$SO_2(^1A_2)$: 800, 300,[50] and 600 cm^{-1} (estimated as in ref 51).
$SO_2(^3A_2)$: 800, 300, and 600 cm^{-1}, transferred from the $^1A_2$ state.
$SO_2(^3B_2)$: the frequencies for this electronic state were taken to be similar to those corresponding to the asymmetric $^1B_2$ state (960, 377, and 211 cm^{-1}.[52]
SO: 1148.2 cm^{-1}.[53]

The following values were used for the rotational constants:
$SO_2(^1A_1)$: A = 2.0274, B = 0.3442, and C = 0.2935 cm^{-1}.[54]
$SO_2(^1A_2)$: the values A = 1.0660, B = 0.3892, and C = 0.2851 cm^{-1} were calculated with the structural parameters of ref 41.
$SO_2(^3A_2)$: A = 0.9978, B = 0.3909, and C = 0.2809 cm^{-1}, calculated with the molecular parameters given in ref 45.
$SO_2(^3B_2)$: A = 1.1579, B = 0.3422, and C = 0.2641 cm^{-1}, calculated with the molecular parameters given in ref 52.
SO: B = 0.72082 cm^{-1}.[53]

The bond energy at 0 K for the ground state of SO_2 was calculated from the enthalpies of formation of SO,[53] O,[53] and SO_2:[49] $\Delta H°_0$ = 130.5 kcal mol^{-1}. The excitation energies of the electronically excited states used are $T_0(^1A_2)$ = 79.9 kcal mol^{-1} [41] and $T_0(^3A_2) = T_0(^3B_2)$ = 75.2 kcal mol^{-1}.[44,45] For the ground electronic state the Morse parameter β = 2.4 Å^{-1} was calculated with the force constant of the dissociating bond, f_{RC}, = 10.34 mdyn Å^{-1}.[55] Similar β values were used for the electronically excited states (see text).

The same Lennard-Jones parameters σ = 4.1 Å and ϵ/k = 328.5k[56] were employed for all electronic states of SO_2. For the bath gases, the Lennard-Jones parameters given in ref 48 were used, and the corresponding collision frequencies were calculated by means of reduced collision integrals.[48,57]

Registry No. SO_2, 7446-09-5; SO, 13827-32-2; O, 17778-80-2; He, 7440-59-7; Ne, 7440-01-9; Ar, 7440-37-1; Kr, 7439-90-9; Xe, 7440-63-3; H_2, 1333-74-0; D_2, 7782-39-0; N_2, 7727-37-9; CO_2, 124-38-9; CH_4, 74-82-8; CF_4, 75-73-0; SF_6, 2551-62-4; C_3F_8, 76-19-7.

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One-Electron Redox Reactions Involving Sulfite Ions and Aromatic Amines

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The one-electron oxidation of aromatic amines by the $\dot{S}O_3^-$ radical and of sulfite and bisulfite ions by aromatic amine radical cations has been investigated. *p*-Phenylenediamine (PDA) and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) were oxidized by $\dot{S}O_3^-$ with rate constants of 5.0 × 10^7 and 5.2 × 10^8 M^{-1} s^{-1}, respectively, in basic solutions. Protonation of the amine reduced the rates considerably (k = 4.2 × 10^6 M^{-1} s^{-1} for PDA at pH 5.25; k = 8.2 × 10^6 M^{-1} s^{-1} for TMPD at pH 4.5). With aniline and *N,N*-dimethylaniline (DMA), the reverse reaction was observed. DMA^+ radical reacted with SO_3^{2-} with k = 9.9 × 10^8 M^{-1} s^{-1} and with HSO_3^- with k < 5 × 10^5 M^{-1} s^{-1}. Aniline radical cation also oxidized SO_3^{2-} rapidly (k = 4 × 10^9 M^{-1} s^{-1}) and HSO_3^- less rapidly (k = 4.8 × 10^6 M^{-1} s^{-1}). The aniline neutral radical reacted too slowly to be measured with either. A secondary product was observed in acid solution of TMPD with an absorption maximum at 455 nm. This was ascribed to a reaction between the $\dot{S}O_3^-$ and $TMPD^{+\cdot}$ radicals.

In earlier publications from this laboratory, we have reported rate constants for the reactions of sulfite radicals and peroxysulfate radicals produced by the pulse radiolysis of aqueous sulfite and sulfite/oxygen solutions.[1,2] In addition, some rate constants for the oxidation of sulfite and bisulfite by free radicals were reported. We have now extended this work to reactions involving aromatic amines.

