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A Radical Chain Mechanism Coupled to Autocatalysis. The Oxidation of *N*,*N*-Dimethyl-*p*-phenylenediamine by Peroxodisulfate

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The oxidation of *N*,*N*-dimethyl-*p*-phenylenediamine ($\bar{R}$) by peroxodisulfate ($S_2O_8^{2-}$) in aqueous solution was studied spectrophotometrically. A complex mechanism which couples a radical chain reaction with an autocatalytic reaction as well as with several consecutive and parallel reactions determines this apparent simple two-step oxidation. Following the formation of only a small amount of *N*,*N*-dimethyl-*p*-semiquinonediimine (S^+), peroxodisulfate almost exclusively oxidizes this organic radical to the corresponding quinonediimine ($\bar{T}$), whereas the sulfate radical (SO_4^-) which is formned by the one-electron reduction of $S_2O_8^{2-}$ preferably oxidizes $\bar{R}$. The rate of this radical chain reaction increases autocatalytically because of a fast synproportionation between $\bar{T}$ and $\bar{R}$, which regenerates up to two molecules S^+ for each molecule S^+ oxidized by $S_2O_8^{2-}$ (and SO_4^-). The contribution of this synproportionation on the oxidation of $\bar{R}$ may become larger than the contribution of the radical chain reaction. During the autocatalytic increase of S^+, two consecutive reactions ($\bar{R} \rightarrow S^+ \rightarrow \bar{T}$) and ($S_2O_8^{2-} \rightarrow SO_4^- \rightarrow SO_4^{2-}$) are coupled with four parallel reactions ($\bar{R} + S_2O_8^{2-} \rightarrow S^+$), ($S^+ + S_2O_8^{2-} \rightarrow \bar{T}$), ($\bar{R} + SO_4^- \rightarrow S^+$), and ($S^+ + SO_4^- \rightarrow \bar{T}$). The synproportionation can be regarded as the pump of the overall reaction. Rate determining is the oxidation of S^+ by peroxodisulfate. Despite this complex mechanism the rate constants for the parallel oxidation of both $\bar{R}$ and S^+ by $S_2O_8^{2-}$, $\bar{k}_1$ and k_2, could be determined by a procedure based on a plot of the formation rate of S^+, measured as change in absorbance, against the corresponding absorbance. At 25 °C, pH = 5.4, and ionic strength 0.025 M, the pH-dependent rate constant $\bar{k}_1$, has the value 1.8 (±0.2) $M^{-1}\ s^{-1}$, whereas the pH-independent rate constant k_2 equals 95 (±4) $M^{-1}\ s^{-1}$.

Introduction

Peroxodisulfate, $S_2O_8^{2-}$, is one of the most powerful oxidants (2.01 V vs NHE), but usually, the rate of oxidation of both inorganic[1−7] and organic[8−13] compounds is low. Sometimes, a radical chain mechanism is assumed.[14−17] First, some sulfate radicals, SO_4^-, are formed because of thermal or light induced dissoziation of $S_2O_8^{2-}$.[18−20] A high concentration of SO_4^- is obtained by flash photolysis[21−28] as well as by pulse radiolysis.[14,22,29,30]

The sulfate radical is not only a strong oxidant (2.43 V vs NHE)[31] but also attacks almost all components of the solution. An electron or a hydrogen atom may be abstracted from a molecule giving another inorganic or organic radical.[25,28] For the electron-transfer reaction, rate constants $>10^9\ M^{-1}\ s^{-1}$ at 25 °C have been found.[22,25,30,34] H abstraction occurs much slower, e.g., the reaction with water, but yields radicals which may initiate further radical chain reactions. The rate constant for the formation of hydroxyl radicals is low ($<10^3\ M^{-1}\ s^{-1}$ at 25 °C).[23,24] Furthermore, this reaction is reversible; that is, a OH radical may react with HSO_4^- (with a hundredful higher rate constant).[23] In the presence of a sufficiently high concentration of an organic compound, this side reaction can therefore mostly be neglected as well as the formation of the peroxodisulfate radical $S_2O_8^-$.[14] Fast and efficient formation of OH radicals occurs in strongly alkaline solutions.[32,33] Furthermore, a reaction of SO_4^- with buffer substances has usually to be taken into account.

According to the radical chain mechanism, the sulfate radical will be regenerated from $S_2O_8^{2-}$ if peroxodisulfate sufficiently fast oxidizes the organic and inorganic radicals created by SO_4^-.[14−17]

Termination of this chain reaction occurs by the reaction of SO_4^- with another radical or by dimerization. The rate constant of dimerization is very high ($>10^9\ M^{-1}\ s^{-1}$ at 25 °C),[21,23−25] but the rate of this reaction is usually low because of the low concentration of SO_4^-. Therefore, in the presence of sufficiently high concentrations of oxidizable compounds, the dimerization can be neglected.[34]

Because of their high reactivity, the concentration of most radicals remains low. Some ion radicals, however, are very stable, even in aqueous solution, e.g., *N*-alkylated *p*-semiquinonediimines, S^+ which are obtained by oxidation of the corresponding *p*-phenylenediamines, $\bar{R}$.[35] $\bar{R}$ refers to the sum of the concentration of the unprotonated (R), the protonated (RH^+), and the doubly protonated phenylenediamine (RH^{2+}). The formation of S^+ can easily be followed spectrophotometrically because *p*-semiquinonediimines exhibit strong and characteristic absorption in the visible region of the spectrum.[36−38] The final oxidation product, the corresponding quinonediimine, $\bar{T}$, is uncolored but exhibits strong absorption around 290 nm.[38] $\bar{T}$ refers to the sum of the concentrations of T^{2+} and the deprotonated compound T^+. A proton is released in neutral and weak acidic solution during the formation of *N*,*N*-dialkylated

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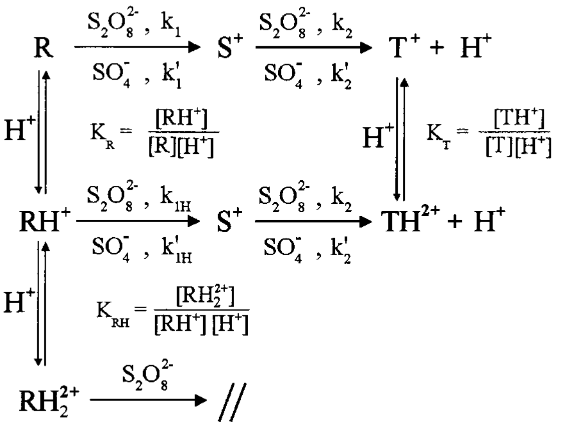
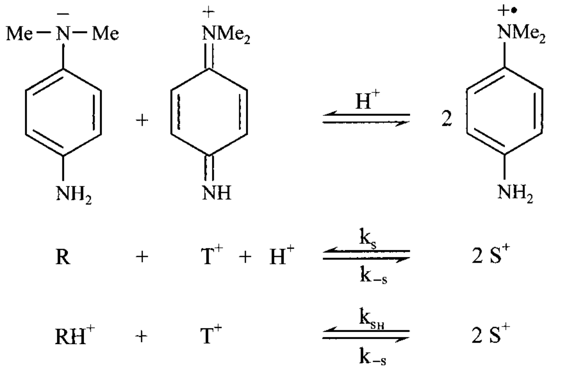
SCHEME 1



p-quinonediimines (as *N,N,N′,N′*-tetraalkylated compounds cannot release a proton, the corresponding quinonediimines always carry two positive charges.) Scheme 1 summarizes the most important reactions of the formnal two-step oxidation of a *p*-phenylenediamine by peroxodisulfate taking into account the oxidation by the sulfate radical.

According to Scheme 1, two consecutive reactions, $\bar{R} \rightarrow S^+ \rightarrow \bar{T}$ and $S_2O_8{}^{2} \rightarrow SO_4{}^- \rightarrow SO_4{}^{2-}$, are coupled with several parallel reactions. Furthermore, the fast redox reaction between $\bar{R}$ and $\bar{T}$ presented in Scheme 2 has to be considered.[36,39]

SCHEME 2



It has already been demonstrated that this synproportionation causes an autocatalytic increase of the rate of oxidation of *p*-phenylenediamines, because the oxidation of S^+ by $S_2O_8{}^{2-}$ not only produces $SO_4{}^-$ but also regenerates the organic radical, S^+.[40,41] This step of the reaction may become rate determining, and thus, the formation rate of semiquinonediimine, $(d[S^+]/dt)$, may predominantly be given by the rate constant of the secondary oxidation, k_2.

This paper deals with the mechanism of this coupled radical chain and autocatalytic reaction which also includes parallel and consecutive reactions chosing the oxidation of *N,N*-dimethyl-*p*-phenylenediamine ($E^\circ_{R/S} = 0.37$ V vs NHE and $E^\circ_{S/T} \cong 0.45$ V vs NHE) as an example. A procedure will be presented which allows the determination of the rate constants of both the primary and the secondary oxidation, $\bar{k}_1$ and k_2, only from the change in absorbance caused by S^+. The most important side reactions such as deamination and consumption of sulfate radicals by buffer substances will be taken into account. With the experimentally determined rate constants for the reaction of $\bar{R}$ and S^+ with $S_2O_8{}^{2-}$, the contribution of peroxodisulfate on the primary and secondary oxidation will be calculated. Furthermore, the analogous contribution of the sulfate radical will be estimated as well as the contribution of the synproportionation between $\bar{R}$ and $\bar{T}$.

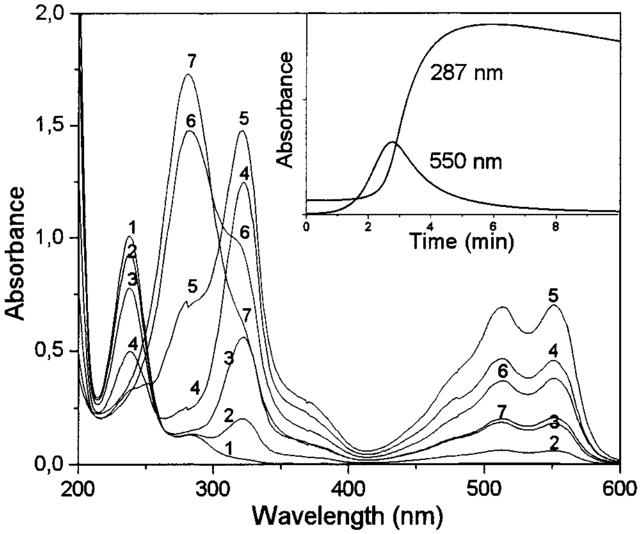


Figure 1. Time-resolved spectra recorded during the oxidation of 1.0 × 10^{-4} M *N,N*-dimethyl-*p*-phenylenediamine with 1.4 × 10^{-4} M $S_2O_8{}^{2-}$ in unbuffered aqueous solution (pH ≈ 4). $T = 25$ °C. The numbers 1−7 refer to the reaction time at 0, 60, 90, 120, 150, 210, and 270 s. Inside figure: absorbance−time curves recorded under the same conditions at 550 and 287 nm respectively.

Experimental Section

N,N-dimethyl-*p*-phenylenediamine•2HCl and potassium peroxodisulfate were p.a. reagents from Merck. The buffer solutions were prepared according to Sørensen from compounds purchased from Merck.

The kinetic experiments were carried out in a spectrophotometer from Biotec (Uvikon 922) equipped with a homemade mixing apparatus and a thermostated flow cuvette (quartz) from Hellma. The optical path length was $b = 1$ cm. Usually, the course of the reaction was followed at the wavelength of maximum absorbance of S^+ in the visible region of the spectrum, i.e., at 550 nm. In addition, some experiments were carried out following the change in absorbance, *A*, at 287 nm, the wavelength of maximum absorbance of T^+. The reaction rate (dA/dt) was obtained either from the derivative calculated by the photometer or by means of a mirror ruler.

Aqueous solutions of the reactants were prepared immediately before use with doubly distilled water which had been degassed and saturated with argon. The solutions of $S_2O_8{}^{2-}$ were kept in the dark in order to avoid light induced dissociation of $S_2O_8{}^{2}$.

All experiments were carried out at 25 °C.

Results

Fundamental Experiments. Figure 1 shows some time-resolved spectra recorded during the oxidation of *N,N*-dimethyl-*p*-phenylenediamine, $\bar{R}$, with a slight excess of $S_2O_8{}^{2}$ in unbuffered solution. First, the characteristic bands of the corresponding p-semiquinonediimine, S^+, appear around 550, 510, and 330 nm. Simultaneously, because of the consumption of $\bar{R}$, the absorbance around 240 nm decreases. When the maximum absorbance in the visible region of the spectrum is almost reached, a shoulder appears at 287 nm which indicates the formation of quinonediimine, $\bar{T}$. This new band increases strongly, whereas simultaneously the absorbance caused by S^+ decreases.

