorption without SO_3^{2-} is that of O^- .

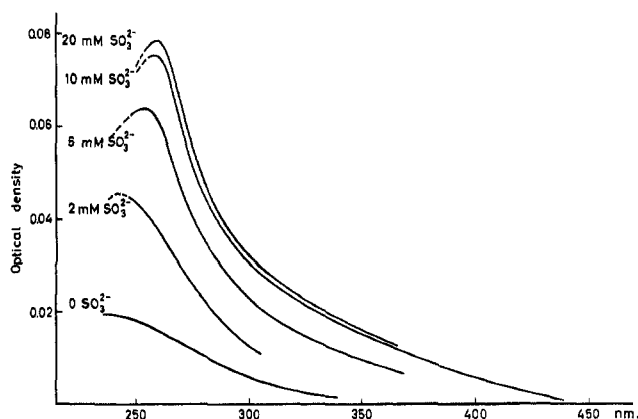


Figure 5. Absorption spectra of SO_3^- in N_2O -saturated solutions, 1 N NaOH, dose 2 krad, optical path length 5.2 cm.

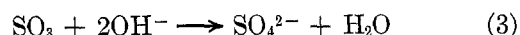
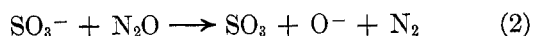
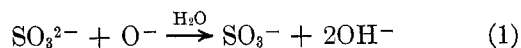
After the end of the pulse, this absorption increased in the first 50 μsec due to $e_{\text{aq}}^- + \text{N}_2\text{O}$. This indicates a relatively long-lived intermediate in the reaction of hydrated electrons with nitrous oxide in strongly alkaline media.

In Ar-saturated solution the hydrated electron absorption was observed at 700 nm, and without sulfite its half-life was 3.5 μsec . If we increased the sulfite concentration, we increased the half-life of the electron, and the kinetics went into pseudo-first-order kinetics with sulfite.

Discussion

In the oxygen-saturated solution the spectrum of SO_3^- is overlapped by the spectrum of O_2^- produced from e_{aq}^- reacting with O_2 . Furthermore, we have the O_3^- absorption, so a much cleaner spectrum of SO_3^- radical ions is obtained from the N_2O -saturated solution.

In Figure 5 the absorption spectra are presented for different sulfite concentrations from zero to 20 mM in N_2O solution. The extinction is increased by increasing of the concentration, and the maximum is shifted 10–20 nm. In this solution we have a chain reaction with $G(-\text{SO}_3^{2-})$ of several thousand measured after γ irradiation. The reactions are assumed to be



From these three reactions it is seen that SO_3^- and O^- are present at the same time. By increasing of the sulfite concentrations the reactions are pushed toward SO_3^- radicals only. The results from 10 and 20 mM sulfite show that 80 to 90% of the total radicals are SO_3^- . If we take the optical densities for 0, 2, 5, 10, and 20 mM sulfite, calculations show that the extinction of 20 mM sulfite has to be corrected by about 10% for the O^- concentration. The computations are

based on reactions 1 and 2 and the rate constant $k_1 = 2.5 \times 10^8 M^{-1} \text{sec}^{-1}$ (see later). The best fit to the experimental values at 260 nm is obtained with $k_2 = (3.5 \pm 1.0) \times 10^7 M^{-1} \text{sec}^{-1}$ and with an extinction coefficient of the SO_3^- radical of $\epsilon_{260} = 1300 \pm 200 M^{-1} \text{cm}^{-1}$. The results are shown in Table I. With no corrections for O^- the directly measured extinction equals $1180 M^{-1} \text{cm}^{-1}$. The rate constant k_1 is calculated from the results from oxygen-saturated solution by using the initial absorptions at 430 nm for different sulfite concentrations. The two competing reactions are reactions 1 and 4



The equation for the competition in reactions 1 and 4 is²¹

$$\frac{D_0}{D} = 1 + \frac{k_1[\text{SO}_3^{2-}]}{k_4[\text{O}_2]}$$

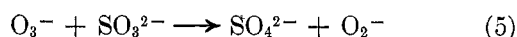
where D_0 is the optical density at 430 nm at a time 1 μsec after the pulse in solutions containing no sulfite ions, and D is the optical density under the same conditions, but with sulfite ions added. The plot of D_0/D as a function of $[\text{SO}_3^{2-}]/[\text{O}_2]$ gives a straight line with intercept 1 and a slope $k_1/k_4 = 0.083$, which gives a rate constant $k_1 = (2.5 \pm 0.5) \times 10^8 M^{-1} \text{sec}^{-1}$ (Figure 6).