The oxidation of aromatic amines by radicals produced by pulse radiolysis in water has been reported.[3-5] The hydroxyl radical adds to the aromatic ring, and the adduct, in a few microseconds, dissociates to give the radical cation.[3,4] The sulfate radical, $SO_4^{-\cdot}$, reacts by direct electron transfer to give the radical cation. Hexacyanoferrate(III) has been used to oxidize many aromatic amines to their cation radicals.[6] Equilibrium constants have been derived for the radical formation from several aromatic diamines and diimines which, coupled with the two-electron redox potential, give one-electron potentials for the diamines.[7] These potentials have been found to correlate with the rate of photographic development of silver halides by several *p*-phenylenediamines in the presence of sulfite.[8]

This study has been prompted also by a desire to understand the autoxidation of SO_2 in aqueous solution, including the effects of added organic compounds and the possible chemical transformation of these organic compounds during autoxidation. $\dot{S}O_3^-$ and $SO_5^{-\cdot}$ are key radicals in the autoxidation of SO_2, and their chemistry must be understood before SO_2 autoxidation is understood.

In this paper we report rate constants for the oxidation of aromatic amines by $\dot{S}O_3^-$ and $SO_5^{-\cdot}$, rate constants for the oxidation of sulfite and bisulfite by aromatic amine radicals, and evidence for a reaction between the sulfite radical and an amine radical cation. In addition, the reaction of NH_2 with sulfite has

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been investigated and rate constants have been measured for the reactions of Br_2^- and I_2^- with SO_3^{2-} and HSO_3^-.

Experimental Section[9]

Sodium sulfite and bisulfite were analytical grade reagents from Fisher and Mallinckrodt, respectively. The amount of S(IV) in the sodium bisulfite was determined by dissolving a sample in 6 M $HClO_4$ and measuring the absorbance at 280 nm. An SO_2 absorptivity $\epsilon_{280} = 367$ M^{-1} cm^{-1} was used.[10] Sodium iodide was from Baker & Adamson, potassium bromide from Fisher, and ammonium hydroxide from Mallinckrodt, all reagent grade. Aniline (AH) was from J. T. Baker, *N*,*N*-dimethylaniline (DMA) and diphenylamine (DPA) were both from Aldrich, *p*-phenylenediamine (PDA) was from Fisher or as the dihydrochloride from J. T. Baker, and two samples of *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine dihydrochloride (TMPD) were from Fisher and Eastman. Water was purified by a Millipore Milli-Q system, and solutions were freshly prepared each day. The pH was adjusted where necessary by using potassium or sodium hydroxide and perchloric acid or was maintained by using phosphate or borate buffers. Solutions were bubbled to saturation with N_2O or a 1:1 N_2O–O_2 mixture and flowed 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 apparatus[11] 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 procesed by a PDP 11/34 minicomputer. First-order rate constants were derived by using a linear least-squares routine. Single-shot transient spectra were obtained by use of a EG&G PAR optical multichannel analyzer with a silicon photodiode array coupled to a Jarrell-Ash Mark X spectrograph.

Results and Discussion

Radiolysis of N_2O-saturated aqueous solutions at pH 3–13 produces the hydroxyl radical predominantly. This radical reacts with sulfite or bisulfite ions to form the sulfite radical very rapidly

$$OH + SO_3^{2-} \rightarrow OH^- + \dot{S}O_3^- \quad (1)$$

$$OH + HSO_3^- \rightarrow H_2O + \dot{S}O_3^- \quad (2)$$

$k_1 = 5.5 \times 10^9$ and $k_2 = 9.5 \times 10^9$ M^{-1} s^{-1}.[12] The hydroxyl radical reacts also with aromatic amines with diffusion-controlled rate constants ($k \sim 10^{10}$ M^{-1} s^{-1})[3] to form initially OH adducts which rapidly lose water or OH^- and yield predominantly the phenylaminyl or the cation radical, e.g.

$$OH + C_6H_5NH_2 \rightarrow HO\text{–}\dot{C}_6H_5NH_2 \rightarrow C_6H_5\dot{N}H + H_2O \quad (3)$$

$$OH + C_6H_5N(CH_3)_2 \rightarrow HO\text{–}\dot{C}_6H_5N(CH_3)_2 \rightarrow C_6H_5\dot{N}^+(CH_3)_2 + OH^- \quad (4)$$

These latter reactions compete effectively with reactions 1 and 2, and therefore, the concentrations of sulfite and of the aromatic amines have to be adjusted in order to favor the desired reaction. The hydrogen atoms, produced in small yield (~10% of OH yield) during the radiolysis, do not interfere in these systems since they do not react with sulfite and their reaction with the aromatic amines yields H adducts that absorb at different wavelengths than the cation or the neutral radicals.