The change of absorbance recorded at 550 and 287 nm respectively is displayed in the inset in Figure 1. The absorbance at 550 nm is directly proportional to the concentration of S^+ (with the absorption coefficient $\epsilon_{S,550} = 1.00 \times 10^4\ M^{-1}\ cm^{-1}$)[37,38] because in the visible region no other compound present in solution causes any measurable absorbance (the concentration of the sulfate radical, SO_4^-, which absorbs around 450 nm[14,21,24,25,29] remains very low).

Although all compounds in solution exhibit absorbances at 287 nm, the concentration of $\bar{T}$ can be calculated by means of the corresponding concentration of S^+ and the known absorption cefficients of $\bar{R}$, S^+, and $\bar{T}$ at this wavelength. Because of the high value of $\epsilon_{T,287}$ ($= 2.2 \times 10^4\ M^{-1}\ cm^{-1}$),[38] the change in absorbance is predominantly given by the formation of $\bar{T}$. The decrease in absorbance after passing the maximum is caused by the acid deamination of $\bar{T}$ at this low pH (see below).

An induction period for the formation of the final product of a two-step reaction is often observed, but it is unusual that also the appearance of the intermediate product is delayed. Moreover, both the formation and the subsequent disappearance of S^+ occurs with a similar rate; that is, the absorbance time curve measured at 550 nm is almost symmetrical. This effect is caused by the autocatalytic process presented in Schemes 1 and 2. At the established pH ($\cong 4$), most of $\bar{R}$ is protonated. As RH^+ and RH_2^{2+} are hardly attacked by $S_2O_8^{2-}$, the reaction begins very slowly by oxidation of the tiny amount of the unprotonated species R with $S_2O_8^{2-}$. The reaction may also be initiated by reactive compounds produced by partial decomposition of $S_2O_8^{2-}$. The consecutive oxidation of the resulting S^+ also begins very slowly. However, because of the synproportionation between $\bar{T}$ and $\bar{R}$ giving two S^+, the concentration of S^+ increases autocatalytically and soon exceeds that of the unprotonated species R. Thus, the rate of oxidation of S^+ by $S_2O_8^{2-}$ becomes higher than the rate of the oxidation of $\bar{R}$ by $S_2O_8^{2-}$. Finally, $\bar{R}$ is almost exclusively oxidized by $\bar{T}$ and by SO_4^-, which is generated as a reactive intermediate because of the reduction of $S_2O_8^{2-}$. According to this mechanism, the formation rate of S^+ should depend in a characteristic way on the initial concentration of both *p*-phenylenediamine, $[R]_o$, and peroxodisulfate, $[S_2O_8^{2-}]_o$. The examples displayed in Figure 2 parts a and b show the influence of a variation of $[R]_o$ on the course of the reaction, whereas Figure 3 parts a and b give some examples for the influence of $[S_2O_8^{2-}]_o$.

Variation of $[R]_o$. For $[R]_o \gg [S_2O_8^2]_o$, the final concentration of *p*-semiquinonediimine, ($[S^+]_{oo}$), given by ($A_{oo}/b\ \epsilon_{S,550}$), should nearly reach twice the initial concentration of peroxodisulfate. As almost no $\bar{T}$ is formed, the reaction might be regarded as a one-step reaction ($\bar{R} \rightarrow S^+$). On the other hand, the absorbance-time curves displayed in Figure 2a do not only show a pronounced induction period (which excludes a simple reaction), but surprisingly, all curves with a concentration of $[R]_o > 1$ mM are almost identical. A thorough evaluation of the experimental results shows that the initial reaction rate seems to be proportional to $[R]_o$ and the induction period is shortened a bit, but the maximum formation rate of S^+ measured as change of absorbance, $v_{max} = (dA_{550}/dt)_{max}$ (dotted line), is independent of $[R]_o$, (see inset in Figure 2a). For $[R]_o \gg [S_2O_8^{2-}]_o$, the autocatalytic formation of S^+ is therefore zero order in $\bar{R}$.

For $[R]_o \leq [S_2O_8^{2-}]_o$, the whole organic compound should finally be converted into quinonediimine. Semiquinonediimine may only appear as an intermediate product. Its maximum concentration should be limited by the initial concentration of *p*-phenylenediamine. The examples displayed in Figure 2b show for this apparent consecutive reaction ($\bar{R} \rightarrow S^+ \rightarrow \bar{T}$) the change in the concentration of S^+ (measured as change in absorbance at 550 nm). The maximum absorbance as well as the rate of both the formation and the disappearance of S^+ is nearly proportional to $[R]_o$. Under these conditions, not only the initial reaction rate but also the autocatalytic reaction is first order in $\bar{R}$. The slope of the straight line in the inset in Figure 2b, which refers to the dependence of the maximum formation rate of S^+ on $[R]_o$, has the value 1.1.

Variation of $[S_2O_8^{2-}]_o$. For $[R]_o \gg [S_2O_8^{2-}]_o$, analogously to the examples displayed in Figure 2a, predominantly semiquinonediimine is formed ($\bar{R} \rightarrow S^+$) and, thus, the final concentration of *p*-semiquinonediimine almost equals $2[S_2O_8^{2-}]_o$. Of course, the final absorbance of the experimental curves displayed in Figure 3a is not constant because $[S_2O_8^{2-}]_o$ is varied. Opposite to the results obtained for a variation of $[R]_o$, the reaction rate strongly increases with increasing initial concentration of peroxodisulfate. The maximum formation rate of S^+, which is determined at about half the final absorbance,

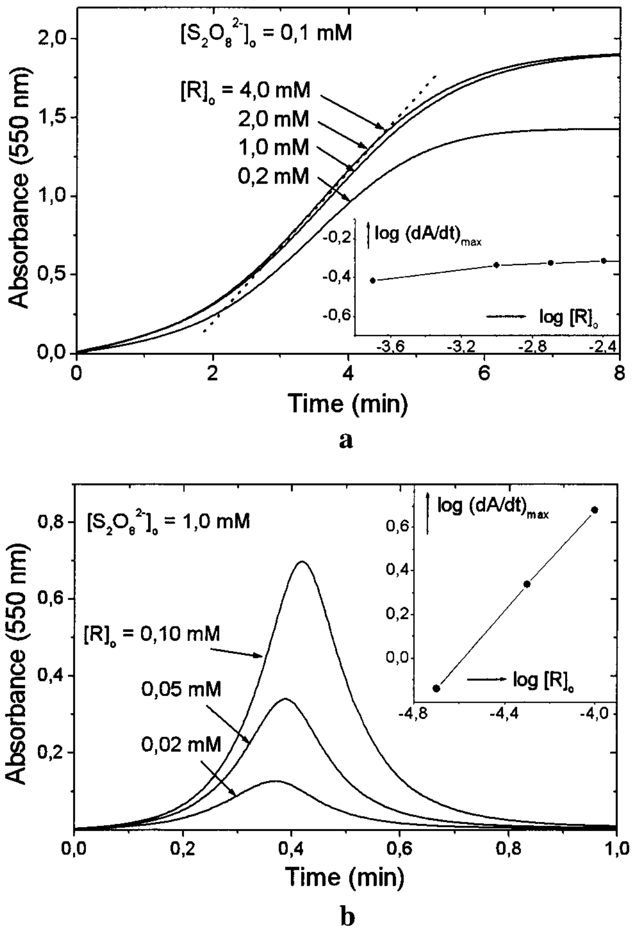
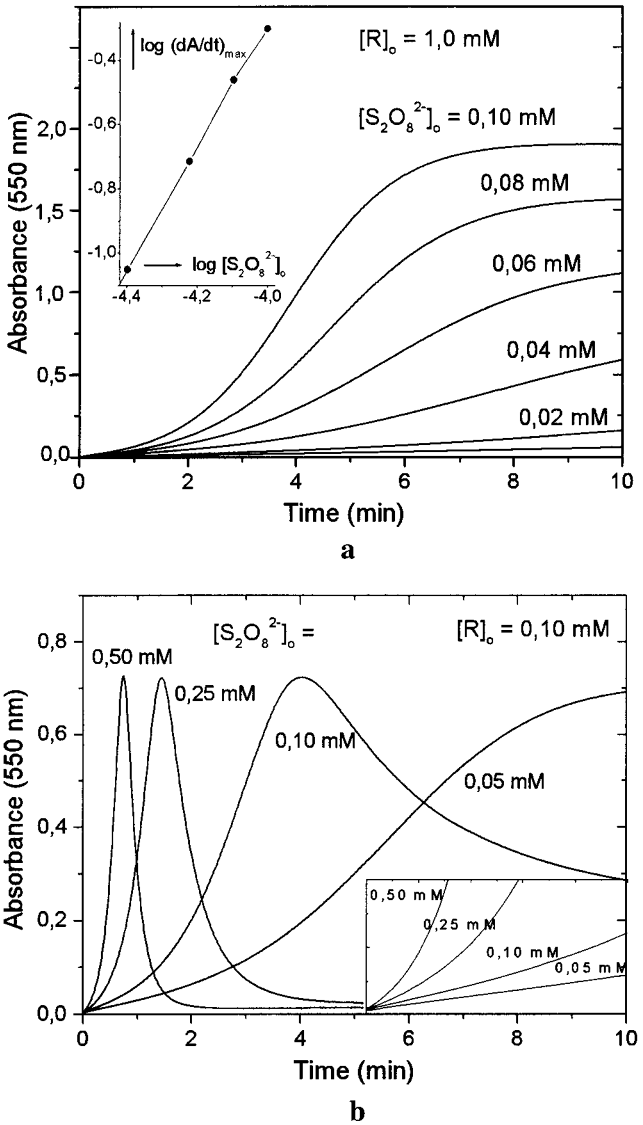


Figure 2. (a) Some examples for the dependence of the formation rate of *p*-semiquinonediimine (recorded as change of absorbance at 550 nm) on the initial concentration of *N*,*N*-dimethyl-*p*-phenylenediamine taking an excess of the organic compound. $[R]_o = 2.0 \times 10^{-4}-4.0 \times 10^{-3}$ M, $[S_2O_8^{2-}]_o = 1.0 \times 10^{-4}$ M. $T = 25$ °C, pH = 5.4−4.6 (0.022 M phosphate buffer). The buffer capacity was not sufficient for high concentrations of *p*-phenylenediamine because this compound was used as a salt with 2 HC1. Dotted line: maximum formation rate of S^+ measured as maximum increase of the absorbance. Inside figure: dependence of the maximum formation rate of S^+ on the initial concentration of *p*-phenylenediamine. (b) Examples for the dependence of the formation rate of *p*-semiquinonediimine on the initial concentration of *N*,*N*-dimethyl-*p*-phenylenediamine taking an excess of peroxodisulfate. $[R]_o = 2.0 \times 10^{-5}-1.0 \times 10^{-4}$ M, $[S_2O_8^2]_o = 1.0 \times 10^{-3}$ M, $T = 20$ °C, pH ≈ 4 (unbuffered). Inside figure: dependence of the maximum formation rate of S^+ on $[R]_o$.



a

b

Figure 3. (a) Some examples for the dependence of the rate of formation of *p*-semiquinonediiimine on the initial concentration of peroxodisulfate chosing a high excess of *p*-phenylenediamine. $[S_2O_8^{2-}]_o = 1.0 \times 10^{-5}$–$1.0 \times 10^{-4}$ M, $[R]_o = 1.0 \times 10^{-3}$ M. $T = 25$ °C, pH = 4.9 (0.022 M phosphate buffer). Inside figure: dependence of the maximum formation rate of S^+ on the initial concentration of peroxodisulfate. (b) Examples for the dependence of the rate of formation of *p*-semiquinonediimine on the initial concentration of peroxodisulfate chosing similar concentrations of R and $S_2O_8^{2-}$ or an excess of the oxidizing compound. $[S_2O_8^{2-}]_o = 5.0 \times 10^{-5}$–$5.0 \times 10^{-4}$ M, $[R]_o = 1.0 \times 10^{-4}$ M. $T = 25$ °C, pH = 5.4 (0.022 M phosphate buffer). Inside figure: first minute of the reactions.

is even proportional to the square of the initial concentration of the oxidizing compound. The slope of the straight line of the graph in the inset in Figure 3a has the high value of 1.93. For $[S_2O_8^{2-}]_o \ll [R]_o$, the reaction is therefore second order in $S_2O_8^{2-}$.