Table I: Measured and Calculated Optical Absorption at 260 nm, Dose 2 krad, Optical Path Length 5.2 cm

	Measured	Calculated
2 mM SO_3^{2-}	0.0375	0.0383
5 mM SO_3^{2-}	0.0610	0.0624
10 mM SO_3^{2-}	0.0745	0.0713
20 mM SO_3^{2-}	0.0780	0.0785

The buildup in 2 mM SO_3^{2-} N_2O -saturated solution has a half-life of 1.5 μsec corresponding to an estimated $k_1 = 2.2 \times 10^8 M^{-1} \text{sec}^{-1}$.

According to Gall and Dorfman²¹ O_3^- is in equilibrium with O^- and oxygen, and the rate constant for the dissociation of O_3^- is $k = (3.3 \pm 0.3) \times 10^3 \text{sec}^{-1}$. The O_3^- disappeared in a pseudo-first-order reaction with sulfite, which is interpreted as a direct reaction between O_3^- and SO_3^{2-} , because a reaction of O^- with sulfite would reform O_3^- through the reactions 1, 6–8. The direct reaction is assumed to be



From a first-order plot we obtained the rate constant $k_5 = (3.5 \pm 1.0) \times 10^4 M^{-1} \text{sec}^{-1}$ (Table II). This rate constant is slightly dependent on OH^- concentration, as Czapski and Dorfman²² have also found for the rate of O_3^- disappearance in oxygenated alkaline solutions. Reaction 5 is consistent with the slow

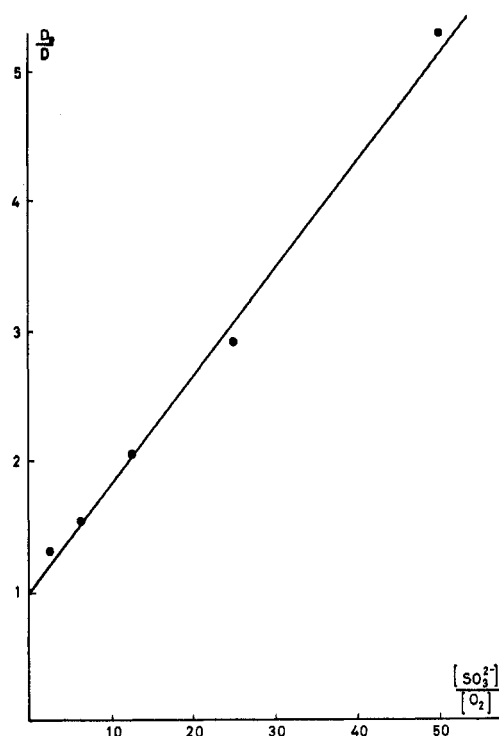


Figure 6. Plot of the competition reaction of O^- between O_2 and SO_3^{2-} . Optical density measured 1 μsec after pulse end at 430 nm. Concentration of $\text{O}_2 = 0.8 \text{mM}$. $k(\text{O}^- + \text{O}_2) = 3 \times 10^9 M^{-1} \text{sec}^{-1}$.²¹

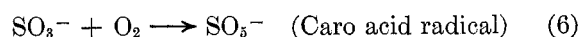
Table II: Rate Constant $k_5(\text{O}_3^- + \text{SO}_3^{2-}) M^{-1} \text{sec}^{-1}$ in Solutions of Different Concentrations of SO_3^{2-} and OH^-

	0.1 N OH^-	0.5 N OH^-	1 N OH^-	2 N OH^-
10 mM SO_3^{2-}	4.5×10^4	...
20 mM SO_3^{2-}	2.75×10^4	2.95×10^4	3.6×10^4	4.1×10^4
40 mM SO_3^{2-}	3.5×10^4	...