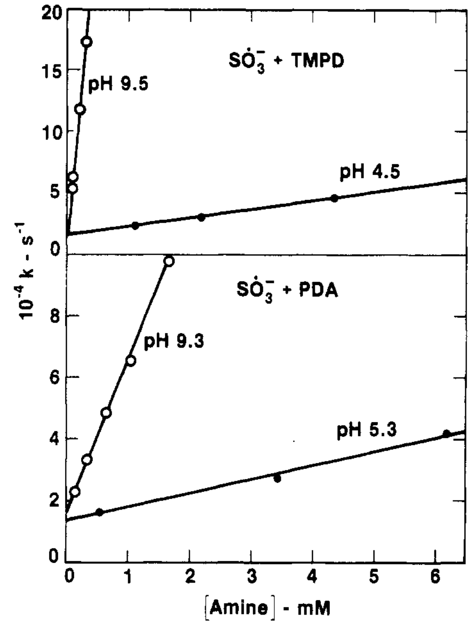

Figure 1. Concentration dependence of the first-order rate constant for reactions of $\dot{S}O_3^-$ with aromatic amines.

TABLE I: Rate Constants for Redox Reactions Involving Sulfite and Aromatic Amines

reaction	pH	k, M^{-1} s^{-1}
$\dot{S}O_3^-$ + TMPD	9.5	$(5.2 \pm 0.6) \times 10^8$
↓↑ pK_a = 6.5		
$\dot{S}O_3^-$ + $TMPDH^+$	4.5	$(8.2 \pm 1.0) \times 10^6$
$\dot{S}O_3^-$ + PDA	9.3	$(5.0 \pm 0.6) \times 10^7$
↓↑ pK_a = 6.1		
$\dot{S}O_3^-$ + $PDAH^+$	5.25	$(4.2 \pm 0.6) \times 10^6$
↓↑ pK_a = 3.3		
$\dot{S}O_3^-$ + $PDAH_2^{2+}$	3.4	$<5 \times 10^5$
$\dot{S}O_3^-$ + DPA	3–7	$<1 \times 10^7$
$SO_5^{-}\cdot$ + DPA	3	$(5 \pm 1) \times 10^7$
$SO_5^{-}\cdot$ + DPA	7	$<1 \times 10^7$
$DMA^{+}\cdot$ + SO_3^{2-}	10.9	$(9.9 \pm 1.0) \times 10^8$
↓↑ pK_a = 7.2	6.8	$(2.0 \pm 0.3) \times 10^8$
$DMA^{+}\cdot$ + HSO_3^-	3.6	$<8 \times 10^5$
$SO_5^{-}\cdot$ + $DMAH^+$	3.6	$(1 \pm 0.2) \times 10^7$
A· + SO_3^{2-}	13	$\sim 0^a$
↓↑ pK_a = 7.2		
A· + HSO_3^-	*a*	~0
↓↑ pK_a = 6.2[a]		
$AH^{+}\cdot$ + SO_3^{2-}	*a*	4×10^9
↓↑ pK_a = 7.2		
$AH^{+}\cdot$ + HSO_3^-	2.5	$(4.8 \pm 0.7) \times 10^6$
$\dot{S}O_3^-$ + AH	13	$<10^6$
$SO_5^{-}\cdot$ + AH	13	$\sim 3 \times 10^6$
$NH_2\cdot$ + SO_3^{2-}	11.5	*a*

[a] See text.

In certain experiments, OH radicals were allowed to react with excess Br^- to form $Br_2^-\cdot$ radicals, which subsequently oxidized either sulfite or the aromatic amine, depending on their relative concentrations.

N,*N*,*N'*,*N'*-*Tetramethyl-p-phenylenediamine* (*TMPD*). This compound was found to be easily oxidized by $\dot{S}O_3^-$ to form the cation radical $TMPD^{+}\cdot$ characterized by its absorption at 560 and 610 nm. The rate constant for oxidation of TMPD (in its basic form) at pH 9.5 was measured to be $(5.2 \pm 0.6) \times 10^8$ M^{-1} s^{-1} (Figure 1 and Table I), which is among the highest rate constants observed for oxidation by sulfite. On the other hand, the reaction becomes very slow in acid solution due to protonation of TMPD (pK_a = 2.2 and 6.35).[13] The value of 8.2×10^6 M^{-1} s^{-1} measured

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(9) Certain commercial equipment, instruments, or materials are identified in this paper in order to specify adequately the experimental procedure. Such identification does not imply recognition 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.

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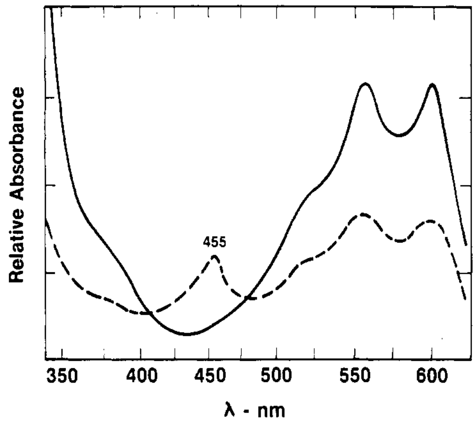

