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Chemical behavior of sulfur trioxide(1-) (SO_3^-) and sulfur pentoxide(1-) (SO_5^-) radicals in aqueous solutions

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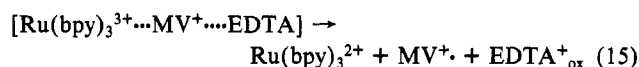
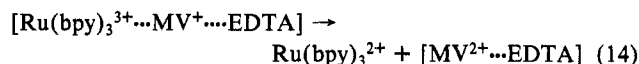
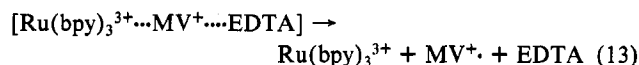
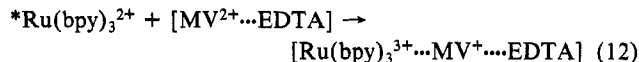
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and must be reconciled by further investigation.

Irrespective of the absolute value of η_{cr} in the presence of EDTA, it is clear that increasing complexation of MV^{2+} with EDTA causes an increase in the cage release yield of redox products. Reactions 12-15 illustrate the role of EDTA as a static scavenger



for $Ru(bpy)_3^{3+}$ within the solvent cage; ion-pair complexation of the metal cations and MV^+ are not shown for the sake of clarity. Hence, $\eta_{cr} = (k_{13} + k_{15})/(k_{13} + k_{14} + k_{15})$.

Although complexation of MV^{2+} with sacrificial donors becomes significant in alkaline solution, the absorbances of the complexes are still too low to compete with a modest concentration of intensely absorbing photosensitizer. However, now the existence of over half of the MV^{2+} as a complex will have kinetic consequences. At pH 11 in 0.1 M EDTA, $k_q = 8.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ which can be attributed to the increased electrostatic repulsion of similarly charged $Ru(bpy)_3^{2+}/EDTA$ and $MV^{2+}/EDTA$ complexes.

We have found^{26,52} as well that the quantum yield of MV^+ formation in the continuous photolysis of the model system in alkaline solution is a strong function of the concentrations of all three components, a phenomenon explained in terms of ion-pair interactions and aggregate formation among the highly charged species that causes variation in η_{cr} .

The fact that the CT complexes absorb light in the visible and near-Uv spectral regions makes them attractive potential candidates for the photochemical formation of high-energy products in the absence of any photosensitizer. Excitation of a CT complex, in which some charge transfer exists even in the ground state, can be seen as producing excited states in which extensive charge separation has been achieved. Unfortunately, the overall yields of redox products from CT complexes are generally rather low.^{11,12,14-16,20,22,25,55,56} We will discuss the photochemistry of the $MV^{2+}/EDTA$ system, and the dependence of $\Phi(MV^+)$ on [acceptor] and/or [donor], in detail in a separate publication.⁵⁷

Acknowledgment. This research was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy. We thank Vincent Malba and Professor G. Jones for many important discussions concerning this work.

Registry No. MV^{2+} , 4685-14-7; $MV^{2+}/EDTA$, 87174-65-0; $MV^{2+}/TEOA$, 87174-66-1; MV^{2+}/Cys , 92096-50-9.

(55) Hilinski, E. F.; Masnovi, J. M.; Amatore, C.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6167-6168.

(56) Gschwind, R.; Haselbach, E. *Helv. Chim. Acta* **1979**, *62*, 941-955.

(57) Prasad, D. R.; Hoffman, M. Z., manuscript in preparation.

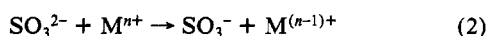
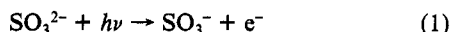
Chemical Behavior of SO_3^- and SO_5^- Radicals in Aqueous Solutions

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The chemistry of the radicals SO_3^- and SO_5^- has been investigated by using pulse radiolysis with kinetic spectrophotometry. Rate constants for the oxidation by SO_3^- of a variety of organic compounds were measured and equilibrium constants determined for the reactions of SO_3^- with chlorpromazine and phenol. SO_3^- was found to be a mild oxidant with a redox potential of $E(SO_3^-/SO_3^{2-}) = 0.63 \text{ V}$ (vs. NHE) at pH > 7 and $E(SO_3^-/HSO_3^-) = 0.84 \text{ V}$ at pH 3.6. The reaction of SO_3^- with O_2 was shown to produce SO_5^- . The oxidation of several compounds by SO_5^- was found to occur more rapidly than their oxidation by SO_3^- . $E(SO_5^-/HSO_5^-)$ was estimated to be approximately 1.1 V at pH 7.

The autoxidation of aqueous solutions of sulfur dioxide ($SO_{2(aq)}$, HSO_3^- , and SO_3^{2-}) has been studied for well over a century (for references to the literature since 1898, see Westley;¹ for recent reviews, see Huie and Peterson² and Hoffmann and Boyce³). It is known that trace amounts of transition metals are required for this reaction⁴ and that it can be initiated by ultraviolet light.^{5,6} In both cases, compounds which are known to be free radical scavengers were observed to inhibit the reaction. This led to the suggestion that both the metal ion catalyzed and the light initiated reactions involved the primary production of the sulfur(V) radical, SO_3^-



followed by a subsequent radical chain reaction.