For $[R]_o \leq [S_2O_8^{2-}]_o$, analogously to the examples presented in Figure 2b, *p*-phenylenediamine is completely converted to quinonediimine ($\bar{R} \rightarrow S^+ \rightarrow \bar{T}$). As demonstrated by the first three examples in Figure 3b, the maximum absorbance is limited by the constant initial concentration of *p*-phenylenediamine. Both the initial reaction rate (see inset in Figure 3b) and the maximum formation rate of S^+ is proportional to $[S_2O_8^{2-}]_o$. Under these conditions, the reaction is therefore first order in $S_2O_8^{2-}$.

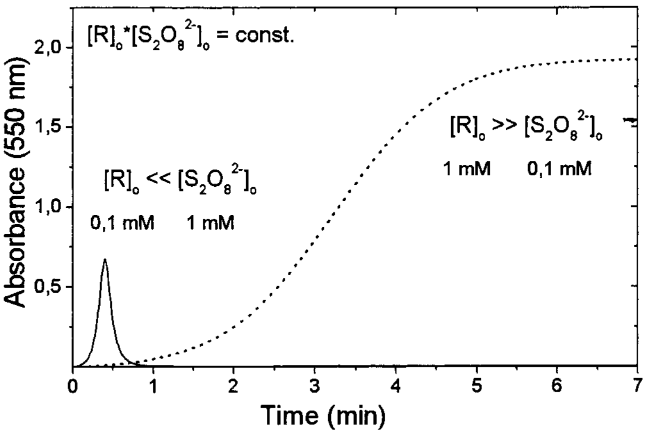


Figure 4. Course of the reaction for a constant product of the initial concentrations $[R]_o[S_2O_8^{2-}]_o = 0.1 \times 10^{-6}$ M but an excess of either peroxodisulfate or *p*- phenylenediamine. $T = 25$ °C, pH ≈ 4 and 3, respectively (unbuffered solution).

TABLE 1

	$[R]_o \gg [S_2O_8^{2-}]_o$		$[R]_o < [S_2O_8^{2-}]_o$	
	order of the reaction at $(dA/dt)_{max}$	final concentration of S^+	order of the reaction at $(dA/dt)_{max}$	maximum concentration of S^+
variation of $[R]_o$	0	constant	1	$\propto [R]_o$
variation of $[S_2O_8^{2-}]_o$	2	$\propto [S_2O_8^{2-}]_o$	≥ 1	constant
final concentration of S^+	$\cong 2[S_2O_8^{2-}]_o$		zero	

Variation of the Ratio ($[S_2O_8^{2-}]_o/[R]_o$). For $[R]_o \ll [S_2O_8^{2-}]_o$ and $[R]_o \gg [S_2O_8^{2-}]_o$ but the same value of the product ($[R]_o{\cdot}[S_2O_8^{2-}]$), absorbance–time curves such as those displayed in Figure 4 are obtained. With an excess of peroxodisulfate (solid line curve), the reaction is much faster than with an excess of *p*-phenylenediamine (dotted curve). Of course, the final products are different, being quinonediimine and semiquinonediimine, respectively.

The most important results of the experiments mentioned so far are summarized in Table 1. The first subcolumn in the second and the third column gives the order of the reaction at the point of the maximum formation rate of S^+, whereas the second subcolumn indicates the change in either the final absorbance (for experiments carried out with an excess of *p*-phenylenediamine) or the maximum absorbance (for experiments with a stoichiometric excess of peroxodisulfate).

Influence of pH. At 4 < pH < 6.5, an increasing pH causes a shortening of the induction period but does not influence the residual shape of the absorbance–time curves. At pH > 7, the induction period disappears completely. The initial reaction rate increases with increasing pH, whereas the autocatalytic reaction is nearly independent of the pH. These results indicate that the oxidation of unprotonated *p*-phenylenediamine occurs faster than the oxidation of the protonated form (see Scheme 1). The total concentration of *p*-phenylenediamine, $[\bar{R}]$, can be expressed by eq 1:

$$[\bar{R}] = [R] + [RH^+] + [RH_2^{2+}] = r[R] \qquad (1)$$

where $r = 1 + K_R[H^+](1 + K_{RH}[H^+])$.

The p*K* values for *N*,*N*-dimethyl-*p*-phenylenediamine are $pK_R = 6.4$ and $pK_{RH} = 2.3$ (at a ionic strength extrapolated to zero), respectively.[38] Therefore, at a pH between 4 and 5, the term *r* almost equals $K_R[H^+]$ ($pK_R \gg$ pH and $pK_{RH} \ll$ pH), and thus,

$[\bar{\mathrm{R}}]$ almost equals $[\mathrm{RH}^+]$. On the other hand, at pH > 7, the term *r* approaches 1, and thus, $[\bar{\mathrm{R}}]$ almost equals [R].

At very low pH, quinonediimine is protonated, too. Analogously to *r* the term, $p = 1 + K_\mathrm{T}[\mathrm{H}^+]$ can be defined. Because of the low value of the protonation constant $\mathrm{p}K_\mathrm{T}$ (= 1.7),[42] at a pH > 4, the factor *p* almost equals 1, and in a very good approximation, $[\mathrm{T}^+]$ equals the total concentration of quinonediimine, $[\bar{\mathrm{T}}]$.

At a pH < 2, protonation of S^+ may occur. On the other hand, at high pH, a proton is released. As all experiments were carried out in the pH range of 3−7, the corresponding equilibria need not be considered here.

Deamination. Even in experiments carried out with a stoichiometric excess of *p*-phenylenediamine, the absorbance measured at both 550 and 287 nm passes through a maximum; that is, the absorbance finally decreases slowly. Furthermore, the maximum absorbance is sometimes lower than expected. The lower and the higher the pH the more pronounced is this effect which is caused by either acid or alkaline deamination of $\bar{\mathrm{T}}$.

In strongly acid solution, quinonediimine reacts with water giving the corresponding *N*-alkylated quinonemonoimine, M^+, and ammonia (as $\mathrm{NH_4}^+$).[42,43] The half time of this acid deamination is about 1 s at pH = 2 and about 100 s at pH = 4. Slow reactions involving $\bar{\mathrm{T}}$ may therefore noticeably be influenced by this side reaction, even at pH > 4 (see inset in Figure 1). Deamination is also caused by the attack of a hydroxide ion at the substituted imino group giving quinonemonoimine, M.[44] The rate of this alkaline deamination which dominates at pH > 7 is proportional to $[\mathrm{OH}^-]$, i.e., increases strongly with increasing pH. Further deamination yields quinone, but this reaction need not to be taken into account here.

The total concentration of quinonemonoimine can be expressed by $[\bar{\mathrm{M}}] = ([\mathrm{M}^+] + [\mathrm{M}])$, and the deamination can be formulated according to eq 2:

$$\bar{\mathrm{T}} \xrightarrow{\bar{k}_\mathrm{D}} \bar{\mathrm{M}} \tag{2}$$

with

$$\bar{k}_\mathrm{D} = \frac{k_{\mathrm{D-acid}}K_\mathrm{T}[\mathrm{H}^+] + k_{\mathrm{D-alk}}[\mathrm{OH}^-]}{p} \tag{2a}$$

The maximum stability of $\bar{\mathrm{T}}$ with regard to deamination is at a pH between 4.5 and 6.5.[42] In this pH range, the deamination for sufficiently fast reactions can usually be neglected.

Influence of Ionic Strength. The rate of the autocatalytic formation of S^+ decreases with increasing ionic strength. A logarithmic plot of the maximum formation rate versus the square root of the ionic strength μ, or better against $[(\mu)^{1/2}/(1 + (\mu)^{1/2})]$, gives straight lines with a negative slope of almost 2 (±0.15).[40]

This dependence indicates that the rate determining step involves a reaction between a positively charged ion (this might be RH^+ or S^+) and a doubly negatively charged ion (this can only be $\mathrm{S_2O_8}^{2-}$). Because of the inverse dependence of the overall reaction rate on the pH mentioned above, the positively charged ion cannot be the protonated *N*,*N*-dimethyl-*p*-phenylenediamine, RH^+, but should be S^+.

Primary Oxidation. Both the unprotonated and protonated form of *p*-phenylenediamine may be oxidized by $\mathrm{S_2O_8}^{2-}$. Equation 3 combines the corresponding parallel reactions given in Scheme 1. As the possibly formed peroxodisulfate radical, $\mathrm{S_2O_8}^{3-}$, rapidly dissociates to sulfate and the sulfate radical, an irreversible reaction can be assumed:

$$\bar{\mathrm{R}} + \mathrm{S_2O_8}^{2-} \xrightarrow{\bar{k}_1} \mathrm{S}^+ + \mathrm{SO_4}^- + \mathrm{SO_4}^{2-} \tag{3}$$

with

$$\bar{k}_1 = \frac{k_1 + k_{1\mathrm{H}}K_\mathrm{R}[\mathrm{H}^+]}{r} \tag{3a}$$

This primary reaction is slow because the transfer of an electron to $\mathrm{S_2O_8}^{2-}$ seems to be difficult. The resulting sulfate radical, however, is a very reactive compound. Particularly, the rate constants for the oxidation of organic compounds by $\mathrm{SO_4}^-$ are usually high ($10^6 - 5 \times 10^9$ $\mathrm{M^{-1}\ s^{-1}}$).[22,25,28,30,34] Fast oxidation of phenylenediamines by $\mathrm{SO_4}^-$ can therefore also be expected, and analogously to (3), eq 4 is formulated:

$$\bar{\mathrm{R}} + \mathrm{SO_4}^- \xrightarrow{\bar{k}_1^\mathrm{I}} \mathrm{S}^+ + \mathrm{SO_4}^{2-} \tag{4}$$

with

$$\bar{k}_1^\mathrm{I} = \frac{k_1^\mathrm{I} + k_{1\mathrm{H}}^\mathrm{I}K_\mathrm{R}[\mathrm{H}^+]}{r} \tag{4a}$$

In most cases, the direct oxidation of an organic compound by $\mathrm{S_2O_8}^{2-}$ is not taken into account. As mentioned above, it is assumed that sulfate radicals which are formed in low concentation as a result of thermal and/or photoinduced dissoziation of $\mathrm{S_2O_8}^{2-}$ initiate a radical chain reaction with several components of solution. In fact, the induction period is shortened when a solution of peroxodisulfate is used which had been kept for some time (e.g., 1 h) at elevated temperature (e.g., 50 °C). The induction period is also shortened a little by strong irradiation of the solution. Effects of this kind will not be discussed here because much more important for the initiating of the reaction is the presence of *p*-semiquinonediimine because of some preoxidation of *N*,*N*-dimethyl-*p*-phenylenediamine (see below).

Secondary Oxidation. Organic radicals may be oxidized by $\mathrm{S_2O_8}^{2-}$ better than nonradical compounds. The corresponding rate constant k_2 may therefore be noticeably higher than the rate constant $\bar{k}_1$. Rate constants up to 10^5 $\mathrm{M^{-1}\ s^{-1}}$ have been reported.[14,15] As a proton is released at pH > 2, the oxidation of *N*,*N*-dimethyl-*p*-semiquinonediimine is formulated according to eq 5:

$$\mathrm{S}^+ + \mathrm{S_2O_8}^{2-} \xrightarrow{k_2} \bar{\mathrm{T}} + \mathrm{SO_4}^- + \mathrm{SO_4}^{2-} + \mathrm{H}^+ \tag{5}$$

On the other hand, the oxidation of S^+ by the sulfate radical should occur with a similar high rate as the oxidation of $\bar{\mathrm{R}}$, i.e., $k_2^\mathrm{I} \cong \bar{k}_1^\mathrm{I}$. Thus, reaction 6 should be much faster than (5):

$$\mathrm{S}^+ + \mathrm{SO_4}^- \xrightarrow{k_2^\mathrm{I}} \bar{\mathrm{T}} + \mathrm{SO_4}^{2-} + \mathrm{H}^+ \tag{6}$$

A low quasistationary concentration of the organic radical should therefore be established. However, in the case of *p*-phenylenediamines, synproportionation occurs which causes a strong increase in the concentration of S^+.