Figure 2. Transient spectra for (solid line) $TMPD^+$ from the reaction Br_2^- with TMPD at pH 3.2 and (dotted line) the products from the reaction of $\dot{S}O_3^-$ with TMPD at pH 4.7: spectra taken at 200 μs after the pulse; dose, 1800 rd; [TMPD] = 0.9 mM; [KBr] = 0.1 M; [$NaHSO_3$] = 0.1 M.

at pH 4.5 is ascribable for the most part to the reactivity of the ~1% basic form present at this pH, indicating that $TMPDH^+$ is at least 100 times less reactive than TMPD. The rate constant decreases further as the pH is lowered and the fully protonated form, $TMPDH_2^{2+}$, is expected to be unreactive toward $\dot{S}O_3^-$. These changes in rate constant result from the changes in the redox potential of TMPD upon protonation.

As the pH of the TMPD solution is lowered below 6, the oxidation of this compound by $\dot{S}O_3^-$ becomes slower and less quantitative as well, i.e. the main absorptions at 560 and 610 nm also decrease. a competing process sets in which results in the formation of an absorption peak at 455 nm (Figure 2). This absorption increases as the pH is lowered. The kinetics of formation of the two absorptions, however, are different; that at 455 nm builds up more slowly and exhibits an induction period (a "foot" in the formation curve). Variations in the dose, i.e. in the initial radical concentration, had little effect on the rate of formation of the 560- and 610-nm absorptions but increased the rate of the 455-nm peak in a manner that indicates a radical–radical reaction. We suggest, therefore, that since at low pH the reactivity of $\dot{S}O_3^-$ toward protonated TMPD is low, this reaction occurs only to a partial extent and after a certain amount of $TMPD^{+}\cdot$ radicals are formed the reaction of these radicals with $\dot{S}O_3^-$ becomes predominant.

$$\dot{S}O_3^- + TMPDH^+ \rightarrow HSO_3^- + TMPD^{+}\cdot \qquad (5)$$

$$\dot{S}O_3^- + TMPD^{+}\cdot \rightarrow \text{product} \qquad (6)$$

Reaction 6 does not appear to result in the reduction or oxidation of $TMPD^{+}\cdot$ since both of the products expected from these processes do not absorb at 455 nm. We speculate, therefore, that the reaction involves addition of $\dot{S}O_3^-$ either on a ring carbon or on a nitrogen. The latter may be more likely since the product may exhibit a charge transfer band corresponding to the observed peak. In order to investigate whether the 455-nm absorption is specific to the sulfite system, we have attempted to observe it in acid solutions in which Br_2^- is used as the oxidant. In this case, however, since Br_2^- oxidizes TMPD rapidly both in its basic and protonated forms, it was not possible to observe any radical–radical $Br_2^-\cdot$ + $TMPD^{+}\cdot$ reaction.

The reaction of the TMPD radical cation with SO_2 has been investigated recently by bubbling SO_2 through an acetonitrile solution of the radical.[14] The rate of reduction of the $TMPD^{+}\cdot$ was found to be second order in $TMPD^{+}\cdot$ and also was observed to increase linearly with increasing water concentration. We also have investigated this reaction, briefly, using pure water. Oxygen was bubbled through a solution containing 0.5 mM TMPD, giving a blue solution with absorption maxima at 560 and 610 nm. The oxygen was bubbled out with nitrogen and the solution mixed with a sodium bisulfite solution (concentration after mixing 7.5 mM HSO_3^-, pH 3.6). The absorption at 610 nm was followed with a Varian/Cary Model 219 spectrophotometer. The signal decreased at a rate second order in the intensity, and the expression $2k/\epsilon = 7 \times 10^{-3}$ s^{-1} was derived. Assuming the reaction is first order in HSO_3^-, as observed by Koschechko et al.,[14] and using $\epsilon = 8.2 \times 10^3$ for the absorptivity,[3] we derived the third-order rate constant $k = 4 \times 10^3$ M^{-2} s^{-1}.

The observed kinetic behavior could be due to one of several possible mechanisms. Koschechko et al.[14] suggested the reaction involved complex formation between the radical ion and SO_2(aq), with a subsequent reaction with another $TMPD^+$ leading to SO_4^{2-}. We suggest, however, that the reaction involves the production and subsequent reactions of $\dot{S}O_3^-$.

$$TMPD^{+}\cdot + SO_3^{2-} \rightleftarrows TMPD + \dot{S}O_3^- \qquad (7)$$

Our pulse radiolysis results show that this electron transfer would be fast with equilibrium far to the left. The small equilibrium amount of $\dot{S}O_3^-$ could undergo self-reaction

$$\dot{S}O_3^- + \dot{S}O_3^- \rightarrow S_2O_6^{2-} \qquad (8a)$$

$$\rightarrow SO_3 + SO_3^{2-} \qquad (8b)$$

or react with $TMPD^+$

$$\dot{S}O_3^- + TMPD^+ \rightarrow SO_3{\cdot}TMPD \qquad (9)$$

$$SO_3{\cdot}TMPD \rightarrow SO_3 + TMPD \qquad (10)$$

This $SO_3{\cdot}TMPD$ adduct could be the radical–radical product we observed at 455 nm in pulse radiolysis experiments.