The production of S(V) by the Ce(IV) oxidation of S(IV) has been confirmed by using ESR.^{7,8} In addition, SO_3^- has been detected by ESR in the reaction of bisulfite with various peroxides,⁹ with a horseradish peroxidase-hydrogen peroxide system,¹⁰ and with prostaglandin hydroperoxidase.¹¹ ESR also has been used to detect SO_3^- in the radiolysis¹² and the photolysis¹³ of bisulfite solutions.

Kinetic studies on SO_3^- have been carried out by using kinetic spectrophotometry with flash photolysis^{14,15} or pulse radiolysis^{14,16,17}

(7) Norman, R. O. C.; Storey, P. M. *J. Chem. Soc. B* **1971**, 1009.

(8) Ozawa, T.; Setaka, M.; Kwan, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3473.

(9) Flockhart, B. D.; Ivin, K. J.; Pink, R. C.; Sharma, R. D. *J. Chem. Soc. D* **1971**, 339.

(10) Mottley, C.; Trice, T. B.; Mason, R. P. *Mol. Pharmacol.* **1982**, *22*, 732.

(11) Mottley, C.; Mason, R. P.; Chignell, L. F.; Sivarejah, K.; Eling, T. S. *J. Biol. Chem.* **1982**, *257*, 5050.

(12) Behar, D.; Fessenden, R. W. *J. Phys. Chem.* **1972**, *76*, 1706.

(13) Chawla, O. P.; Arthur, N. L.; Fessenden, R. W. *J. Phys. Chem.* **1973**, *77*, 772.

(14) Hayon, E.; Treinin, A.; Wilf, J. *J. Am. Chem. Soc.* **1972**, *94*, 47.

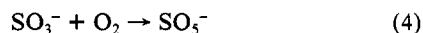
(15) Subhani, M. S.; Kauser, F. *Rev. Roum. Chim.* **1978**, *23*, 1129.

- (1) Westley, F. *NBS Spec. Publ. (U.S.)* **1982**, No. 360.
 (2) Huie, R. E.; Peterson, N. C. In "Trace Atmospheric Constituents"; Schwartz, S. E., Ed.; Wiley: New York, 1983; Chapter 2.
 (3) Hoffmann, M. R.; Boyce, S. D. In "Trace Atmospheric Constituents"; Schwartz, S. E., Ed.; Wiley: New York, 1983; Chapter 3.
 (4) Titoff, A. Z. *Phys. Chem., Stoichiomet. Verwandtschaftsl.* **1903**, *45*, 641.
 (5) Mathews, J. H.; Weeks, M. E. *J. Am. Chem. Soc.* **1917**, *39*, 635.
 (6) Bäckström, H. L. *J. J. Am. Chem. Soc.* **1927**, *49*, 1460.

as a radical source. Quantitative rate data from this earlier work are limited mostly to the self-reaction of the SO_3^- radical



Rate data on the production of SO_5^- from the reaction of SO_3^- with O_2 are even more limited



as are data on the self-reaction of the SO_5^- radical.¹⁴

In order to understand fully the free radical oxidation of SO_2 in aqueous solutions, it is necessary to have a basic understanding of the chemistry of the radicals involved. The objective of the work reported here is to begin to establish the chemical behavior of the radicals SO_3^- and SO_5^- .

In an earlier publication, we reported rate constants for the reactions of SO_3^- and SO_5^- with ascorbic acid and trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid). In the present work, we extend this investigation to the reactions of SO_3^- with phenol, *p*-methoxyphenol, and chlorpromazine and the reactions of SO_5^- with promethazine, phenol, *p*-methoxyphenol, and I^- . The reaction system involving SO_3^- , O_2 , and ascorbic acid was investigated more thoroughly, and rate constants for the reaction of SO_3^- with O_2 and the SO_5^- with HSO_3^- were derived. In addition, rate constants for the reactions of the phenoxyl radical, the promethazine radical, and I_2^- with S(IV) were also measured.

Using both the kinetic results and some equilibrium measurements, we have derived a redox potential for the SO_3^- radical and estimated a value for the SO_5^- radical, which can be used to predict the reactivity of these radicals toward other species.

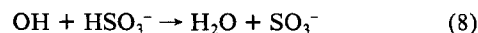
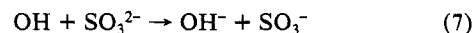
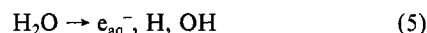
Experimental Section¹⁸

Sodium sulfite and bisulfite were analytical grade reagents from Fisher and Mallinckrodt, respectively. Sodium iodide was from Baker & Adamson and sodium perchlorate from G. F. Smith, both reagent grade. Sodium ascorbate, *p*-methoxyphenol, chlorpromazine [2-chloro-10-(3-dimethylamino)propyl]phenothiazine], and promethazine [10-(2-dimethylamino)propyl]phenothiazine] were from Sigma. Phenol was from Mallinckrodt. Water was purified by a Millipore Milli-Q system. Solutions were prepared freshly before irradiation and the pH was adjusted where necessary by using sodium hydroxide or perchloric acid. Solutions were bubbled to saturation with either N_2O or $\text{N}_2\text{O}-\text{O}_2$ mixtures and allowed to flow through an irradiation cell with a 2-cm optical path perpendicular to the electron beam. The flow rate was sufficient to replenish the solution in the cell between pulses.