Synproportionation. Quinonediimine reacts with *p*-phenylenediamine giving the semioxidized form (see Scheme 2). Both the protonated and the unprotonated form of *p*-phenylenediamrnine may be oxidized. In the latter case, the transfer of a proton is necessary. As the rate constants $\bar{k}_s$ ($\geq 1.1 \times 10^6$ M^{-1} s^{-1} at 25 °C)[36,39] and k_{-s} ($\geq 4.0 \times 10^4$ M^{-1} s^{-1} at 25 °C)[39] are much higher than the rate constants $\bar{k}_1$ and k_2, the equilibrium according to eq 7 will almost (but not completely) be established after the formation of a small amount of $\bar{T}$. It should be mentioned that the synproportionation is catalyzed by all compounds which are able to offer a proton:[39]

$$\bar{R} + \bar{T} \underset{k_{-s}}{\overset{\bar{k}_s}{\rightleftharpoons}} S^+ + S^+ \tag{7}$$

with

$$\bar{k}_s = \frac{k_s + k_{SH}K_R[H^+]}{r} \tag{7a}$$

The relation between the pH-dependent equilibrium constant $\bar{K}_s$ and the pH-independent synproportionation constant $K_s = [S^+]^2/[R][T^+][H^+]$ is given in eq 8:

$$\bar{K}_s = \frac{[S^+][S^+]}{[\bar{R}][\bar{T}]} = K_s\frac{[H^+]}{rp} \tag{8}$$

For *N*,*N*-dimethyl-*p*-phenylenediamine, the synproportionation constant was determined to be $K_s = 7.0 \times 10^7$ M^{-1} (at 25 °C)[38,45] At a pH between 4 and 5, the term r almost equals $K_R[H^+]$ and the term $p = 1$. In this pH range, the synproportionation constant $\bar{K}_s$ is independent of pH and given by the ratio $(K_S/K_R) = 28$ (25 °C). At both pH < 3 and pH > 6, the value of $\bar{K}_s$ becomes smaller.

Mass-Balance Equations. During the whole course of the reaction, the sum of the actual concentration of $[\bar{R}]$, $[S^+]$, $[\bar{T}]$, and $[\bar{M}]$ should equal the initial concentration of *p*-phenylenediamine, $[R]_o$:

$$[R]_o = [\bar{R}] + [S^+] + [\bar{T}] + [\bar{M}] \tag{9}$$

As long as side reactions of SO_4^- with other components in solution can be neglected, a similar equation is valid for the initial concentration of peroxodisulfate, $[S_2O_8^{2-}]_o$, taking into account that $S_2O_8^{2-}$ can accept two electrons:

$$[S_2O_8^{2-}]_o = [S_2O_8^{2-}] + 0.5[S^+] + [\bar{T}] + [\bar{M}] + 0.5[SO_4^-] \tag{10}$$

Because of the high reactivity of SO_4^-, its concentration remains low, and thus, the last term in (10) can usually be omitted.

Determination of the Rate Constants $\bar{k}_1$ and k_2 from ($d[S^+]/dt$) and ($d[\bar{T}]/dt$). The kinetic equation for the formation of semiquinonediimine, ($d[S^+]/dt$), is obtained considering the eqs 3−7:

$$d[S^+]/dt = \bar{k}_1[\bar{R}][S_2O_8^{2-}] + \bar{k}_1^I[\bar{R}][SO_4^-] - k_2[S^+][S_2O_8^{2-}] - k_2^I[S^+][SO_4^-] + 2\bar{k}_s[\bar{R}][\bar{T}] - 2k_{-s}[S^+]^2 \tag{11}$$

Analogously, the formation rate of quinonediimine, ($d[\bar{T}]/dt$), is obtained from eqs 5−7 and 2:

$$d[\bar{T}]/dt = k_2[S^+][S_2O_8^{2-}] + k_2^I[S^+][SO_4^-] - \bar{k}_s[\bar{R}][\bar{T}] + k_{-s}[S^+][S^+] - \bar{k}_D[\bar{T}] \tag{12}$$

In the aqueous stock solution of $S_2O_8^{2-}$, several reactive oxidizing compounds may be present because of reactions of SO_4^-, formed by decomposition of some molecules of $S_2O_8^{2-}$ with water and buffer substances. Therefore, immediately after mixing the reacting compounds, fast oxidation of some $\bar{R}$ may occur. Furthermore, a small amount of the *p*-phenylenediamine salt is already oxidized because of the method of preparation and the kind of storage. Reactions of this kind are not included in (11) and (12) because they only influence the initial reaction rate. It should also be stressed that such reactive compounds are not necessary to start the oxidation reaction.

According to (2), the formation rate of quinonemonoimine, ($d[\bar{M}]/dt$), is given by

$$d[\bar{M}]/dt = \bar{k}_D[\bar{T}] \tag{13}$$

At a pH between 4 and 6, deamination occurs much slower than the oxidation and needs mostly not to be taken into account. The decrease in *p*-phenylenediamine, ($d[\bar{R}]/dt$), is obtained by combining (3), (4), and (7), as well as according to (9) by the sum of the terms ($d[S^+]/dt$), ($d[\bar{T}]/dt$), and ($d[\bar{M}]/dt$), i.e., by the sum of (11)−(13):

$$-d[\bar{R}]/dt = \bar{k}_1[\bar{R}][S_2O_8^{2-}] + \bar{k}_1^I[\bar{R}][SO_4^-] + \bar{k}_s[\bar{R}][\bar{T}] - k_{-s}[S^+]^2 \tag{14}$$

In the absence of side reactions, the change in the concentration of SO_4^- can be formulated by combination of (3)−(6):

$$d[SO_4^-]/dt = \bar{k}_1[\bar{R}][S_2O_8^{2-}] - \bar{k}_1^I[\bar{R}][SO_4^-] + k_2[S^+][S_2O_8^{2-}] - k_2^I[S^+][SO_4^-] \tag{15}$$

The terms concerning the dissociation of $S_2O_8^{2-}$ and the dimerization are not included in eq 15 because, under the experimental conditions applied here, their influence on the reaction of interest is very small.

The decrease in $[S_2O_8^{2-}]$ is given by the kinetic eq 16, not considering the thermal decomposition and the dimerization as well as any other side reactions:

$$-(d[S_2O_8^{2-}]/dt) = \bar{k}_1[\bar{R}][S_2O_8^{2-}] + k_2[S^+][S_2O_8^{2-}] \tag{16}$$

The change in $[S_2O_8^{2-}]$ cannot be followed photometrically, but it can be expressed by the increase in the products of the oxidation. Differentiation of (10) neglecting the low concentration of SO_4^- and suitable combination with (11)−(13) gives

$$-\frac{d[S_2O_8^{2-}]}{dt} = \frac{1}{2}\frac{d[S^+]}{dt} + \frac{d[\bar{T}]}{dt} + \frac{d[\bar{M}]}{dt}$$

$$= \frac{1}{2}\bar{k}_1[\bar{R}][S_2O_8^{2-}] + \frac{1}{2}k_2[S^+][S_2O_8^{2-}] + \frac{1}{2}\bar{k}_1^I[\bar{R}][SO_4^-] + \frac{1}{2}k_2^I[S^+][SO_4^-] \tag{17}$$

This equation equals (16) because for ($d[SO_4^-]/dt$) = 0 according to (15) the sum of the terms with $[SO_4^-]$ equals the sum of the terms with $[S_2O_8^{2-}]$:

$$\bar{k}_1^I[\bar{R}][SO_4^-] + k_2^I[S^+][SO_4^-] = \bar{k}_1[\bar{R}][S_2O_8^{2-}] + k_2[S^+][S_2O_8^{2-}] \tag{18}$$

The difference of the right-hand side terms and the left-hand side terms of (18) (which gives ($d[SO_4^-]/dt$)) is small, but each of these terms is much larger than the term ($d[SO_4^-]/dt$). This definition is better than the steady-state assumption because

$[SO_4^-]$ is very low but may strongly change during the course of the reaction.

As long as deamination can be neglected, the formation of S^+ and $\bar{T}$ can therefore be described according to eq 19:

$$\frac{1}{2}\frac{d[S^+]}{dt} + \frac{d[\bar{T}]}{dt} = \bar{k}_1[\bar{R}][S_2O_8^{\ 2-}] + k_2[S^+][S_2O_8^{\ 2-}] \quad (19)$$

This equation is also obtained by addition of (11)−(15) after dividing (11) and (15) by the factor 2 and neglecting the terms $(d[\bar{M}]/dt)$ and $(d[SO_4^-]/dt)$. The terms concerning the synproportionation and disproportionation disappear as well as all terms with $[SO_4^-]$.

As mentioned above, the concentration of semiquinonediimine, $[S^+]$, as well as its formation rate, $(d[S^+]/dt)$, can be determined very accurately from the absorbance A_{550}, measured at the wavelength of maximum absorbance of S^+ in the visible region of the spectrum. The concentration of quinonediimine, $[\bar{T}]$, and its formation rate, $(d[\bar{T}]/dt)$, can be calculated from the change in absorbance at 287 nm, A_{287}.

With the absorption coefficients of $\bar{R}$ (at the chosen pH), S^+, and $\bar{T}$, $\epsilon_{R,287}$, $\epsilon_{S,287}$ and $\epsilon_{T,287}$, for each concentration of S^+ considering (9) and neglecting $[\bar{M}]$, the corresponding concentration of $\bar{T}$ is given by

$$[\bar{T}] = \frac{A_{287} - A_{o,287} - (\epsilon_{S287} - \epsilon_{R,287})b[S^+]}{b(\epsilon_{T,287} - \epsilon_{R,287})} \quad (20)$$

$A_{o,287}$ refers to the initial absorbance which depends on the initial concentration of $\bar{R}$ and on the pH. Most often, during oxidation, the contribution of $\bar{M}$ to the absorption at 287 nm is low and need not to be taken into account.

The formation rate of quinonediimine, $(d[\bar{T}]/dt)$, is therefore given by

$$d[\bar{T}]/dt = \frac{(dA_{287}/dt) - (\epsilon_{S,287} - \epsilon_{R,287})b\,(d[S^+]/dt))}{b(\epsilon_{T,287} - \epsilon_{R,287})} \quad (21)$$

In principle, it is also possible to determine the concentration of quinonemonoimine, $[\bar{M}]$, from the absorbance at a suitable wavelength, e.g., at 245 nn (pH > 6) or at 270 nm (pH < 6), but it is more convenient to calculate the term $\bar{k}_D[\bar{T}]$ by means of the rate constant of deamination which can be determined separately.

To obtain a simple relation which allows the determination of the rate constants $\bar{k}_1$ and k_2, eq 19 is divided by $[S_2O_8^{2-}]$. Furthermore, $[\bar{R}]$ is substituted according to (9) neglecting $[\bar{M}]$. The term $(\bar{k}_D[\bar{T}]/[S_2O_8^{2-}])$ has only to be included if deamination cannot be neglected. A plot of the left-hand side term of the resulting eq 22, Y, against $[S^+]$ gives a graph with the intercept $\bar{k}_1[R]_o$. Most often, an almost straight line is obtained because at pH < 6, $k_2 \gg \bar{k}_1$, such that the term $\bar{k}_1[\bar{T}]$ can only cause a slight deviation. The slope of this straight line equals $(k_2 - \bar{k}_1)$:

$$Y = \frac{0.5\,(d[S^*]/dt) + (d[\bar{T}]/dt)}{[S_2O_8^{\ 2-}]} = \bar{k}_1[R]_o - \bar{k}_1[\bar{T}] + (k_2 - \bar{k}_1)[S^+] \quad (22)$$

For $[R]_o > 2\,[S_2O_8^{2-}]_o$, only positive values of $(d[S^+]/dt)$ appear (a succeeding slow decrease of the maximum concentration of S^+ is caused by deamination), whereas for $[S_2O_8^2]_o > 0.5\,[R]_o$, also negative values of $(d[S^+]/dt)$ have to be taken into account.

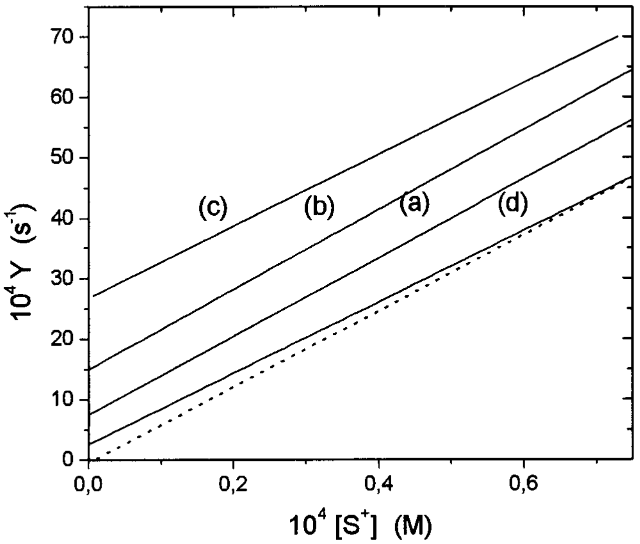


Figure 5. Some examples for a plot of Y according to eq 22. (a) $[R]_o = 5.0 \times 10^{-4}$ M, $[S_2O_8^{2-}]_o = 5.0 \times 10^{-5}$ M, $T = 25$ °C, pH 5.3 (0.033 M phosphate buffer). (b) Conditions such as those in part a but with $[R]_o = 1.0 \times 10^{-3}$ M. (c) Conditions such as in part a but with $[R]_o = 2.0 \times 10^{-4}$ M and pH = 6.1. (d) Conditions such as in part a but with $[R]_o = 2.0 \times 10^{-4}$ M and $[S_2O_8^{2-}]_o = 5.0 \times 10^{-4}$ M.