(see later). The absorption was stable for minutes, which is consistent with O_2^- , if it does not react with sulfite. Furthermore, it also explains our results in the hydrogen peroxide solutions, where the chain oxidation of SO_3^{2-} is quenched because of the O_2^- formation.

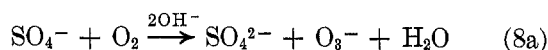
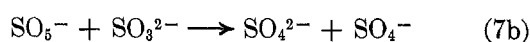
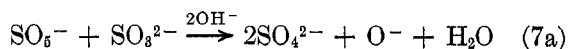
The chain mechanism in the N_2O system is given by reactions 1–3. In the oxygenated system, we can assume that, beginning with reaction 1, a proper selection from the following reaction can be made to describe the buildup of O_3^- and the chain carrier.

increase in optical density at shorter wavelengths in oxygenated solutions (Figure 4). The spectrum from 250 to 300 nm resembles the tail of the O_2^- spectrum and the extinctions are about the same as for O_2^-



(21) B. L. Gall and L. M. Dorfman, *J. Amer. Chem. Soc.*, **91**, 2199 (1969).

(22) G. Czapski and L. M. Dorfman, *J. Phys. Chem.*, **68**, 1169 (1964).

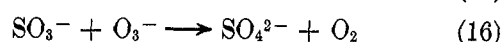
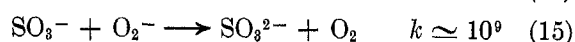
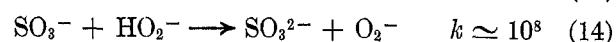
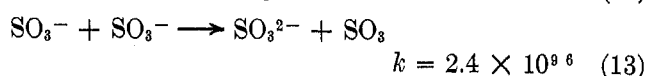
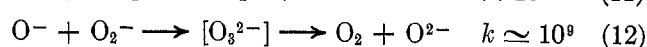
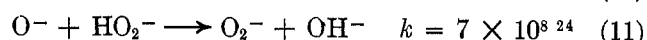
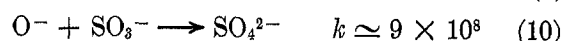
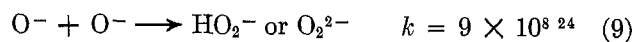


The sulfite radical reacts with oxygen and probably forms a complex (Caro acid radical) rather than causing an electron transfer. An electron transfer would yield O_2^- , which is contradictory to a chain reaction. The radical of Caro acid then reacts with a sulfite ion in the strongly alkaline media, giving sulfate and an O^- radical or an SO_4^- radical (reactions 7a and b). If the chain mechanism consists of 1, 6, and 7a, the O^- radical is the chain carrier as in the N_2O system, and reaction 4 is then responsible for the O_3^- buildup. If the reactions are 1, 6, and 7b, the produced SO_4^- radical must react with both O_2 and SO_3^{2-} (reactions 8a and b) to form O_3^- and SO_3^- radicals. Reaction 8a then explains the buildup of O_3^- and SO_3^- is the chain carrier. The SO_5^- radical has an absorption in the far-ultraviolet, but the extinction is much lower than that of the SO_3^- radical. The SO_4^- radical absorbs in the region 270–500 nm, and the extinction coefficients for the two radicals have been determined by Roebke, *et al.*,²³ and equals $300 \text{ M}^{-1} \text{ cm}^{-1}$ at 260 nm for SO_3^- and $700 \text{ M}^{-1} \text{ cm}^{-1}$ at 325 nm for SO_4^- .

Under our experimental conditions we cannot prove the existence of the SO_4^- radical, because of the absorption of SO_3^- , O_2^- , and O_3^- . At 325 nm, however, the optical density is very weak and the other radicals (SO_3^- , O_2^- , and O_3^-) are known to contribute to the absorption at that wavelength, and thus the concentration of SO_4^- has to be very low. This may indicate that SO_4^- radicals are not formed or that reactions 8a and b are much faster than the corresponding reactions for SO_3^- and SO_5^- (6 and 7a or b).