The pulse radiolysis apparatus¹⁹ consists of a Febetron 705 accelerator supplying 50-ns pulses of 2-MeV electrons. The dose per pulse was usually 500 rd, determined by using KSCN dosimetry. The optical detection system used a Varian 300-W xenon lamp, separated from the cell by a shutter, and a monochromator and photomultiplier located in a separate room from the irradiation region. The kinetic traces were digitized by a Tektronix 7612 transient recorder and processed by a PDP 11/34 minicomputer. First-order rate constants were derived by using a linear least-squares routine.

Results and Discussion

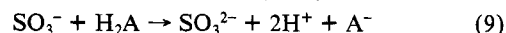
Formation of SO_3^- . The SO_3^- radicals were produced by the reaction of OH with sulfite or bisulfite in irradiated aqueous solutions containing N_2O .



Reactions 7 and 8 are practically diffusion controlled; $k_7 = 5.5 \times 10^9$ and $k_8 = 9.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ have been reported.²⁰ Sulfite and bisulfite ions do not react with e_{aq}^- and thus do not compete with reaction 6. Under our experimental condition, i.e., sulfite concentrations $\geq 1 \text{ mM}$ and pH 3–12, SO_3^- radicals are formed with a yield of $G = 6$ (radicals/100 eV) in less than 1 μs after the pulse. The small yield of H atoms (<10%) usually can be neglected.

The optical absorption spectrum of SO_3^- has been reported¹⁴ to have $\lambda_{\text{max}} = 255 \text{ nm}$ with $\epsilon_{\text{max}} = 1000 \text{ M}^{-1} \text{ cm}^{-1}$. We rarely used this absorption to monitor the reactions of SO_3^- with other solutes. Instead, we have followed the formation of the product radicals at longer wavelengths.²¹ The second-order decay of SO_3^- was reported to take place with $2k = 1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.¹⁴ Most of our experiments were carried out with a dose per pulse of ~ 500 rd, and the reactions of SO_3^- with solutes were usually complete within $\sim 100 \mu\text{s}$, so that the $\text{SO}_3^- + \text{SO}_3^-$ reaction had no significant contribution. Nevertheless, in most cases the solute concentrations were varied to allow correction for any possible contribution to the overall kinetics by the second-order decay. Most of the product radicals from the reactants studied are quite stable, at least on the time scale of a pulse radiolysis experiment. It was therefore possible to seek conditions under which an observable equilibrium would be obtained. Under these conditions, however, the $\text{SO}_3^- + \text{SO}_3^-$ reaction could become important and was accounted for.

Redox Reactions of SO_3^- . In a preliminary report²² we have described the oxidation of ascorbate by SO_3^-



and the dependence of k_9 upon pH. The pH dependence of the rate constant corresponded to the acid-base equilibria of ascorbic acid



with $\text{p}K_1 = 4.2$ and $\text{p}K_2 = 11.5$.²³ The values of k_9 were found to be $<10^6$, 9×10^6 , and $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for H_2A , HA^- , and A^{2-} , respectively.

The rate constants for oxidation of ascorbate by SO_3^- are considerably lower than the values reported for oxidation by I_2^- (1.4×10^8 at pH 7),²⁴ Br_2^- (1×10^9 at pH 7),²⁴ Cl_2^- (6×10^8 at pH 2),²⁵ and CO_3^- (1.1×10^9 at pH 11).²⁵ By using the Marcus relation²⁶ and the known redox potentials for the above radicals²⁷ we can estimate the redox potential for $\text{SO}_3^-/\text{SO}_3^{2-}$ to be in the range 0.5–0.7 V, assuming that all the reactions involve outer-sphere electron transfer. In an attempt to improve this value we have examined other oxidation reactions of SO_3^- and some radical reactions producing SO_3^- .

p-Methoxyphenol has a redox potential of 0.4 V at pH >12 and 0.6 V at pH 7.²⁸ This compound was found to be oxidized readily by SO_3^- , with $k = 4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at pH 9.2, $1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at pH 11.7, and $1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at pH 12.4. At the latter pH, $[\text{SO}_3^{2-}]$ was varied between 1 mM and 2 M and, except

(16) Zagorski, Z. P.; Sehested, K.; Nielsen, S. O. *J. Phys. Chem.* **1971**, *75*, 3510.

(17) Erikson, T. E. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 208.

(18) Certain commercial equipment, instruments, or materials are identified in this paper in order to specify adequately the experimental procedures. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified are necessarily the best available for the purpose.

(19) Simic, M. G.; Hunter, E. P. L. In "Radioprotectors and Anticarcinogens"; Academic Press: New York, 1983; pp 449–460.

(20) Adams, G. E.; Boag, J. W. *Proc. Chem. Soc., London* **1964**, 112.

(21) All of the radicals studied in the present work have been reported previously. Their absorption maxima are as follows: ascorbate radical, 360 nm; phenoxyl, 400 nm; *p*-methoxyphenoxyl, 420 nm; TMPD⁺, 565 nm; chlorpromazine cation radical, 525 nm.

(22) Huie, R. E.; Neta, P. *Environ. Res.*, in press.

(23) Kortum, G.; Vogel, W.; Andrussov, K. "Dissociation Constants of Organic Acids in Aqueous Solution"; Butterworths: London, 1961.