p-Phenylenediamine (*PDA*). This compound was found to be oxidized by $\dot{S}O_3^-$ more slowly than TMPD, as expected from its higher redox potential. The rate constant for the basic form is only 5.0×10^7 M^{-1} s^{-1} (Figure 1 and Table I). The observed rate constant at pH 5.25 (4.2×10^6 M^{-1} s^{-1}) can be ascribed completely to the reaction of the basic form present at this pH. In fact, the rate decreases further upon lowering the pH and it appears that both $PDAH^+$ and $PDAH_2^{2+}$ are not oxidized by $\dot{S}O_3^-$. At pH 5.2 we attempted to measure an equilibrium constant for

$$\dot{S}O_3^- + PDA \rightleftarrows SO_3^{2-} + PDA^{+}\cdot \qquad (11)$$

We find that even at this pH the equilibrium is still driven to the right. Although we were unable to establish equlibrium, we estimate that the equilibrium constant at this pH is greater than 250; therefore $E(\dot{S}O_3^-/SO_3^{2-}) - E(PDA^{+}\cdot/PDA) > 0.14$ V. Since $E(\dot{S}O_3^-/SO_3^{2-})$ is 0.74 at pH 5.2,[2] $E(PDA^{+}\cdot/PDA) < 0.6$ V. This value would appear to disagree with $E = 0.7$ V at pH 7, derived from an extrapolation from measurement at pH 13.5.[5] That extrapolation assumes that the radical does not protonate above pH 7. The present result for pH 5.2 and the previous result from pH 13.5 would be consistent if the PDA radical cation has a pK_a ~ 9. This value is reasonable in view of pK_a ~ 7 for the aniline radical and the higher pK_a of the PDA molecule compared to that of aniline.

The spectrum monitored upon reaction of $\dot{S}O_3^-$ with PDA in basic solution (Figure 3) exhibits maxima at 460–490 nm and is in agreement with the reported spectrum for the radical produced by other reactions.[3] The absorption decreases at lower pH as was the case with TMPD, and the kinetic traces indicate a contribution from a radical–radical reaction ($\dot{S}O_3^-$ + PDA·) at pH 3.4, but no new absorption was found under these conditions to confirm this process. It is possible that the reactions occurring in these solutions are similar to those taking place in TMPD solutions, but because the main radical absorption is at lower wavelengths with PDA, the product of the $\dot{S}O_3^-$ + PDA· reaction is masked by this absorption (unlike the case of TMPD where they are well separated).

Diphenylamine (*DPA*). The limited solubility in water of this amine limited the concentration range over which its oxidation could be studied. This results in the rather high upper limit given in Table I for its reaction with $\dot{S}O_3^-$ ($k < 10^7$ M^{-1} s^{-1}). At pH

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[14] Koschechko, V. G.; Titov, V. E.; Pokhodenko, V. D. *React. Kinet. Catal. Lett.* **1984**, *24*, 31.

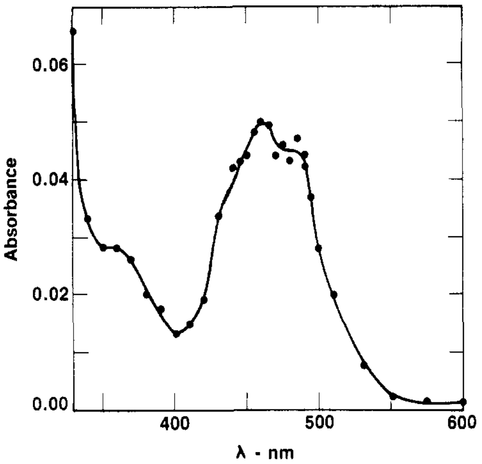

Figure 3. Transient spectra for PDA^+ from the reaction of $\dot{S}O_3^-$ with PDA. The spectra were taken point by point from the maximum value of the absorption at each wavelength. [PDA] = 0.9 mM; $[Na_2SO_3]$ = 0.1 M; dose 500 rd.