Some examples for a plot according to (22) are displayed in Figure 5. Graphs a−c refer to experiments carried out with an excess of *p*-phenylenediamine. Graph d was obtained from an experiment with an excess of peroxodisulfate (solid line for positive values of $(d[S^+]/dt)$; dotted line for the negative values).

The term $\bar{k}_1[\bar{T}]$ is too small to influence the slope of the solid line curves noticeably, and therefore, straight lines are obtained. The ratio of the intercept of these straight lines and $[R]_o$ yields the rate constant $\bar{k}_1$ (at the chosen pH), whereas the slope gives the difference in the rate constants, $(k_2 - \bar{k}_1)$. Because of the small value of $\bar{k}_1$ at pH = 5.3 (1.5 ± 0.2 M^{-1} s^{-1}), the slope of graphs a, b, and d almost equals the rate constant k_2 (64 ± 3 M^{-1} s^{-1} at the ionic strength 0.039 M). At the higher pH = 6.1, which was chosen in experiment c, the value of $\bar{k}_1$ is larger ($=13 \pm 2$ M^{-1} s^{-1}), and therefore, the slope of graph c is smaller than the slope of the other solid line curves.

In experiments carried out with an excess of peroxodisulfate, the term $\bar{k}_1[\bar{T}]$ cannot be omitted, especially after passing the maximum concentration of S^+. Therefore, the slope of the dotted graph d is larger than the slope of the corresponding solid line. Furthermore, the intercept of the dotted line is almost zero. This is obvious, because after complete oxidation the term $\bar{k}_1[\bar{R}]$ becomes zero ($\bar{k}_1[R]_o = \bar{k}_1[\bar{T}]$). The slight negative value of the intercept results from deamination and corresponds to the neglected term $(d[\bar{M}]/dt)/[S_2O_8^2]$. The rate constant k_2 can be obtained from the slope of both the solid line and the dotted line curve of graph d. This supports the assumption that this rate constant not only determines the disappearance of S^+ but also its formation.

Determination of $\bar{k}_1$ and k_2 only from d[S$^+$]/d*t*. During the course of the reaction, the synproportionation equilibrium will not be established perfectly, although the corresponding kinetic terms do not appear in (22). This phenomenum will be discussed later in more detail. However, also with an only approximately established equilibrium, the concentration of both $\bar{R}$ and $\bar{T}$ can be calculated for any concentration of S^+ by combining (8) with

(9) and neglecting the deamination, i.e., taking the concentration of quinonemonoimine to be zero:

$$[\bar{R}] = \frac{[R]_o - [S^+]}{2} \pm \frac{1}{2}\sqrt{([R]_o - [S^+])^2 - \frac{([S^+])^2}{\bar{K}_{S,app}/4}} \quad (23)$$

$$[\bar{T}] = \frac{[R]_o - [S^+]}{2} \mp \frac{1}{2}\sqrt{([R]_o - [S^+])^2 - \frac{([S^+])^2}{\bar{K}_{S,app}/4}} \quad (24)$$

The calculation of $[\bar{T}]$ is not only useful if further compounds in solution exhibit an absorbance around 287 nm but also offers the opportunity to restrict the measurements to the visible region of the spectrum. A procedure for a simple determination of the apparent equilibrium constant, $\bar{K}_{S,app}$, which almost equals the synproportionation constant $\bar{K}_s$ is given below.

Differentiation of (24) gives a relation between the change in $d[\bar{T}]$ and $d[S^+]$:

$$2d[\bar{T}] = \left(\pm \frac{([R]_o - [S^+]) + [S^+]/(\bar{K}_{S,app}/4)}{\sqrt{([R]_o - [S^+])^2 - [S^+]^2/(\bar{K}_{S,app}/4)}} - 1\right) d[S^+] \quad (25)$$

Thus, eq 22 can be transformed to eq 26:

$$\pm \frac{B}{2[S_2O_8^{2-}]}(d[S^+]/dt) = \bar{k}_1[R]_o - \bar{k}_1[\bar{T}] + (k_2 - \bar{k}_1)[S^+] \quad (26)$$

with

$$B = \frac{([R]_o - [S^+]) + [S^+]/(\bar{K}_{S,app}/4)}{\sqrt{([R]_o - [S^+])^2 - [S^+]^2/(\bar{K}_{S,app}/4)}} \quad (27)$$

and

$$[S_2O_8^{2-}] = [S_2O_8^{2-}]_o - 0.5[S^+] - [\bar{T}] \quad (28)$$

If deamination cannot be neglected, the difference $([R]_o - [\bar{M}])$, instead of $[R]_o$, has to be taken. Furthermore, on the left-hand side of (26), the term $(\bar{k}_D[\bar{T}]/[S_2O_8^{2-}])$ has to be added, and in eq 28, the term [M] has to be added.

Multiplication of (26) with $b\epsilon_{S,550}$ thus taking the absorbance $A_{550} = \epsilon_{S,550}b[S^+]$ instead of $[S^+]$ gives

$$Z = \pm \frac{B}{2[S_2O_8^{2-}]}(dA_{550}/dt) = \bar{k}_1\epsilon_{S,550}b[R]_o - \bar{k}_1\epsilon_{S,550}b[\bar{T}] + (k_2 - \bar{k}_1)A_{550} \quad (29)$$

In the absence of deamination, the reaction rate given by the decrease in $[S_2O_8^{2-}]$ can therefore be measured by the change in absorbance caused by only one of the products. The change in absorbance (dA_{550}/dt) can be determined at any point of the absorbance-time curve by means of a suitable method, e.g., with a mirror ruler or recorded directly as the derivative curve.

For experiments with $[R]_o > 2[S_2O_8^{2-}]_o$, only positive values of $(d[S^+]/dt)$ appear, and the positive sign has to be used in (26) and (29). On the other hand, for $[S_2O_8^{2-}]_o > 0.5[R]_o$, also negative values of $(d[S^+]/dt)$ have to be taken into account. Then for the second part of the reaction, the negative sign has to be applied. For the maximum concentration, $[S]_{max}$, eqs 26 and 29 are not defined because both $(d[S^+]/dt)$ and the term under the square root become zero. It has to be stressed that in contrast to (22), eqs 26 and 29 can only be applied when the synproportionation equilibrium is nearly established. Details on the limits of application are given below.

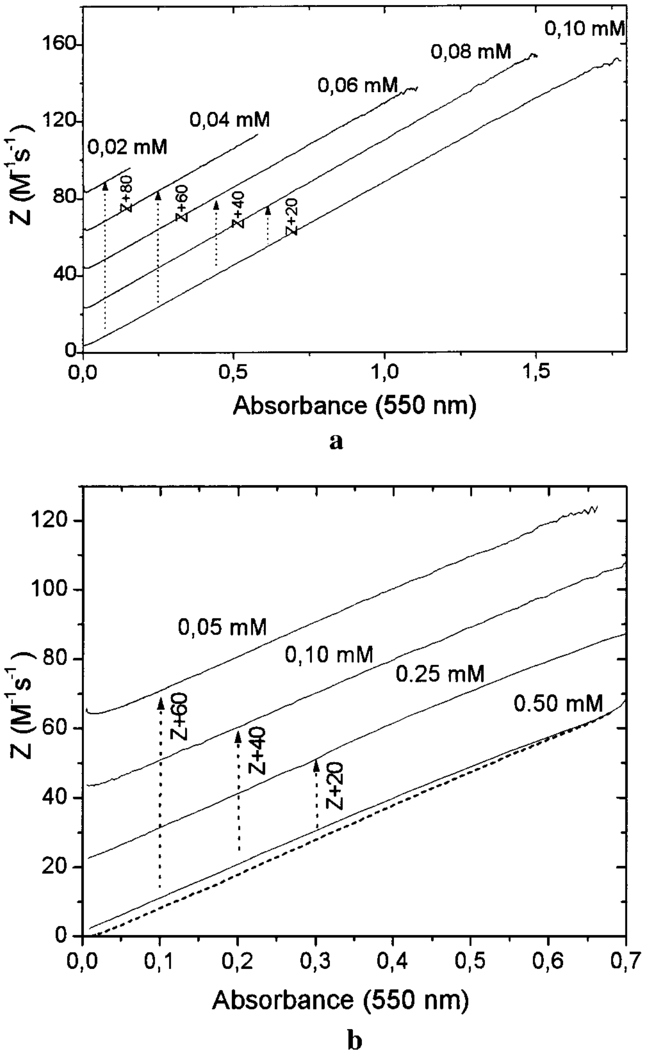


Figure 6. (a) Plot of Z according to eq 29 for the graphs displayed in Figure 3a. $[R]_o = 1.0 \times 10^{-3}$ M, $[S_2O_8^{2-}]_o = 2.0 \times 10^{-5}$–$1.0 \times 10^{-4}$ M, pH = 4.9. All graphs have almost the same slope and the same intercept. For a better presentation, the graphs are shifted vertically. The graphs were obtained from the derivate curves. The noise results from the not very accurately determined slope near the maximum absorbance. For the synproportionation constant, the value $\bar{K}_s = 28$ was chosen. (b) Plot of Z according to eq 29 for the graphs displayed in Figure 3b. $[R]_o = 1.0 \times 10^{-4}$ M, $[S_2O_8^{2-}]_o = 5.0 \times 10^{-5}$–$5.0 \times 10^{-4}$ M, pH = 5.4. All graphs have almost the same slope and the same intercept. For a better presentation, the graphs are shifted vertically. For the apparent synproportionation constant, the value $\bar{K}_{S,app} = 27.2$ was determined. The dotted graph was obtained from the negative slope of the absorbance–time curve.

A plot of Z against the corresponding absorbance gives graphs such as those displayed in Figure 6a for the experiments presented in Figure 3a, i.e., for $[R]_o > 2[S_2O_8^{2-}]_o$. Despite the strong increase in the reaction rate with increasing $[S_2O_8^{2-}]_o$, both the slope and the intercept of all straight lines are almost the same. For a better presentation, the graphs are separated by a vertical shift.

Graphs with almost the same slope (solid lines in Figure 6b) result for a plot of Z calculated from the data of the first part (increasing absorbance) of the experimental curves presented in Figure 3b, i.e., for $[S_2O_8^{2-}]_o \geq [R]_o$ (and also for $[S_2O_8^{2-}]_o = 0.5[R]_o$).

The dotted line corresponds to the data for the second part of the reaction (decreasing absorbance). The small difference from the solid line graph results from the term $\bar{k}_1\epsilon_{S,550}b[\bar{T}]$.

The intercept of the solid line graphs in Figure 6 allows the determination of the rate constant $\bar{k}_1$ (0.6 ± 0.1 M^{-1} s^{-1} at pH = 4.9 and 1.8 ± 0.2 M^{-1} s^{-1} at pH = 5.4), whereas the slope corresponds to the difference ($k_2 - \bar{k}_1$) and thus gives the rate constant k_2 (95 ± 4 M^{-1} s^{-1} at the ionic strength 0.025 M). The values correspond to those obtained from graphs such as those displayed in Figure 5 taking into account the dependence of $\bar{k}_1$ on the pH and the dependence of k_2 on the ionic strength. This coincidence proves that (29) can be applied instead of (22).

A plot of $\bar{k}_1$ according to (3) against $[H^+]$ (which is not very convenient because of the large scale of the abscissa) may give the value of the rate constant k_1 from the intercept and that of the rate constant k_{1H} from the slope.

It is obvious that the value of the rate constant $\bar{k}_1$ influences the slope of the graphs according to (22) and (29). The higher the value of $\bar{k}_1$, the flatter will the straight line be, whereas a change in the concentration of $\bar{R}$ only causes a parallel shift (see the graphs displayed in Figure 5). Because of the dependence of the rate constant k_2 on the ionic strength, the slope also depends on the kind and the concentration of all components in solution.

Side Reactions. For $[S_2O_8{}^{2-}]_o \gg [R]_o$, the absorbance-time curve is almost symmetrical (see Figure 3b). On the other hand, for $[S_2O_8{}^{2-}]_o = [R]_o$, the decrease in absorbance occurs noticeably slower than the increase. It may therefore be useful to compare the increase and the decrease in absorbance, (dA_{550}/dt), at a given absorbance.

In the absence of any side reaction, e.g., deamination, and assuming almost established synproportionation equilibrium for a given concentration of S^+, the term *B* has the same value for positive and negative values of ($d[S^+]/dt$) or (dA_{550}/dt). However, for negative values, the concentration of $S_2O_8{}^{2-}$ is by a factor *x* lower. This factor is given by the ratio of the concentrations of $S_2O_8{}^{2-}$ calculated according to (28). The factor *x* approaches 1 for a high ratio ($[S^+]/[S^+]_{max}$) as well as for a high value of the equilibrium constant $\bar{K}_s$.