(24) Schöneshöfer, M. Z. *Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1972**, *27B*, 649.

(25) Redpath, J. L.; Willson, R. L. *Int. J. Radiat. Biol. Relat. Stud. Phys., Chem. Med.* **1973**, *23*, 51.

(26) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966; **1957**, *26*, 867, 872.

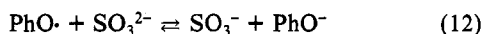
(27) Endicott, J. F. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleishauer, P. D., Eds.; Wiley-Interscience: New York, 1975; p 81.

for an increase in k up to $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ due to the higher ionic strength, there was no evidence for an equilibrium; i.e., the yield of the *p*-methoxyphenoxy radical was quantitative even at the highest concentration of sulfite. From this result we estimate an equilibrium constant $K \geq 10^4$ and $\Delta E \geq 0.24 \text{ V}$.

The rate constant for the reaction of SO_3^- with phenol, which has a redox potential of ≥ 0.6 ,²⁸ was investigated by pulsing a solution of 0.1 M Na_2SO_3 and 0.05 M phenol at pH 11.1. The results suggested a rate constant of $< 10^4 \text{ M}^{-1} \text{ s}^{-1}$. By investigating the system with phenol in excess, so that phenoxy radicals were produced after the pulse instead of sulfite radicals,



we were able to observe the equilibrium

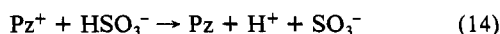


By varying $[\text{SO}_3^{2-}]$ from 0.01 to 0.39 M at $[\text{PhO}^-] = 0.35 \text{ M}$, and from 0.001 to 0.03 M at $[\text{PhO}^-] = 0.15 \text{ M}$, and by determining both $[\text{PhO}^-]$ at equilibrium from the absorbance at 400 nm as well as the rate constant for approach to equilibrium (for details, see ref 28), we were able to derive an equilibrium constant of $K_{12} = 17 \pm 5$. The forward and reverse rate constants were calculated to be $k_{12} = 1 \times 10^7$ and $k_{-12} = 6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. The redox potential different is thus calculated to be $\Delta E = 72 \pm 8 \text{ mV}$.

Promethazine and chlorpromazine have known one-electron oxidation potentials (0.86 and 0.78 V, respectively)²⁹ that do not change with pH in the acid region. We have, therefore, attempted to determine the redox potential of SO_3^- against these compounds. The promethazine cation radical was produced by reaction with Br_2^{30}

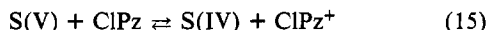


and found to oxidize bisulfite



with $k_{14} = 6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at pH 3.6, 1.6×10^7 at pH 5.0, 5.0×10^7 at pH 5.5, 1.0×10^8 at pH 6.1, and 1.2×10^8 at pH 6.6. The increase in k_{14} is in accord with the expected increase in ΔE with pH for reaction 14 due to the acid-base equilibria of HSO_3^- . However, equilibrium conditions were not established even at the lower pH owing to slow electron-transfer rate and fast decay (of $\text{SO}_3^- + \text{SO}_3^-$ and, possibly, $\text{SO}_3^- + \text{Pz}^+$).

Experiments at pH 3.6 with 0.05–0.1 M HSO_3^- and 1–10 mM chlorpromazine gave sufficiently high rates of electron transfer to establish the equilibrium



The equilibrium constant was determined by measuring the equilibrium absorbance at 525 nm due to the chlorpromazine radical cation as a function of the chlorpromazine concentration. The total amount of radicals was constant ($\pm 5\%$) from pulse to pulse and was determined, in terms of chlorpromazine radical absorbance, A , by using the oxidation of chlorpromazine with $(\text{SCN})_2^-$, which is known to go to completion.^{30c} The equilibrium constant was calculated by

$$K = \frac{[\text{S(IV)}]}{[\text{ClPz}]} \frac{[\text{ClPz}^+]}{[\text{S(V)}]} = \frac{[\text{S(IV)}]}{[\text{ClPz}]} \frac{A'}{A - A'}$$

where A' is the absorbance at a particular set of solute concentrations. From the results, given in Table I, we derive $K_{15} = 11 \pm 2$.

The rate constants k_{15} and k_{-15} were estimated to be $\sim 5 \times 10^6$ and $\sim 5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, respectively, but could not be determined very accurately. From K_{15} we calculate $\Delta E = 61 \pm 5 \text{ mV}$, and

TABLE I: Equilibrium Measurements for Reaction 15

$[\text{SO}_3^{2-}]$, M	$[\text{ClPz}]$, mM	$A' \times 10^{2a}$	$A'/(A - A')$	K
0.1	0	≤ 0.05		
0.1	2	1.59	0.22	10.9
0.1	4	2.78	0.45	11.3
0.1	6	3.58	0.67	11.2
0.1	8	3.995	0.81	10.2
0	2	8.91 (A) ^b		

^a Dose per pulse 580 rd, optical pathlength 2 cm, pH 3.6.

^b Determined in the presence of 0.1 M KSCN.