3, $SO_5^-\cdot$, which has a higher reduction potential than $\dot{S}O_3^-$, reacted with DPA with a rate constant of $k = 5 \times 10^7$ M^{-1} s^{-1}. At pH 7, the rate constant for this reaction was too slow to measure, probably due to the decrease in the redox potential of $SO_5^-\cdot$ as the pH is increased.[2]

N,N-Dimethylaniline (*DMA*). DMA and aniline are expected to have higher redox potentials than the preceding amines—higher, also, than the sulfite radical. Indeed, no oxidation of these amines by $\dot{S}O_3^-$ could be detected. Therefore, the oxidation of sulfite by the amine cation radical was investigated

$$DMA^{+}\cdot + SO_3^{2-} \rightarrow DMA + \dot{S}O_3^- \qquad (12)$$

The cation radical $DMA^{+}\cdot$ was produced by reaction of DMA with either OH or Br_2^-. Addition of sulfite to the solution increases the decay rate of $DMA^{+}\cdot$, and the first-order rates were linearly dependent on $[SO_3^{2-}]$. From such plots $k_{12} = 9.9 \times 10^8$ M^{-1} s^{-1} (Table I) was derived. This rate constant was also found to be pH dependent. The results at lower pH values (Table I), in fact, indicate that $DMA^{+}\cdot$ does not oxidize HSO_3^-. The upper limit of $k < 8 \times 10^5$ M^{-1} s^{-1} measured at pH 3.6 can be completely ascribed to reaction of $DMA^{+}\cdot$ with the SO_3^{2-} present at this pH.

We also attempted to measure the equilibrium constant for reaction 12 at pH 10. At $[DMA]/[SO_3^{2-}] \sim 100$, an obvious equilibrium was obtained. The subsequent decay of the radicals (due to $\dot{S}O_3^- + \dot{S}O_3^-$ and, possibly, $\dot{S}O_3^- + DMA^+$) made it impossible to derive an accurate value for the equilibrium constant. An approximate value of $K_{12} = 240$ was derived, leading to $E(DMA^+/DMA) - E(SO_3^-/SO_3^{2-}) \approx 0.14$ V. Therefore, $E(DMA^+/DMA) \approx 0.77$ V at pH 10.

In the presence of O_2, we monitored the oxidation of DMA by $SO_5^-\cdot$, $k = 1 \times 10^7$ M^{-1} s^{-1} at pH 3.6. Thus, DMA is an example of a compound which can catalyze the oxidation of sulfite by O_2 through reaction 12 followed by reactions

$$\dot{S}O_3^- + O_2 \rightarrow SO_5^-\cdot \qquad (13)$$

and

$$SO_5^-\cdot + DMA \rightarrow SO_5^{2-} + DMA^{+}\cdot \qquad (14)$$

This type of catalysis has been discussed before,[2] and it requires that the reduction potential of the compound falls between those for $SO_5^-\cdot$ and $\dot{S}O_3^-$.

Aniline (*AH*). Aniline is expected to have a higher redox potential than DMA, and therefore, its cation radical is expected to oxidize sulfite more rapidly than does $DMA^{+}\cdot$. The cation radical of aniline, $AH^{+}\cdot$, however, exists only in acid solutions, while in basic solution it deprotonates to the neutral radical.

$$AH^{+}\cdot \rightleftarrows A\cdot + H^+ \qquad (15)$$

Experiments at pH 11–13 indicate that the oxidation reaction $A\cdot + SO_3^{2-}$ does not take place with a measurable rate constant ($k < 10^4$ M^{-1} s^{-1}). In the acid range we observe the oxidation of bisulfite

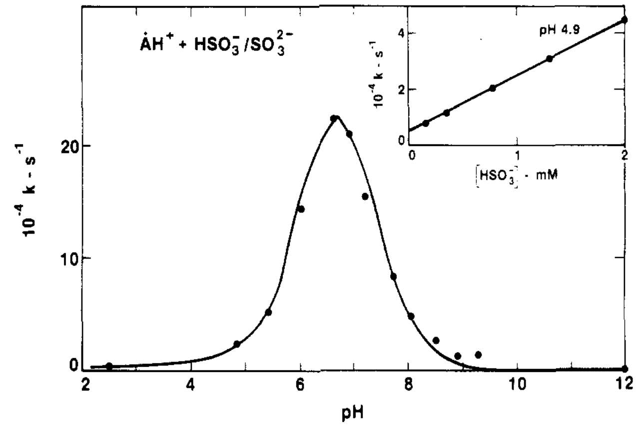

Figure 4. First-order rate constant for the reaction of the aniline radical cation with SO_3^{2-}/HSO_3^-. [aniline] = 5.5 mM; [S(IV)] = 1.0 mM. Insert: dependence of first-order rate constant on $[HSO_3^-]$ at pH 4.9.