Sometimes, the experimentally found difference in the reaction rate is larger than calculated according to the factor *x*. This indicates that some sulfate radicals are consumed in side reactions diminishing the actual concentration of $S_2O_8{}^{2-}$.

In aqueous solution, predominantly $\bar{T}$ may be attacked by $SO_4{}^-$, whereas in buffered solution, also reactions with the compounds of the buffer may take place. The examples displayed in Figure 7 show that phosphate ions are rather resistant against $SO_4{}^-$, whereas phthalate ions are attacked rapidly by $SO_4{}^-$. Analogous experiments have shown that also citrate ions rapidly react with $SO_4{}^-$. These results agree with the reported relatively low values for the rate constants of the reaction of the sulfate radical with $HPO_4{}^{2-}$ (1.2 × 10^6 M^{-1} s^{-1})[46] and $H_2PO_4{}^-$ (<7 × 10^4 M^{-1} s^{-1})[47] as well as with the high reaction rate of $SO_4{}^-$ of with some derivates of benzoic acid.[22]

For a quantitative interpretation of these results, the dependence of the reaction rate on both the pH and the ionic strength has also to be taken into account.

Determination of the Apparent Synproportionation Constant $\bar{K}_{S,app}$. The value of the apparent equilibrium constant, $\bar{K}_{S,app}$, can be obtained from experiments carried out with an excess of $S_2O_8{}^{2-}$. Under these conditions, the absorbance–time curve passes through a maximum (see the curves in Figures 2b and 3b). If the concentration of quinonemonoimine, [M], and other side products can be neglected for the established synproportionation equilibrium, the concentration of $\bar{T}$ should equal that of residual $\bar{R}$, and thus, with (9), the concentration of both residual $\bar{R}$ and already formed $\bar{T}$ can be expressed by the maximum concentration of semiquinonediimine, $[S^+]_{max}$:

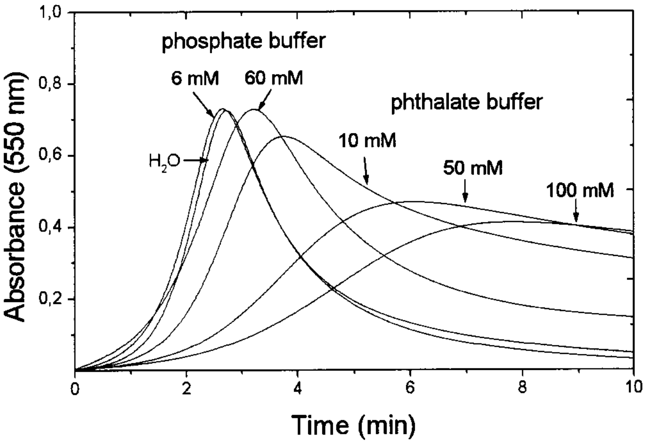


Figure 7. Influence of kind and concentration of buffer ions on the formation rate of *p*-semiquinonediimine. The first and the third curves were recorded in the presence of phosphate buffer (pH = 5.4), the second curve was recorded in unbuffered solution, and the last three experiments were carried out in the presence of phthalate buffer (pH = 4.0). The ionic strength was not kept constant.

$$\bar{K}_{S,app} = 4\frac{([S^+]_{max})^2}{([\bar{R}]_o - [S^+]_{max})^2} \tag{30}$$

It is noticeable that the initial concentration of $S_2O_8{}^{2-}$ does not have any direct influence on the determination of $\bar{K}_{S,app}$ according to this procedure, but it influences the deviation of its value from that of the real equilibrium constant $\bar{K}_s$.

Discussion

According to eq 17, the rate of the decrease in $S_2O_8{}^{2-}$ is given by four terms which describe the oxidation of $\bar{R}$ and S^+ by $S_2O_8{}^{2-}$ and $SO_4{}^-$. Analogous to the definition of mole fraction, the partial contribution of each of these oxidation steps on the total consumption of peroxodisulfate can be expressed by the fraction of a single term and the sum of all terms. Taking into account that according to (18) this sum equals ($\bar{k}_1[\bar{R}] + k_2[S^+]$) $[S_2O_8{}^{2-}]$ as well as ($\bar{k}_1^I[\bar{R}] + k_2[S^+]$)$[SO_4{}^-]$, oxidation coefficients f_i can be defined which describe the specific contribution of each oxidation step on the total oxidation.

Thus, the oxidation of $\bar{R}$ with $S_2O_8{}^{2-}$ is expressed by the oxidation coefficient f_1, and the oxidation of S^+ is expressed with $S_2O_8{}^{2-}$ by the oxidation coefficient f_2:

$$f_1 = 0.5\frac{\bar{k}_1[\bar{R}]}{(\bar{k}_1[\bar{R}] + k_2[S^+])} = \frac{0.5}{1 + (k_2/\bar{k}_1)([S^+]/[\bar{R}])} \tag{31a}$$

$$f_2 = 0.5\frac{k_2[S^+]}{(\bar{k}_1[\bar{R}] + k_2[S^+])} = \frac{0.5}{1 + (k_1/\bar{k}_2)([\bar{R}]/[S^+])} \tag{31b}$$

The factor 0.5 takes into account that $S_2O_8{}^{2-}$ carries out only 50% of the total oxidation. The other 50% are performed by the sulfate radical. The oxidation of $\bar{R}$ with $SO_4{}^-$ is expressed by the oxidation coefficient f_1^{I}, whereas the oxidation of S^+ with SO_4^- is defined by the oxidation coefficient f_2^{I}:

$$f_1^{\mathrm{I}} = 0.5\,\frac{\bar{k}_1^{\mathrm{I}}[\bar{\mathrm{R}}]}{(\bar{k}_1^{\mathrm{I}}[\bar{\mathrm{R}}] + k_2^{\mathrm{I}}[\mathrm{S}^+])} = \frac{0.5}{1 + (k_2^{\mathrm{I}}/\bar{k}_1^{\mathrm{I}})([\mathrm{S}^+]/[\bar{\mathrm{R}}])} \tag{32a}$$

$$f_2^{\mathrm{I}} = 0.5\frac{k_2^{\mathrm{I}}[\mathrm{S}^+]}{(\bar{k}_1^{\mathrm{I}}[\bar{\mathrm{R}}] + k_2^{\mathrm{I}}[\mathrm{S}^+])} = \frac{0.5}{1 + (\bar{k}_1^{\mathrm{I}}/k_2^{\mathrm{I}})([\bar{\mathrm{R}}]/[\mathrm{S}^+])} \tag{32b}$$

The sum of all four oxidation coefficients equals 1. The value of each term may range from $0 < f_i < 0.5$:

$$1 = f_1 + f_2 + f_1^{\mathrm{I}} + f_2^{\mathrm{I}} \tag{33a}$$

Furthermore, eq 33b is valid

$$(f_1 + f_2) = (f_1^{\mathrm{I}} + f_2^{\mathrm{I}}) = 0.5 \tag{33b}$$

Contribution of $S_2O_8^{2-}$ on the Oxidation of $\bar{R}$ and S^+. The contribution of peroxodisulfate on the oxidation of $\bar{R}$ and S^+, respectively, can be calculated according to (31a) with the experimentally determined rate constants $\bar{k}_1$ and k_2. Figure 8a shows for the second experimental curve presented in Figure 3b the change in the oxidation coefficients f_1 and f_2 during the course of the reaction (dashed−dotted curves). Displayed is also the decrease in $[\bar{R}]$ and $[S_2O_8^{2-}]$, as well as the change in $[S^+]$ and $[\bar{T}]$. For a better presentation, the normalized concentrations $([R]/[R]_o)$, $([S^+]/[R]_o)$, $([\bar{T}]/[R]_o)$, as well as $([S_2O_8^{2-}]/[R]_o)$ (right-hand-side scale) have been chosen. The concentrations of $\bar{R}$ and $\bar{T}$ were calculated according to (23) and (24), respectively, with $\bar{K}_s = 28$, and the concentration of $S_2O_8^{2-}$ was calculated according to (28).

Because $k_2 \gg \bar{k}_1$, the term $k_2[S^+]$ soon equals $\bar{k}_1[\bar{R}]$. Therefore, after the formation of only a small amount of S^+, the coefficients f_1 and f_2 become equal (=0.25). Further increase in $[S^+]$ causes a strong increase in the ratio (f_2/f_1), and the maximum value of f_2 (=0.5) is approached. The succeeding decrease in S^+ because of the formation of $\bar{T}$ does not cause a decrease in f_2 because the concentration of $\bar{R}$ also becomes very low. This behavior of the oxidation coefficients f_1 and f_2 proves that, in accordance with the assumed radical chain mechanism, peroxodisulfate predominantly oxidizes the organic radical, S^+. The oxidation of $\bar{R}$ should therefore preferably be carried out by the sulfate radical. Of course, SO_4^- might also react with S^+, thus, terminating the radical chain reaction.

Contribution of the Sulfate Radical on the Oxidation of $\bar{R}$ and S^+. The contribution of SO_4^- on the total oxidation could not be calculated from (32a) and (32b) because the rate constants $\bar{k}_1^{\mathrm{I}}$ and k_2^{I} could not be determined with the methods applied here. The oxidation coefficients f_1^{I} and f_2^{I} were calculated according to (32) from an estimated ratio of the rate constants $(\bar{k}_1/k_2^{\mathrm{I}})$. For $(\bar{k}_1^{\mathrm{I}}/k_2^{\mathrm{I}}) = 0.1$ the change in the oxidation coefficients f_1^{I} and f_2^{I} is displayed in Figure 8a by the dashed curves.

Common Contribution of $S_2O_8^{2-}$ and SO_4^-. The common contribution of $S_2O_8^{2-}$ and SO_4^- on the oxidation of $\bar{R}$ and S^+, respectively, can be regarded as the primary and secondary oxidation. It is given by the sum of the corresponding oxidation coefficients f_i as $(f_i + f_i^{\mathrm{I}})$. The graphs displayed in Figure 8b show this for three different assumed ratios $(\bar{k}_1^{\mathrm{I}}/k_2^{\mathrm{I}})$.

For the low ratio $(\bar{k}_1^{\mathrm{I}}/k_2) = 0.02$, which almost equals the experimentally determined ratio of the rate constants k_1 and k_2, the secondary oxidation soon dominates (dashed curves). The example displayed for the ratio 0.1 (dashed−dotted curves) corresponds to that of Figure 8a (addition of the dashed−dotted and dashed curves). Equal contribution of the primary and secondary oxidation is only reached at a higher concentration of S^+. This effect is more pronounced for the ratio $(\bar{k}_1^{\mathrm{I}}/k_2^{\mathrm{I}}) = 1$, but also in this case, the contribution of the secondary oxidation exceeds that of the primary oxidation some time before the maximum concentration of S^+ is reached (dotted curves). A higher ratio is unlikely because there is no reason the sulfate radical should attack the neutral organic compound easier than the organic radical.

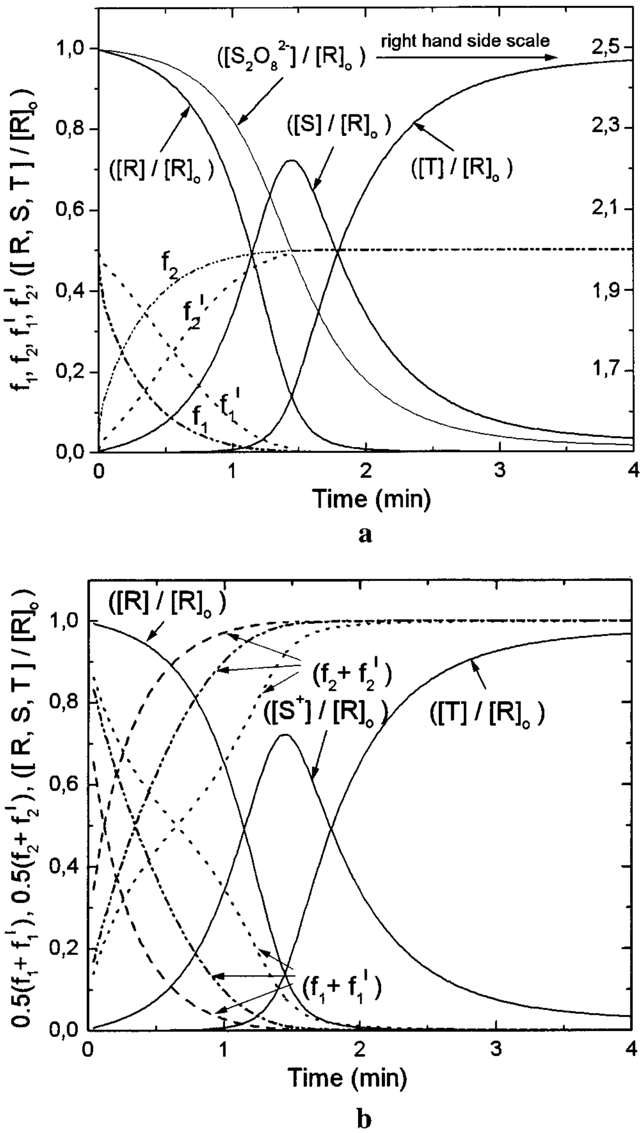


Figure 8. (a) Change of the relative concentrations of the differently oxidized species of *p*-phenylenediamine during the course of the reaction for the second experiment displayed in Figure 3b ($[R]_o = 0.1$ mM, $[S_2O_8^{2-}]_o = 0.25$ mM). Furthermore, the change of the oxidation coefficients f_1 and f_2 is displayed (dashed−dotted curves) as well as the change of the factors f_1^{I} and f_2^{I} for $(\bar{k}_1^{\mathrm{I}}/k_2^{\mathrm{I}}) = 0.1$ (dashed lines). (b) Plot similar to that in Figure 8a but according to eq 32b for the sum of the factors $(f_1 + f_1^{\mathrm{I}})$ and $(f_2 + f_2^{\mathrm{I}})$ which gives the relative contribution of the oxidation of *p*-phenylenediamine and *p*-semiquinonediimine by both peroxodisulfate and the sulfate radical. Three different ratios of the rate constants $\bar{k}_1^{\mathrm{I}}$ and k_2^{I} have been assumed: $(\bar{k}_1^{\mathrm{I}}/k_2^{\mathrm{I}}) = 0.02$ (dashed curves), 0.1 (dashed−dotted curves), and 1.0 (dotted curves).