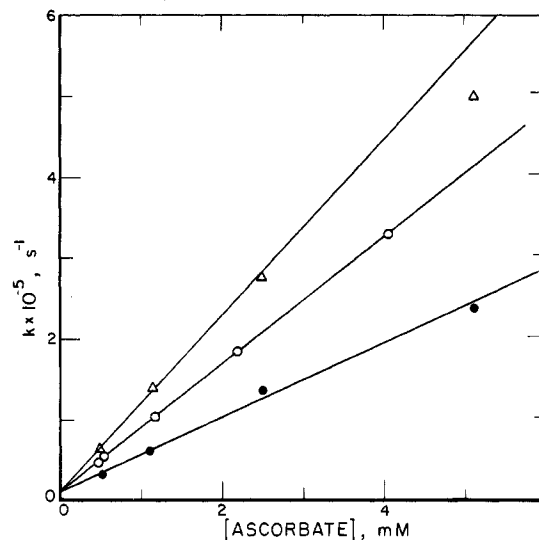
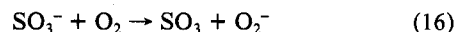
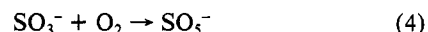


Figure 1. First-order rate constant for the reaction of SO_5^- with ascorbate at pH 6.8: open circles, 0.05 M NaHSO_3 ; open triangles, 0.05 M NaHSO_3 + 0.5 M NaClO_4 ; solid circles, 0.5 M NaHSO_3 .

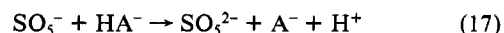
from $E = 0.78 \text{ V}$ for ClPz we derive $E = 0.84 \text{ V}$ for $\text{SO}_3^-/\text{HSO}_3^-$ at pH 3.6.

Finally, we have measured the rate constant for the reaction of I_2^- with HSO_3^- to produce SO_3^- at pH 6.7. The I_2^- radical was produced by the pulse radiolysis of 4 mM NaI solution and the HSO_3^- concentration varied over the range 1–4 mM. A rate constant of $6.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ was derived.

Reaction of SO_3^- with O_2 and Reaction of SO_5^- with HSO_3^- . Replacing the pure N_2O stream with a 1:1 mixture of N_2O and O_2 resulted in the much more rapid oxidation of the organic substrates, typically a tenfold increase. Under the experimental conditions employed, O_2 does not participate in the initial chemistry after the pulse, but, rather, will react with the sulfite radical. Addition and electron transfer have been suggested as possible routes for this reaction

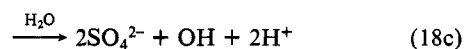
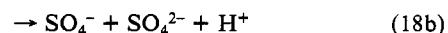
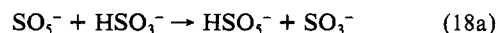


As we reported in our preliminary communication,²² the measured rates for the oxidation of ascorbate do not agree with the formation of O_2^- and must correspond to



The values of k_{17} were found to be 2×10^6 and $1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for H_2A and HA^- , respectively.

In addition to reacting with ascorbic acid, SO_5^- also can react with bisulfite, which is in great excess. Three possible paths have been suggested for this reaction:



Since both OH and SO_4^- very rapidly oxidize HSO_3^- , these paths

(28) Steenken, S.; Neta, P. *J. Phys. Chem.* **1982**, *86*, 3661.

(29) Pelizzetti, E.; Mentasi, E. *Inorg. Chem.* **1979**, *18*, 583.

(30) (a) Willson, R. L. *Biochem. Soc. Trans.* **1974**, *2*, 1082. (b) Pelizzetti, E.; Meisel, D.; Mulac, W. A.; Neta, P. *J. Am. Chem. Soc.* **1979**, *101*, 6954. (c) Bahnmann, D.; Asmus, K. D.; Willson, R. L. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1661.

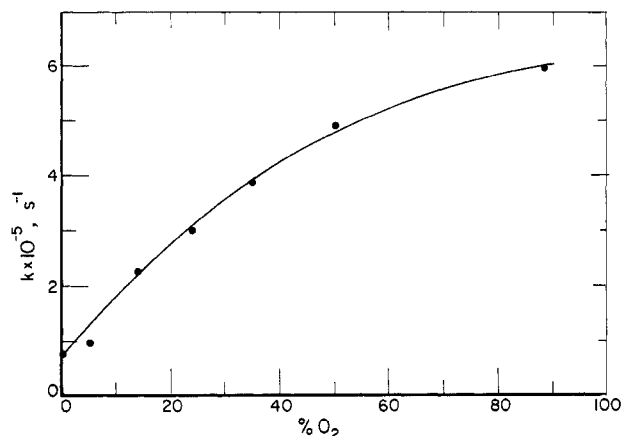
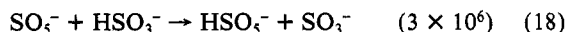
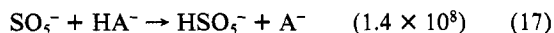
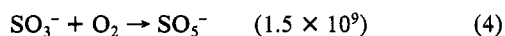
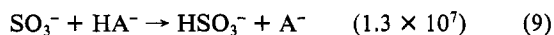


Figure 2. First-order rate constant for the oxidation of ascorbate following the pulse radiolysis of a mixture of 5 mM ascorbic acid–0.05 M NaHSO₃–0.5 M NaClO₄, saturated with a N₂O:O₂ mixture. The proportion of O₂ in the gas stream is indicated. The circles are the experimental points, the line was calculated (see text).

will have the same impact on measured rates under our experimental conditions.