$$AH^{+}\cdot + HSO_3^- \rightarrow AH_2^+ + \dot{S}O_3^- \qquad (16)$$

with $k_{16} = 4.8 \times 10^6$ M^{-1} s^{-1}. Direct monitoring of the reaction

$$AH^{+}\cdot + SO_3^{2-} \rightarrow AH + \dot{S}O_3^- \qquad (17)$$

is not possible because of the overlapping pK_a values for $AH^{+}\cdot/A\cdot$ and HSO_3^-/SO_3^{2-} ($pK_a = \sim 7.2$),[15] and in fact, the pH dependence of the rate constant (Figure 4) shows a maximum at pH ~6.7. In order to fit the data in Figure 4, we assume that oxidation takes place only by $AH^{+}\cdot$ and not by $A\cdot$. Oxidation of SO_3^{2-} by $A\cdot$ was shown to be unobservable, and therefore, oxidation of HSO_3^- by $A\cdot$ can also be assumed to be negligible (since HSO_3^- is usually oxidized more slowly than SO_3^{2-}; see below). This leads to the following equation for the observed first-order rate constant

$$k_{obsd} = \left(1 + \frac{K_{AH}}{[H^+]}\right)^{-1}\left(\frac{k_{16}S_T}{1 + K_s/[H^+]} + \frac{k_{17}S_T}{1 + [H^+]/K_s}\right) \qquad (18)$$

where S_T is the total S(IV) concentration, K_s the SO_3^{2-}/HSO_3^- equilibrium constant, and K_{AH} and the $AH^+/A\cdot$ equilibrium constant. We get the best fit with the experimental data if we assume $k_{17} = 4.0 \times 10^9$ M^{-1} s^{-1} and $pK_a(AH^{+}\cdot/A\cdot) = 6.2$. The finding that k_{17} is higher than k_{12} is in agreement with the higher redox potential of aniline. The pK_a of 6.2 derived from these data (with $pK_S = 7.2$) is lower than that determined from plots of absorbance vs. pH ($pK_a = 7.0$)[16] or from the rate of reaction of $AH^{+}\cdot$ with ClO_2^- vs. pH (to be published).

Oxidation of aniline by $SO_5^-\cdot$, if it occurs, may be observable at high pH, where $A\cdot$ does not react with sulfite rapidly. Experiments at pH 13 with 0.1–0.2 M SO_3^{2-} and 10–40 mM aniline in the presence of $N_2O:O_2$ = 1:1 gave indication for the occurrence of the reaction

$$SO_5^-\cdot + AH \rightarrow HSO_5^- + A\cdot \qquad (19)$$

with $k_{19} \sim 3 \times 10^6$ M^{-1} s^{-1}. This value is much lower than those found for the other amines.

$NH_2\cdot$. We have attempted to oxidize sulfite with the aminyl radical, NH_2, produced by the reaction of OH with NH_3 at pH 11.5.[17] We found no evidence for sulfite oxidation. We note that the rate constants for oxidation of several compounds by the radicals $\dot{S}O_3^-$ or $NH_2\cdot$ are practically identical, suggesting that these two radicals have very similar redox potentials, assuming

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TABLE II: Rate Constants for Oxidation of Sulfite and Bisulfite Ions by Radicals

reaction	pH	k, $M^{-1}\ s^{-1}$
$I_2^- + SO_3^{2-}$	11	$(1.9 \pm 0.3) \times 10^8$
	6.7	$(1.0 \pm 0.2) \times 10^7$
$I_2^- + HSO_3^-$	3	$(1.1 \pm 0.2) \times 10^6$
$Br_2^- + SO_3^{2-}$	10	$(2.6 \pm 0.3) \times 10^8$
$Br_2^- + HSO_3^-$	4.2	$(6.9 \pm 0.9) \times 10^7$
$OH\cdot + SO_3^{2-}$		5.5×10^9 [a]
$OH\cdot + HSO_3^-$		9.5×10^9 [a]
$(\text{promethazine})^{+}\cdot + SO_3^{2-}/HSO_3^-$	6.6	1.2×10^8 [b]
$(\text{promethazine})^{+}\cdot + HSO_3^-$	3.6	6×10^5 [b]

[a] Reference 12. [b] Reference 2.

these reactions are only outer-sphere electron transfer.

Summary and Conclusion

The aromatic amines studied in the present work span a wide range of one-electron reduction potentials, from 0.27 V[5] for TMPD to around 1 V (vs. NHE) for aniline. The reduction potential for $\dot{S}O_3^-$ falls roughly in the middle of this range and that for $SO_5^-\cdot$ near the upper limit.[2] Therefore, while $\dot{S}O_3^-$ oxidizes TMPD and PDA, SO_3^{2-} is oxidized by $DMA^+\cdot$ and $AH^+\cdot$, and the rate constants for both types of processes vary with redox potentials. Oxidation of the aromatic amines becomes more difficult as the molecules are protonated while oxidation by the aromatic amine radicals is more favorable when these are protonated or in a cation-radical form. These trends would be expected to reflect the pH effect on redox potentials.

Attempts to measure redox potentials for the aromatic amines by establishing equilibria with the $\dot{S}O_3^-/SO_3^{2-}$ couple were usually thwarted by the slowness of the electron transfer relative to the radical decay processes. For the $PDA^+\cdot/PDA$ couple we were able to derive an upper limit on the redox potential (<0.6 V at pH 5.2), and for the $DMA^+\cdot/DMA$ couple we derived an approximate value (0.77 V at pH 10). From the fact that aniline is not oxidized by $\dot{S}O_3^-$ but is oxidized slowly by $SO_5^-\cdot$ at high pH, we can estimate that the reduction potential for the couple $AH/A\cdot$ is around 1 V.