Contribution of the Synproportionation to the Oxidation of $\bar{R}$. To avoid a confusing number of coefficients, the contribution of the synproportionation, r_{syn}, has also been referred to the consumption of peroxodisulfate:

$$r_{syn} = \frac{\bar{k}_s[\bar{R}][\bar{T}] - k_{-s}[S^+]^2}{(\bar{k}_1[\bar{R}] + k_2[S^+])[S_2O_8{}^{2-}]} \tag{34}$$

The difference ($\bar{k}_s[\bar{R}][\bar{T}] - k_{-s}[S^+]^2$) gives the degree of deviation from the synproportionation equilibrium and can be regarded as the pump of the autocatalytic reaction. A simple relation between r_{syn} and the oxidation coefficients f_i is obtained from the ratio of the kinetic eqs 14 and 16 taking into account (18) as well as (19) and neglecting the term concerning the deamination:

$$\frac{-(d[\bar{R}]/dt)}{-(d[S_2O_8{}^{2-}]dt)} = 2(f_1 + f_1^I) + r_{syn} \tag{35}$$

According to (9) and (10), the terms $-(d[\bar{R}]/dt)$ and $-(d[S_2O_8{}^{2-}]/dt)$ can be expressed by $(d[S^+]/dt) + (d[\bar{T}]/dt)$ and $0.5(d[S^+]/dt) + (d[\bar{T}]/dt)$, respectively. Furthermore, the coefficients for the primary oxidation are substituted by those for the secondary oxidation. Suitable rearrangement of the resulting equation gives (36):

$$r_{syn} = \frac{0.5(d[S^+]/dt)}{0.5(d[S^+]/dt) + (d[\bar{T}]/dt)} - 1 + 2(f_2 + f_2^I) \tag{36}$$

Based on this equation some limiting cases will be considered.

(a) For $(d[\bar{T}]/dt) \ll (d[S^+]/dt)$, the fraction in (36) is almost 1, and thus, r_{syn} equals $2(f_2 + f_2^I)$. As in the beginning of the reaction, the oxidation coefficients f_2 and f_2^I are near zero, r_{syn} will also be $\ll 1$, and $\bar{R}$ is predominantly oxidized by $S_2O_8{}^{2-}$ and $SO_4{}^-$.

(b) The formation of S^+ causes a strong increase in the coefficient f_2 (see Figure 8a). Its maximum value, $f_2 = 0.5$, is sometimes reached before noticeable formation of $\bar{T}$ begins. As a consequence, r_{syn} may become > 1; that is, $\bar{R}$ is also oxidized indirectly by $\bar{T}$.

(c) If $(d[\bar{T}]/dt) \ll (d[S^+]/dt)$ but both coefficients f_2 and f_2^I approach their maximum value 0.5, also r_{syn} reaches its maximum value, $r_{syn} = 2$. Because the coefficients f_1 and f_1^I are close to zero, the primary oxidation loses its importance. Almost all *p*-phenylenediamine is indirectly oxidized by $\bar{T}$. The limiting value 2 indicates the maximum autocatalytic increase of S^+, but rate determining remains the oxidation of S^+ by $S_2O_8{}^{2-}$. Each molecule of $S_2O_8{}^{2-}$ gives two molecules of $\bar{T}$: one molecule directly, and the other one indirectly via the oxidation of S^+ by $SO_4{}^-$. Two molecules of $\bar{T}$ then react with two molecules of $\bar{R}$ and give four molecules of S^+.

(d) As soon as noticeable formation of $\bar{T}$ takes place, the fraction in (36) becomes <1. A possible increase in r_{syn} because of an increase in the coefficients f_2 and f_2^I may therefore be canceled. Under these conditions, the value of r_{syn} depends on several parameters.

(e) When $(d[S^+]/dt)$ becomes zero, also the fraction in (36) reaches the value zero. This occurs at the end of the reaction for experiments carried out with a stoichiometric excess of $\bar{R}$ as well as at the maximum of the absorbance−time curve (at 550 nm) for experiments performed with a stoichiometric excess of $S_2O_8{}^{2-}$. In the first case, which is not of special interest here, also $(d[\bar{T}]/dt) = 0$, whereas in the second case, the formation of quinonediimine occurs with its maximum rate. At this point of the reaction, r_{syn} therefore equals the term $(2f_2 + 2f_2^I - 1)$ and is ≤ 1. For $f_2 \rightarrow 0.5$ and $f_2^I \rightarrow 0.5$, the term r_{syn} would approach 1. This would mean that as many molecules of S^+ oxidized by $S_2O_8{}^{2-}$ are regenerated by synproportionation. (One molecule of $S_2O_8{}^{2-}$ oxidizes directly and indirectly (with $SO_4{}^-$) two molecules of S^+ which are recovered by the reaction of one molecule of $\bar{T}$ with one molecule of $\bar{R}$. One molecule of $\bar{T}$ does not participate in the synproportionation reaction.) Under these conditions, no autocatalysis takes place, but the oxidation of $\bar{R}$ occurs exclusively by the synproportionation reaction. Usually, the coefficient f_2^I will not reach the value 0.5; that is, the coefficient f_1^I will be larger than 0, and therefore, some *p*-phenylenediamine will also be oxidized by the sulfate radical according to the radical chain mechanism.

(f) A negative value of $(d[S^+]/dt)$, which appears in experiments with a stoichiometric excess of $S_2O_8{}^{2-}$, decreases the ratio r_{syn} even if the coefficient f_2^I reaches its maximum value 0.5. When all $\bar{R}$ is consumed, the rate of decrease in S^+, $-(d[S^+]/dt)$, equals the formation rate of $\bar{T}$, $(d[\bar{T}]/dt)$, and the fraction in (36) has the value of −1. Thus, r_{syn} becomes zero. This is obvious because after the consumption of all $\bar{R}$ no synproportionation can take place anymore.

Contribution of the Radical Chain Reaction. In a normal two-electron consecutive reaction, the concentration of S^+ can only reach a high value if the secondary oxidation occurs much slower than the primary oxidation. Otherwise, a low quasi-stationary concentration will be established, and the ratio $([S^+]/[\bar{R}])$ is given by eq 37, which is obtained by combining (18) with (11) not considering the terms that are due to synproportionation and disproportionation and taking $(d[S^+]/dt) = 0$:

$$\left[\frac{[S^+]}{[\bar{R}]}\right]_{qst} = \sqrt{\frac{\bar{k}_1\bar{k}_1^I}{k_2 k_2^I}} \tag{37}$$

With $\bar{k}_1^I = k_2^I$, this ratio would equal the square root of $(\bar{k}_1/k_2)$; that is, it would be $\ll 1$. Because of the low concentration of S^+, the resulting sulfate radical would predominantly react with $\bar{R}$ thus regenerating S^+. The reaction of $SO_4{}^-$ with S^+ terminates this radical chain reaction and is therefore unfavorable.

Of course, eq 37 has also to be valid for a radical chain reaction, i.e., with both $r_{syn} = 0$ and $(d[S^+]/dt) = 0$. This results in $(f_2 + f_2^I) = 0.5$ and $(f_1 + f_1^I) = 0.5$. On the assumption that $S_2O_8{}^{2-}$ exclusively attacks S^+ ($f_2 = 0.5$ and $f_1 = 0$), the coefficient f_1^I has to be 0.5, and therefore, the coefficient f_2^I has to be zero, because the sum of all factors is 1. This seems to be unlikely, and therefore, some oxidation of *p*-phenylenediamine by peroxodisulfate has to be taken into account also for a simple radical chain mechanism.

Because of the influence of the synproportionation, the concentration of S^+ is not limited by eq 37. The stationarity of S^+ is restricted to the small region in the maximum of the absorbance−time curve. On the other hand, at the beginning, the radical chain reaction may strongly influence the course of the reaction. Opposite to a normal radical chain mechanism, the reaction of $SO_4{}^-$ with S^+ does not terminate the chain. It even accelerates the radical chain reaction because of the autocatalytic increase of S^+, which then by reaction with $S_2O_8{}^{2-}$ produces more sulfate radicals. Computer-based simulations have shown that the concentration of $SO_4{}^-$ remains very low but increases almost proportional to the increase in S^+. For experiments with an excess of $\bar{R}$, the maximum concentration of $SO_4{}^-$ is usually reached at the maximum formation rate of S^+.

Estimation of the Ratio of the Rate Constants $\bar{k}_1^I$ and k_2^I. For (d[S$^+$]/d*t*) = 0, from equations (36) and (34) results

$$r_{syn} = \frac{(\bar{k}_s[\bar{R}][\bar{T}] - k_{-s}[S^+]^2)_{S,max}}{(\bar{k}_1[\bar{R}] + k_2[S^+])_{S,max}[S_2O_8{}^{2-}]_{S,max}} = 2(f_2 + f^I_2)_{S,max} - 1 \quad (38)$$

The concentration of S$^+$ can accurately be determined. A slight error in the calculated values of f_2 and $[S_2O_8{}^{2-}]$ does not have a strong influence. The concentration of $\bar{T}$ may be exactly determined from measurements in the UV, and thus, the concentration of $\bar{R}$ can also be calculated. With the exact knowledge of the rate constants $\bar{k}_s$ and $\bar{k}_{-s}$, the determination of the oxidation coefficient f^I_2 should therefore be possible. Thus, with (32b), the ratio $(\bar{k}_1^I/k_2^I)$ may be estimated which then allows the calculation of f^I_1 and f^I_2 for any point of the reaction.

Estimation of the Deviations from the Equilibrium Constants $\bar{K}_s$ and $K_{S,app}$. Rearrangement of (38) gives (for S_{max})

$$\frac{\bar{k}_s[\bar{R}][\bar{T}]}{k_{-s}[S^+]^2} = 1 + (2f_2 + 2f^I_2 - 1)\frac{(\bar{k}_1[\bar{R}] + k_2[S^+])[S_2O_8{}^{2-}]}{k_{-s}([S^+])^2} \quad (39)$$

For the established equilibrium, the term on the left-hand side of this equation would have the value 1. The lower the ratio (k_2/k_{-s}), the smaller will the last term in this equation be. For *N*,*N*-dimethyl-*p*-phenylenediamine, this ratio is <0.001. Therefore, even in the presence of a high excess of $S_2O_8{}^{2-}$, the deviation of the right-hand side term from the value 1 is small. Therefore, a plot of the experimental results according to (29), which is based on the apparent synproportionation constant $\bar{K}_{S,app}$ (see eqs 23−27), gives reliable results. The constant $\bar{K}_{S,app}$ is a little smaller than $\bar{K}_s = (\bar{k}_s/k_{-s})$ but larger than the term $([S^+])^2/([\bar{R}][\bar{T}])$.