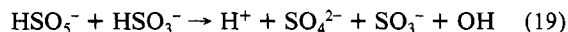
To assess the impact of reaction 18, we measured the rate constant for the reaction of SO₅⁻ with ascorbate at pH 6.8 in the presence of 0.05 and 0.5 M HSO₃⁻ (Figure 1). The ionic strength was adjusted to 0.5 M with NaClO₄. It is apparent that reaction 18 slows the measured rate at 0.5 M HSO₃⁻. In addition, the results in Figure 1 also reveal another effect. In the solution containing 0.05 M HSO₃⁻ and 0.5 M NaClO₄, a line drawn through the three lower ascorbate concentrations extrapolates to predict a higher rate constant than that measured for 5 mM ascorbate. This is because the rate of the reaction of SO₅⁻ with ascorbate, reaction 17, is approaching the rate of the reaction of SO₃⁻ with O₂. This provides an opportunity to derive rate constants for this latter reaction and for reaction 18. This was done by using a solution of 0.05 M HSO₃⁻, 0.5 M NaClO₄, and 5 mM ascorbate, saturated with various N₂O:O₂ mixtures. Rate constants for the appearance of the ascorbate radical were measured and the concentration of oxygen was calculated by using the ratio of oxygen in the gas stream and the solubility of O₂ in a 0.5 M NaCl solution (1.1 mM).³¹ The initial concentration of SO₃⁻ was taken to be 3 μM. Both sets of data were modeled,³² and the best fit was obtained by using the rate constants shown (in M⁻¹ s⁻¹):



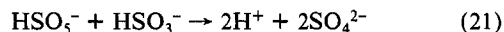
The experimental points and the calculated curve are given in Figure 2.

Possible complications in the above analysis arise from possible impurities introduced with the added sodium perchlorate and from secondary reactions of HSO₅⁻. The lack of any change in the intercept in Figure 1 upon the addition of sodium perchlorate rules out any direct contribution of added impurities to SO₃⁻ loss. We cannot rule out completely some possible catalytic influence of impurity metal ions added with the sodium perchlorate, but the very high rate constant that would be required for the radical-metal ion interaction and the excellent fit to the data using just the above four reactions make such a contribution highly unlikely.

Some secondary reactions of HSO₅⁻ could also contribute to the rate of formation of the ascorbate radical



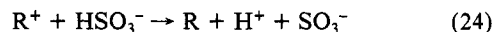
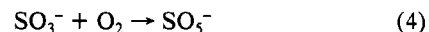
(The alternate paths



would make no contribution.)

The occurrence of reaction 19 or 20 at a rate sufficient to influence the kinetic results requires that the yield of A⁻ increase upon the addition of O₂. Within the variability of the electron pulse (±5%), there was no change in the yield.

Other Reactions of SO₅⁻. We have carried out pulse radiolysis studies of the reactions of SO₅⁻, formed by the reaction of SO₃⁻ with O₂, with several additional compounds. Complications, however, frequently prevented the successful derivation of rate constants. Bubbling O₂ through solutions of some of the compounds resulted in their oxidation. In some cases, the added compound appeared to catalyze the reaction of O₂ with HSO₃⁻, leading to a lower, and unknown, oxygen concentration. Finally, if the redox potential of the compound is between that of SO₃⁻ and SO₅⁻, the following chain reaction is possible:



The net effect is to slow the buildup of R⁺, leading to too low a value of the rate constant. These problems lead to some ambiguity in the results for SO₅⁻ reactions obtained from the pulse radiolysis of bisulfite solutions saturated with N₂O–O₂ mixtures.

A striking example of these difficulties comes from our attempt to study the pulse radiolysis of a solution containing 20 mM NaI and 20 mM NaHSO₃, saturated with a 1:1 mixture of N₂O and O₂. Both SO₃⁻ and I₂⁻ are produced in the initial chemistry after the pulse and SO₃⁻ rapidly forms SO₅⁻. The redox potential of I₂⁻, 1.13 V, is near that expected for SO₅⁻, so the objective of the experiment was to determine if I₂⁻ was produced or consumed subsequent to this initial chemistry. The results showed that I₂⁻ was being lost, but much less rapidly than for an O₂-free solution. This suggests that the redox potential for SO₅⁻ is slightly less than 1.13 V. These experiments were severely complicated by a large decrease in the observed rate of loss of I₂⁻ (from pulse to pulse). The rate became very slow and began to show what appeared to be an induction period. Since the reaction mixture was flowed through the irradiation cell rapidly enough to ensure that only fresh solution is irradiated, this suggested either the iodide or the sulfite or both were being oxidized in the storage vessel.

The pulse radiolysis of a solution containing 0.1 M NaHSO₃ and 1 mM promethazine (*E* = 0.86 V), bubbled either with N₂O or a N₂O–O₂ mixture, was investigated. With no O₂ present there was no production of the promethazine radical. With a 1:1 mixture of N₂O and O₂, the radical was produced with an apparent rate constant of 1.5 × 10⁸ M⁻¹ s⁻¹. The radical buildup curves, however, each had a "foot", almost like an induction period. In addition, the pH of the solution decreased from 3.6 to 3.2 during the experiment (~20 min). This suggests that HSO₅⁻ was being oxidized by O₂ and that the steady-state O₂ concentration was reduced. Computer modeling indicated that a reduction in the O₂ concentration to about 0.1 mM would lead to curves similar to those observed.