Subtracting the absorption at 260 nm of O_2^- formed in the reaction $e_{\text{aq}}^- + \text{O}_2$ and taking into account the amount of O_3^- formed for different SO_3^{2-} concentrations, we find an extinction coefficient for the SO_3^- radical in oxygenated solutions which is slightly lower than the $1300 \text{ M}^{-1} \text{ cm}^{-1}$ found in N_2O solutions. This is probably due to the lower extinction of the SO_5^- radical as compared to that of the SO_3^- radical. In 20 mM SO_3^{2-} solutions, where 30% of the O^- reacts with O_2 , the extinction coefficient is measured to be $1150 \text{ M}^{-1} \text{ cm}^{-1}$. From this the concentration of SO_5^- radicals present in 20 mM SO_3^{2-} is less than 15%. This means that the rate of reactions 6 and 7a or 6, 7b, 8a, and b is of the same order of magnitude as of reaction 2 in N_2O solutions. It is difficult to say which reaction is the rate-determining step, but reaction 6 is probably faster ($k_6 \sim 10^9$) than the sulfite radical reacting with N_2O (reaction 2).

The chain-terminating reactions are assumed to be



These reactions together with reaction 4 give an explanation of the increase in the measured $G(-\text{O}_2)$ values with decrease of dose rate. Computed values for different dose rates and for different concentrations of sulfite and oxygen are in fair agreement with the results for $G(-\text{O}_2)$ determined in the polarographic measurements, in spite of the fact that many of the rate constants have to be assumed. Reactions 11 and 14 explain why hydrogen peroxide quenches the sulfite oxidation in solutions where peroxide concentrations are comparable to the sulfite concentration.

Reactions 9, 10, and 13 and, in O_2 solutions, 12 and 15 are the important reactions at high dose rates. Computation shows that variation in pulse lengths from 0.5 to 4 μsec has little effect on the G values. At very high dose rates the G values are very low, but there still seems to be a short-chain reaction, which it is difficult to explain by the reactions proposed. Reaction 15 offers at the same time an explanation of a smaller absorption than expected of O_2^- after SO_3^- and O_3^- have decayed away. From a time 1 msec after the pulse where SO_3^- has disappeared, the increase at 285 nm (Figure 4) is about half of the decrease at 430 nm, which corresponds to $\epsilon_{\text{O}_2^-}^{285} \simeq 850 \text{ M}^{-1} \text{ cm}^{-1}$, in good agreement with reported values.²⁵

Reactions 5 and 16 are responsible for the decay kinetics of the O_3^- radical. At higher concentrations of sulfite, the maximum is lower because of reaction 5. At higher dose rates the maximum is reached more quickly mainly because of reaction 16.

In the γ irradiation, the important reactions in O_2 solutions are 14 and 15, and because of the low concentrations of O_2^- and HO_2^- the chain is very long. In N_2O solutions the chain-breaking mechanism (reactions 9–14) is not very efficient before either N_2O or SO_3^{2-} is almost consumed.

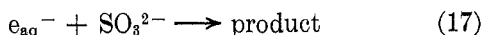
In Ar-saturated solutions the e_{aq}^- reacts with SO_3^{2-} , but very slowly. The half-life of the e_{aq}^- is increased by increasing of the SO_3^{2-} concentration. The half-life in a 20 mM SO_3^{2-} solution is about 10

(23) W. Roebke, M. Renz, and A. Henglein, *Int. J. Radiat. Phys. Chem.*, **1**, 39 (1969).

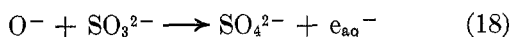
(24) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotopes*, **18**, 493 (1967).

(25) J. Rabani and S. O. Nielsen, *J. Phys. Chem.*, **73**, 3736 (1969).

μsec , and at higher concentrations the decay kinetics become first order in sulfite. The rate constant for (17)



is estimated from the half-life of 9 μsec in 50 mM SO_3^{2-} to $k_{17} \leq 1.5 \times 10^6 M^{-1} \text{sec}^{-1}$, which is in agreement with $1.3 \times 10^6 M^{-1} \text{sec}^{-1}$ found by Anbar and Hart.³ The reason for examining e_{aq}^- in Ar-saturated solution was the possible exclusion of the reaction



which would replace reaction 1. There are no indications at all at 700 nm of an additional e_{aq}^- production in Ar-saturated solution even with 40 mM SO_3^{2-} , so we are justified in leaving the reaction out of consideration. Furthermore, reaction 18 would be in contradiction to the proposed chain mechanism in O_2 solutions.