The difference $(\bar{k}_s[\bar{R}][\bar{T}] - k_{-s}[S^+]^2)_{S,max}$ not only demonstrates the contribution of synproportionation on the primary oxidation but also gives the degree of deviation of the apparent synproportionation constant $\bar{K}_{S,app}$ from the real equilibrium constant $\bar{K}_s$. High values of the rate constants $\bar{k}_s$ and k_{-s} are therefore necessary to apply (26) and (29), respectively; that is, the synproportionation reaction has to be sufficiently fast. For *N*,*N*-dimethyl-*p*-phenylendediamine, these rate constants have been determined by stopped-flow experiments as 1.1 × 10^6 and 4.0 × 10^4 M^{-1} s^{-1} at 25 °C.[39] Thus, the deviation from the synproportionation equilibrium is smaller than 1%. On the other hand, the determination of the ratio $(\bar{k}_1^I/k_2^I)$ becomes more difficult.

Influence of the Oxidation Coefficients f_i on the Term *Y*. The contribution of $S_2O_8{}^{2-}$ and $SO_4{}^-$ on the primary and secondary oxidation respectively can also be demonstrated by considering the term Y more in detail. For this purpose, both (19) and (17) are divided by $[S_2O_8{}^{2-}]$. Furthermore, the ratio $([SO_4{}^-]/[S_2O_8{}^{2-}])$ is substituted by the terms given in eq 18, and the oxididation coefficients are introduced. Thus, analogously to (22), eqs 40a and 40b are obtained:

$$Y = \bar{k}_1[\bar{R}] + k_2[S^+] \quad (40a)$$

$$Y = 0.5\bar{k}_1[\bar{R}] + 0.5k_2[S^+] + 0.5\frac{f^I_i}{f_1}\bar{k}_1[\bar{R}] + 0.5\frac{f^I_2}{f_2}k_2[S^+] \quad (40b)$$

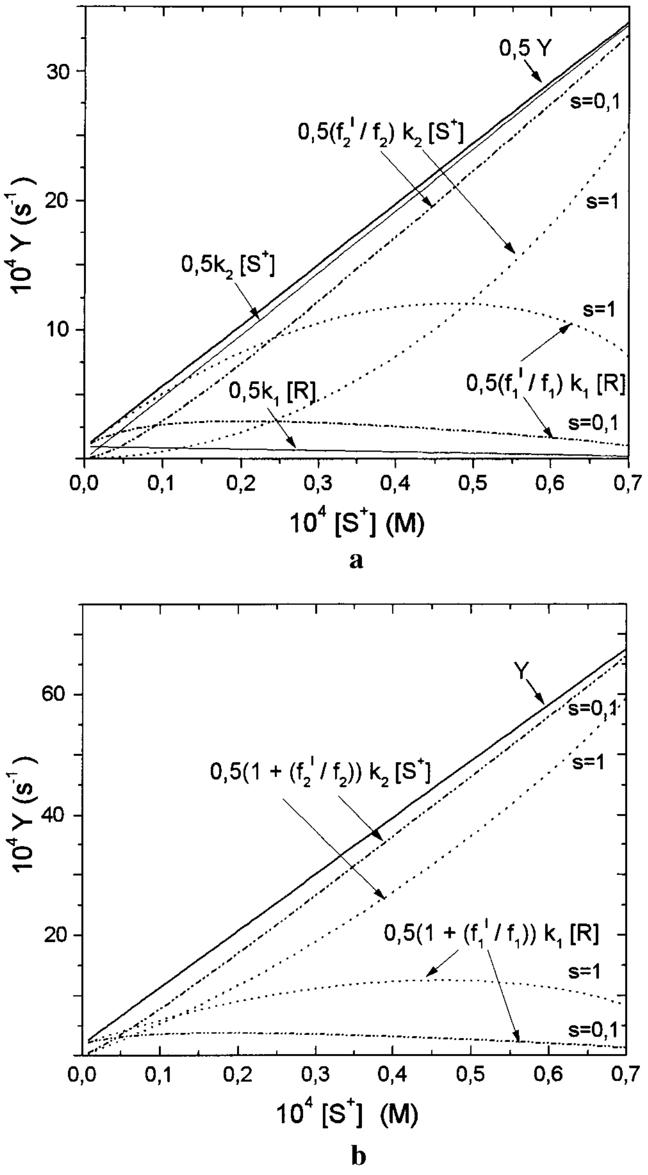


Figure 9. (a) Plot of the calculated terms according to eq 40 for $[R]_o$ = 0.1 mM and $[S_2O_8{}^{2-}]_o$ = 0.25 mM assuming for $s = (\bar{k}_1^I/k_2^I)$ the values 0.1 and 1.0. (b) Plots similar to those presented in Figure 9a but according to (41) for the demonstration of the contribution of the total primary and secondary oxidation.

A comparison of eq 40a with eq 40b may cause some confusion because (40b) seems to equal (40a) only when the ratio of the coefficients have the value 1. However, the sum of the last two terms in (40b) can equal the sum of the first two terms for many ratios of the last terms. This is demonstrated by the graphs displayed in Figure 9a which show the dependence of the individual terms of eq 40b, as well as the sum of both the first two terms and the last two terms, on the concentration of semiquinonediimine for the experiment already presented in Figure 8a.

The single terms were calculated with the experimentally determined kinetic constants $\bar{k}_1$ and k_2. The coefficients f_1 and f_2 could also be calculated based on experimental results, whereas the coefficients f^I_1 and f^I_2 were calculated according to the estimated ratios $(\bar{k}_1^I/k_2^I) = s = 0.1$ and 1.0.

At any point on the abscissa, the sum of the terms $0.5\bar{k}_1[\bar{R}]$ and $0.5k_2[S^+]$ gives the value of 0.5*Y* (thick solid line). The same value results from the addition of the last two terms of (40b) although the single graphs may show a strong deviation from a straight line (addition of the dotted curves as well as addition of the dashed−dotted curves).

Rearrangement of (40b) gives (41) which describes the common contribution of $S_2O_8^{2-}$ and SO_4^- on the primary and the secondary oxidation:

$$Y = 0.5\left(1+\frac{f_1^{\mathrm{I}}}{f_1}\right)\bar{k}_1[\bar{\mathrm{R}}] + 0.5\left(1+\frac{f_2^{\mathrm{I}}}{f_2}\right)k_2[\mathrm{S}^+] \qquad (41)$$

The corresponding graphs are displayed in Figure 9b for the two assumed ratios $(\bar{k}_1^{\mathrm{I}}/k_2^{\mathrm{I}}) = s = 0.1$ and 1.0, respectively. The addition of the graphs (dashed−dotted line or dotted line respectively) at any point of the abscissa gives the value of Y (thick solid line).

The influence of synproportionation cannot be detected directly from the plots in Figure 9a,b because the term Y only refers to the decrease in the concentration of peroxodisulfate. On the other hand, it is obvious that at least as many molecules phenylenediamine have to be oxidized as molecules semiquinonediimine.

For $(\mathrm{d}[\bar{\mathrm{T}}]/\mathrm{d}t) \approx 0$, a comparison of (11) with (17) or (19) may also cause some irritation. In (17) and (19), the terms for the primary oxidation appear with a positive sign, but in eq 11, they appear with negative signs. If the synproportionation equilibrium is established, the term $\bar{k}_\mathrm{s}[\bar{\mathrm{R}}][\bar{\mathrm{T}}]$ would cancel the term $k_{-\mathrm{s}}[\mathrm{S}^+]^2$. An always positive value of the formation rate of S^+ is therefore only possible when the term $\bar{k}_\mathrm{s}[\bar{\mathrm{R}}][\bar{\mathrm{T}}]$ exceeds the term $k_{-\mathrm{s}}[\mathrm{S}^+]^2$. As mentioned above, the difference $(\bar{k}_\mathrm{s}[\bar{\mathrm{R}}][\bar{\mathrm{T}}] - k_{-\mathrm{s}}[\mathrm{S}^+]^2)$ can therefore be regarded as the pump of the autocatalytic reaction. This term should be large in order to regenerate with high efficiency semiquinonediimine, but it cannot be larger than twice the sum $(\bar{k}_1[\bar{\mathrm{R}}] + k_2[\mathrm{S}^+])$. Otherwise, the factors f_i would become negative.

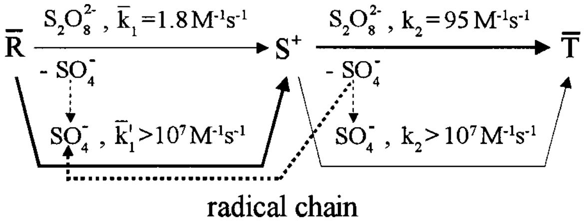
Limits of Accuracy. A plot according to (22) or (29) yields a reliable value of the rate constant k_2 even if the concentration of *p*-phenylenediamine is not well defined. Because $\bar{k}_1[\bar{\mathrm{R}}] \ll 0.5k_2[\mathrm{S}^+]$, the slope of the straight line is hardly influenced. For experiments carried out with an excess of peroxodisulfate, a slight error in the concentration of this compound does not noticeably influence the accuracy of the determination of the rate constants. Only for experiments carried out with an excess of *p*-phenylenediamine, the concentration of peroxodisulfate strongly influences the position of the graphs and thus the value of the rate constants. Therefore, the determination of the rate constant k_2 may be more accurate from experiments carried out with an excess of peroxodisulfate.

Conclusions

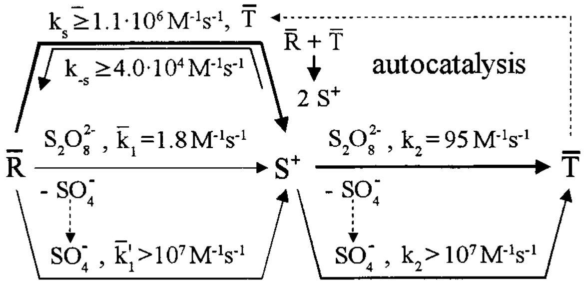
The example presented here shows that an apparent simple reaction between only two compounds, *N*,*N*-dimethyl-*p*-phenylenediamine and peroxodisulfate, may follow a very complex mechanism. Two consecutive reactions $(\bar{\mathrm{R}} \rightarrow \mathrm{S}^+ \rightarrow \bar{\mathrm{T}})$ and $(S_2O_8^{2-} \rightarrow SO_4^- \rightarrow SO_4^{2-})$ are coupled with four parallel reactions $(\bar{\mathrm{R}} + S_2O_8^{2-} \rightarrow \mathrm{S}^+)$, $(\mathrm{S}^+ + S_2O_8^{2-} \rightarrow \bar{\mathrm{T}})$, $(\bar{\mathrm{R}} + SO_4^- \rightarrow \mathrm{S}^+)$, and $(\mathrm{S}^+ + SO_4^- \rightarrow \bar{\mathrm{T}})$. Two of these reactions establish a radical chain because of the production (regeneration) of the sulfate radical $(\mathrm{S}^+ + S_2O_8^{2-} \rightarrow \bar{\mathrm{T}} + SO_4^-)$ and the regeneration of S^+ $(\bar{\mathrm{R}} + SO_4^- \rightarrow \mathrm{S}^+ + SO_4^{2-})$. In Scheme 3, these reactions are stressed by thick arrows.

If only this mechanism would be valid, a quasistationary low concentration of S^+ would be established. However, the fast redox reaction between $\bar{\mathrm{T}}$ and $\bar{\mathrm{R}}$ causes autocatalysis and the concentration of S^+ increases. In Scheme 4, the most important steps of this autocatalysis are indicated by thick arrows. Furthermore, both $\bar{\mathrm{R}}$ and S^+ may be oxidized by SO_4^- with a similar rate. The synproportionation can be regarded as the pump of the overall reaction.

SCHEME 3



SCHEME 4



Despite the very complex mechanism, the determination of the most important rate constants does not cause serious problems. On the other hand, the evaluation of accurate values demands the maintenance of several parameters such as pH and ionic strength. This may cause some problems because the sulfate radical not only oxidizes the organic compounds of interest but also many other compounds present in solution.

It might be possible that many other redox reactions of this kind occur according to a similar mechanism. For example, the oxidation of succinic acid by $S_2O_8^{2-}$ was found to be zero order in the organic compound.[11] A zero order dependence was also found for the oxidation of manganese(II)[6] and dodeca-tungstocobaltate(II).[7] An autocatalytic mechanism will not be detected, however, when only a few experiments with a high excess of peroxodisulfate, i.e., under pseudo-first-order conditions, are carried out. An apparent first order dependence was found for the oxidation of *N*,*N*,*N′*,*N′*-tetramethyl-*p*-phenylenediamine[12] and the corresponding tetraethyl compound.[13] Under the chosen experimental conditions, the induction period could not be observed, and thus, from the increase in the product concentration, the rate constant for the primary oxidation was calculated, although the rate of the reaction might be determined by the rate constant of the secondary reaction. For this reason, at least some experiments under extreme conditions such as those displayed in Figure 4 should be carried out, to detect any deviation from an assumed simple mechanism.

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References and Notes

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