For some molecules, however, the system appeared to behave properly. As we reported in a preliminary communication, trolox reacts with SO₅⁻ at pH 9 with a rate constant of 1.2 × 10⁷ M⁻¹ s⁻¹. This is more than 10 times the rate constant for the SO₃⁻ reaction (~10⁶ M⁻¹ s⁻¹). Oxygen sensitivity of trolox precluded measurements at higher pH. The reaction of ascorbic acid with SO₅⁻, also reported previously, was measured up to pH 6.8. Rate constants of 2 × 10⁶ and 1.4 × 10⁸ M⁻¹ for H₂A and HA⁻, respectively, were derived.

(31) Narita, E.; Lawson, F.; Han, K. N. *Hydrometallurgy* **1983**, *10*, 21.

(32) Brown, R. L. *Natl. Bur. Stand., [Tech. Rep.] NBSIR (U.S.) NBSIR-81-2281* 1981.

TABLE II: Summary of Rate Constants

reaction	pH	k , $\text{M}^{-1} \text{s}^{-1}$
$\text{SO}_3^- + \text{ascorbic acid}$	<3	< 10^6
$\text{SO}_3^- + \text{ascorbate ion}$	5–10	9×10^6
$\text{SO}_3^- + \text{ascorbate dianion}$	>12	3×10^8
$\text{SO}_3^- + \text{trolox}$	9	$\sim 10^6$
$\text{SO}_3^- + p\text{-methoxyphenol}$	9.2	4×10^7
$\text{SO}_3^- + p\text{-methoxyphenol}$	11.7	1.0×10^8
$\text{SO}_3^- + p\text{-methoxyphenol}$	12.4	1.2×10^8
$\text{SO}_3^- + \text{phenol}$	11.1	6×10^5
$\text{Ph}\dot{\text{O}} + \text{SO}_3^{2-}$	11.1	1×10^7
$(\text{Promethazine})^+ + \text{HSO}_3^-$	3.6	6×10^5
$(\text{Promethazine})^+ + \text{HSO}_3^-$	5.0	1.6×10^7
$(\text{Promethazine})^+ + \text{HSO}_3^-$	5.5	5.0×10^7
$(\text{Promethazine})^+ + \text{HSO}_3^-$	6.1	1.0×10^8
$(\text{Promethazine})^+ + \text{HSO}_3^-$	6.6	1.2×10^8
$(\text{CIPz})^+ + \text{HSO}_3^-$	3.6	$\sim 5 \times 10^5$
$\text{SO}_3^- + \text{CIPz}$	3.6	$\sim 5 \times 10^6$
$\text{I}_2^- + \text{HSO}_3^- (\text{SO}_3^{2-})$	6.7	6.5×10^7
$\text{SO}_3^- + \text{O}_2$	6.8	1.5×10^9
$\text{SO}_5^- + \text{ascorbic acid}$	<4	2×10^6
$\text{SO}_5^- + \text{ascorbate ion}$	5–10	1.4×10^8
$\text{SO}_5^- + \text{HSO}_3^-$	6.8	3×10^6
$\text{SO}_5^- + \text{trolox}$	9	1.2×10^7
$\text{SO}_5^- + p\text{-methoxyphenol}$	6.7	$\sim 5 \times 10^5$
$\text{SO}_5^- + p\text{-methoxyphenol}$	9.2	5.5×10^7
$\text{SO}_5^- + p\text{-methoxyphenol}$	11.7	1.3×10^8

Rate constants for the reaction of SO_5^- with p -methoxyphenol were measured at pH 6.7, 9.2, and 11.1. Values of $\sim 5 \times 10^5$, 5.5×10^7 , and $1.3 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$ were derived, only slightly greater than those measured for the SO_3^- reaction. For phenol, at pH 11.1, a rate constant of $\sim 8 \times 10^4 \text{ M}^{-1} \text{s}^{-1}$ for SO_5^- was measured. In both these systems, loss of O_2 and the phenolic reactant could have been important.

Conclusion

The rate constants measured in this work are summarized in Table II, along with the results reported earlier.²² Although the rate measurements allow an approximate calculation of the SO_3^- oxidation potential, a more reliable value is derived from the equilibrium measurement for the SO_3^- -chlorpromazine reaction. At pH 3.6, this value is 0.84 V. The potential at any other pH can be calculated from

$$E = E_0 + 0.059 \log \frac{K_1 K_2 + K_1 [\text{H}^+] + [\text{H}^+]^2}{K_r + [\text{H}^+]}$$

where K_1 and K_2 are the dissociation constants for H_2SO_3 (1.39×10^{-2})³³ and HSO_3^- (6.3×10^{-8}),¹⁴ respectively, K_r the dissociation constant for HSO_3 , and E_0 the potential at pH 0. K_r is unknown, but the absence of any change in the ESR spectrum¹³ over the pH range 2.2–12.5 suggests it is larger than 10^{-2} . Therefore, the above equation predicts that in the pH 2–7 range the potential will change by 59 mV for every unit of pH change and above the pK_a of HSO_3^- (7.2) the potential will remain unchanged at 0.63 V. This is in agreement with the upper limit of 0.89 V proposed in a study of the reaction of sulfite with copper(III) tetraglycine.³⁴