We feel confident that the absorption at 700 nm in the Ar-saturated solution is due to e_{aq}^- absorption (measured $\epsilon = 1.5 \times 10^4 M^{-1} \text{cm}^{-1}$) and not to the species HSO_3^{2-} (or SO_3^{3-}) as proposed by Adams and Boag⁵ as responsible for the absorption at 720 nm in oxygen-saturated solutions. Dogliotti and Hayon⁶ have not observed the transient in N_2O -saturated solutions, but, on adding N_2O , they have found an in-

crease of more than a factor of 2 over the transient at 275 nm. The reason for the observation in air-saturated solutions is that the thermal oxidation of sulfite with oxygen in neutral media is so fast that the oxygen is consumed immediately. Recalculation of the data in Figure 1 (ref 6) with $\epsilon_{e_{\text{aq}}^-} = 1.58 \times 10^4 M^{-1} \text{cm}^{-1}$ ²⁶ gives an ϵ of about $1000 M^{-1} \text{cm}^{-1}$ for the absorption at 275 nm compared with ours of $1300 M^{-1} \text{cm}^{-1}$ at 260 nm. The first-order rate constant reported $k = 1.9 \times 10^4 \text{sec}^{-1}$ in 20 mM SO_3^{2-} for the species absorbing at 720 nm, may be recalculated as a pseudo first order giving $k(e_{\text{aq}}^- + \text{SO}_3^{2-}) = 1 \times 10^6 M^{-1} \text{sec}^{-1}$ compared with that of Anbar and Hart³ of $1.3 \times 10^6 M^{-1} \text{sec}^{-1}$ and ours of $1.5 \times 10^6 M^{-1} \text{sec}^{-1}$. From a competition study in which they used NO_3^- ions, Dogliotti and Hayon⁶ have estimated the rate constant $k(e_{\text{aq}}^- + \text{SO}_3^{2-}) \leq 2 \times 10^6 M^{-1} \text{sec}^{-1}$.

Acknowledgments. We are indebted to E. J. Hart and H. Fricke for discussions of this work. We wish to thank O. L. Rasmussen for performing the computer calculations. We greatly appreciate the skillful assistance of the accelerator staff, and one of us (Z. P. Z.) is indebted to the Danish Atomic Energy Commission for the fellowship granted.

(26) E. J. Hart, *Science*, **146**, 19 (1964).

Autodetachment Lifetimes, Attachment Cross Sections, and Negative Ions

Formed by Sulfur Hexafluoride and Sulfur Tetrafluoride

by P. W. Harland and J. C. J. Thynne*¹

Chemistry Department, Edinburgh University, Edinburgh, Scotland (Received December 21, 1970)

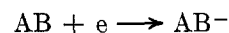
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The formation of long-lived temporary negative ion states in sulfur tetrafluoride and sulfur hexafluoride has been studied. The autodetachment lifetimes of SF_4^{-*} and SF_6^{-*} are 16.3 ± 0.3 and $68 \pm 2 \mu\text{sec}$, respectively. The measured ratio of the cross sections for electron attachment to SF_6 and SF_4 was 109 ± 6 ; this leads to a value of $10.7 \pm 0.6 \times 10^{-17} \text{cm}^2$ for the electron attachment cross section of sulfur tetrafluoride. This is some two orders of magnitude smaller than the cross section of the hexafluoride. The $\text{SF}_3\text{-F}$ bond dissociation energy has been estimated to be $\leq 3.6 \text{eV}$ and a value of $2.9 \pm 0.1 \text{eV}$ deduced for the electron affinity of sulfur trifluoride.

Introduction

When an electron interacts with a molecule, one of several processes may occur depending on the energy of the electron and the nature of the molecule. Of these, the processes which lead to negative ion formation are conventionally classified as (i) resonance capture,

which occurs with low-energy electrons (usually 0–2 eV)



(1) Correspondence should be addressed to Department of Trade and Industry, Room 506, Abell House, John Islip Street, London S. W. 1, England.