The kinetics of one-electron oxidation of sulfite are strongly dependent upon pH, with HSO_3^- being less readily oxidized than SO_3^{2-}. The ratio between the reactivities of these two ions is very large (~3 orders of magnitude, Table I) when the reduction potential of the oxidant is not very high ($DMA^+\cdot$, $AH^+\cdot$) (see also promethazine radical cation in Table II), but it decreases for I_2^- to ~200, for Br_2^- to ~4, and for OH it vanishes (although in this case the mechanism may involve addition of OH to SO_3^{2-}/HSO_3^- or abstraction of a hydrogen atom).

The kinetic and equilibrium results we have obtained for the one-electron-transfer reaction involving sulfite and the sulfite radical provide general information useful for understanding the varied phenomena associated with the autoxidation of sulfite. First, weak oxidants oxidize sulfite much faster than bisulfite; the stronger the oxidant, the less the difference. Second, the oxidation of reductants by $\dot{S}O_3^-$ is, typically, pH dependent due to the pH dependence of the $\dot{S}O_3^-$ redox potential.[2] This effect can be complicated considerably by protonation equilibria associated with the reductant. Third, the electron-transfer rates are very fast compared to the rates of autoxidation. Therefore, even if the free energy is unfavorable, for a reaction such as reaction 7 the small amount of $\dot{S}O_3^-$ produced can participate in secondary reactions. In the case of $TMPD^+\cdot$, this leads to its reduction. This probably also happens in the reduction of Fe(III) by bisulfite. Finally, $\dot{S}O_3^-$ can react very rapidly with O_2 ($k_{13} \sim 1.5 \times 10^9\ M^{-1}\ s^{-1}$)[2] leading to $SO_5^-\cdot$, which is a stronger oxidant. If the redox potential of a reactant is between that of $\dot{S}O_3^-$ and $SO_5^-\cdot$, rapid catalysis of the autoxidation can take place.

$$M^{n+} + SO_3^{2-} \rightleftarrows M^{(n-1)+} + \dot{S}O_3^- \tag{20}$$

$$\dot{S}O_3^- + O_2 \rightarrow SO_5^-\cdot \tag{13}$$

$$SO_5^-\cdot + M^{(n-1)+}H^+ \rightarrow HSO_5^- + M^{n+} \tag{21}$$

Subsequent reactions of HSO_5^- would increase the yield of this chain and possibly even lead to chain branching.

Registry No. PDA, 106-50-3; TMPD, 100-22-1; $DMA^+\cdot$, 34529-89-0; $AH^+\cdot$, 34475-46-2; $TMPDH^+$, 19513-44-1; $PDAH^+$, 19513-42-9; $PDAH_2^{2+}$, 33087-41-1; DPA, 122-39-4; $DMAH^+$, 17835-98-2; $SO_3^-\cdot$, 12210-38-7; HSO_3^-, 15181-46-1; SO_5^-, 12509-93-2; SO_3^{2-}, 14265-45-3.

Electric Polarization and Birefringence of a Molecule Having Two Equivalent Interacting Dipoles

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(Received: May 23, 1984; In Final Form: December 5, 1984)

The static electric polarization and birefringence of a molecule having two equivalent interacting dipoles are calculated. It is emphasized that, in obtaining averages for this system with the intramolecular interaction by using the Maxwell–Boltzmann distribution function, special care neglected in previous studies should be taken. Various new aspects of the present results are discussed.

I. Introduction

The calculation of the observable quantities, such as the electric polarization and the electric birefringence, induced by an external electric field on a fluid or a solution consisting of molecules having internal freedom is concerned with how to obtain the ensemble average of the overall dipole moment or the optical anisotropy of the molecule projected onto a suitable laboratory coordinate system. The internal motion is governed by an intramolecular potential function which may be conveniently expressed in terms of the molecular coordinate system. When an external electric field is applied, the molecules are subjected to a potential function V

$$V = V_{ex} + V_i$$

where V_{ex} is the potential energy due to the interaction of the dipoles on the molecule with an external field and V_i is the intramolecular potential function.

From the fundamental result of classical statistical mechanics the probability of molecules taking generalized coordinates $q = (q_1, q_2, \ldots)$ and their conjugate momenta $p = (p_1, p_2, \ldots)$ in the range of q, $q + dq$ and p, $p + dp$ is given by

$$C \exp(-H/k_B T)\ dp\ dq \tag{1}$$

where C is a constant, H is the Hamiltonian which is the sum of the kinetic energy K and potential V, k_B is the Boltzmann constant,

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