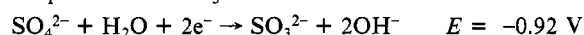
Using this value of 0.63 V for the sulfite radical-sulfite ion couple and the potential difference between the sulfite radical and the phenoxyl radical of 0.072 V, we can now calculate a redox potential of $E = 0.70 \text{ V}$ for the phenoxyl radical-phenoxide ion couple at pH 11.1 and $E = 0.90 \text{ V}$ at pH 7. Previously, only a

lower limit of 0.60 V for this couple was estimated.²⁸

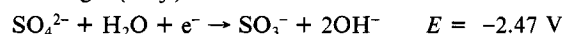
Although the experimental approach taken precluded the measurement of an equilibrium constant for a SO_5^- reaction, the rate measurements do provide some information on its redox potential. First, the experiments with I_2^- suggest the potential of SO_5^- is close to 1.1 V at pH 6.7. In the pH range 3.2–3.6, the experiments with promethazine suggest the potential is greater than 0.86 V. The kinetic results for SO_5^- reacting with ascorbate also support a redox potential in this range.

Like HSO_3 , HSO_5 is probably a strong acid with a pK of less than 2. The first dissociation constant for H_2SO_5 is large^{35,36} ($\text{pK} < 2$), and the second pK has been reported to be 9.88 at 15°C .³⁶ Taking the value of the SO_5^- redox potential at pH 6.7 to be 1.1, the potential will increase to 1.4 at pH 2 and stay at about 0.9 above pH 10.

Knowing the redox potential for the reduction of SO_3^- allows us to calculate its oxidation potential from the known two-electron redox potential for SO_3^{2-} :



Subtracting $E(\text{SO}_3^-) = 0.63$ from twice this value leads to



This suggests that SO_3^- can act as both a mild oxidant or a strong reductant. It may be difficult to demonstrate the reducing power of SO_3^- since many oxidants will react with sulfite ions thermally before the SO_3^- radicals are produced in the radiolysis. Moreover, SO_3^- may react by addition rather than reduction, as it does with O_2 .

The observations reported in this paper on the reactivity of SO_3^- and the formation and reactivity of SO_5^- are important for understanding the biological consequences of S(IV) , which can enter the body by inhalation of atmospheric SO_2 , the ingestion of bisulfite food preservatives, or the breakdown of sulfur-containing compounds like methionine. It has been known for some time that the reactive intermediates formed during the oxidations of bisulfite bring about the destruction of amino acids,³⁷ the breakdown of DNA,³⁸ lipid oxidation,³⁹ and the inactivation of papain.⁴⁰ This could be accomplished directly by the oxidation of these compounds by SO_3^- or SO_5^- , or indirectly by reaction of HSO_5^- (formed from the one-electron reduction of SO_5^-). In addition to being a powerful oxidant [$E(\text{HSO}_5^-/\text{HSO}_4^-) = 1.82 \text{ V}$],⁴¹ peroxymonosulfate can react with unsaturated organics in the presence of ketones to produce epoxides⁴² and directly with primary amines to produce nitroso compounds.⁴³ In the oxidation of Na_2SO_3 solution, the production of an oxidant with the properties of HSO_5^- has been reported with a yield of up to 30%.⁴⁴

Acknowledgment. The research described herein was supported in part by the Office of Basic Energy Sciences of the U.S. Department of Energy.

Registry No. CIPz, 50-53-3; CIPz⁺, 34468-21-8; Pz⁺, 38878-40-9; O_2 , 7782-44-7; $\text{Ph}\dot{\text{O}}$, 2122-46-5; SO_3^{2-} , 14265-45-3; HSO_3^- , 15181-46-1; I_2^- , 12190-71-5; SO_3^- , 12210-38-7; SO_5^- , 12509-93-2; ascorbic acid, 50-81-7; ascorbate ion, 299-36-5; ascorbate dianion, 63983-50-6; trolox, 56305-04-5; p -methoxyphenol, 150-76-5; phenol, 108-95-2.

(35) Spiro, M. *Electrochim. Acta* **1979**, *24*, 313.

(36) Kyrki, J. *Ann. Univ. Turku., Ser. A* **1963**, *61*.

(37) Yang, S. F. *Environ. Res.* **1973**, *6*, 395.

(38) Hayatsu, H.; Miller, R. C. *Biochem. Biophys. Res. Commun.* **1972**, *46*, 120.

(39) Kaplan, D.; McJilton, C.; Lucht, D. *Arch. Environ. Health* **1975**, *30*, 507.

(40) Fujimoto, S.; Nakagawa, T.; Ishimitsu, S.; Ohara, A. *Chem. Pharm. Bull.* **1983**, *31*, 992.

(41) Steele, W. V.; Appelman, E. H., Jr. *J. Chem. Thermodyn.* **1982**, *14*, 337.

(42) Edwards, J. O.; Pater, R. H.; Curci, R.; DiFuria, F. *Photochem. Photobiol.* **1979**, *30*, 63.

(43) March, J. "Advanced Organic Chemistry"; McGraw-Hill: New York, 1977; p 1109.

(44) Deuvyst, E. A. P.; Ettel, V. A.; Mosolu, M. A. *CHEMTECH* **1979**, *426*.

(33) Huss, A.; Eckert, A. *J. Phys. Chem.* **1977**, *81*, 7268.

(34) Anast, J. M.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 2319.