its success can be readily judged. For families of similar compounds (like the acenes, the polyphenyls, etc.), the method can easily predict crystal structures in which the space group is the same as that of the parent compound, and some cell parameters are changed. This task has been accomplished for a number of thiophene oligomers.[24] In general, the approach outlined here can be useful whenever partial structural or spectroscopic information is available; then, trial structures can be generated, and the calculated crystal properties can be matched to the experimental ones.

The procedure should become more and more selective, and therefore efficient, with increasing molecular polarity and when stronger directional pointers are present, as is the case for hydrogen bonding. Of course, the empirical potentials must be appropriately updated to deal with such systems.[25] Generalization of the method to include more complex interaction potentials and to take into account any combination of symmetry operators is being considered for future work.

Acknowledgment. Preliminary accounts of this method have been presented at the Mendel Cohen Memorial Symposium (Rehovot, February 1990), at the Symposium on Chemistry and Structure (Swiss Crystallographic Society, Zurich, March 1990), at the NATO Advanced Research Workshop on Electron Crystallography (Erice, April 1990), and at the XVIII Congress of the International Union of Crystallography (Bordeaux, July 1990). Financial support from MURST-Fondi 40% is gratefully acknowledged. Copies of the computer programs used are available from the author at the electronic mail address GAVEZ at IMISIAM.

Supplementary Material Available: Table X, with C-atom coordinates for all the calculated structures, and Appendix I, Cartesian coordinate model of the nuclei, Appendix II, Generation of translation vectors, and Appendix III, Use of the PCK83 program (16 pages). Ordering information is given in any current masthead.

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One-Electron Reduction of *N*-Bromosuccinimide. Rapid Expulsion of a Bromine Atom[†]

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Abstract: By means of pulse radiolysis *N*-bromosuccinimide, SBr, was reduced to its radical anion, SBr$^{\bullet-}$. Evidence is presented that SBr$^{\bullet-}$ rapidly fragments into the succinimide anion, S$^-$, and a free bromine atom, Br$^{\bullet}$, which is converted into $Br_2^{\bullet-}$ by reacting with Br$^-$ present. The rate constant of hydrogen abstraction by Br$^{\bullet}$ from 2-propanol and methanol have been determined. The carbon-centered radical of *tert*-butyl alcohol was also found to react with SBr yielding $Br_2^{\bullet-}$ in the presence of Br$^-$.

Introduction

Succinimidyl radical chemistry has long been dominated by a lively discussion[1–4] about the possible existence of two-electron isomeric succinimidyl radicals, to which were assigned the π and σ states.[1e] This suggestion was eventually abandoned,[1a] but in the system *N*-bromosuccinimide(SBr)/bromine/substrate quantification of the end products appears to demand the existence of a third chain carrier.[1a,3] Attempts to generate succinimidyl radical from SBr via a one-electron reductive pathway initially looked promising,[5,6] but later it turned out that the reactions observed could be better explained by a polar mechanism.[7,8] Lasting facts from these studies were provided by the isolation and X-ray structural elucidation of SBr···Br$^-$ complexes[9,10] which seem to play an important role in the chemistry of SBr, as, for example, indicated by a catalytic effect of bromide ion upon the electron-transfer oxidative properties of SBr toward ferrocene,[11] in the formation of tribromide ion in the thermal decomposition of SBr/bromide solutions in acetonitrile[12] and in halogen heteroexchange reactions between *N*-halosuccinimide and halide ion.[13] The existence and stability of SBr/Br$^-$ complexes lend credibility

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[†] Keywords: *N*-bromosuccinimide, pulse radiolysis, one-electron reduction, bromine atom, succinimidyl radical.

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Table I. Rate Constants Determined in This Work[f]

reaction	k	lit. value
$e^{-aq} + \mathrm{SBr}$	2.9×10^{10}	
$(\mathrm{CH_3})_2(\mathrm{OH})\mathrm{C}^{\bullet} + \mathrm{SBr}$	2.2×10^{9}	
$\mathrm{Br}^{\bullet} + (\mathrm{CH_3})_2\mathrm{CHOH}$	4.5×10^{5}	
$\mathrm{Br}^{\bullet} + \mathrm{CH_3OH}$	1.3×10^{4}	
$\mathrm{O_2}^{\bullet-} + \mathrm{SBr}$	4.8×10^{8}	
$\mathrm{OH}^{\bullet} + \mathrm{SBr}$	3.6×10^{8}	
$\mathrm{Br}^{\bullet} + \mathrm{Br}^-$	$1.0 \pm 0.5 \times 10^{10}$	$1.1 \pm 0.1 \times 10^{10}$[a]
$\mathrm{Br_2}^{\bullet-} + \mathrm{Br}^{\bullet} + \mathrm{Br}^-$	$4.6 \pm 1 \times 10^{4}$	3.5×10^{4}[b]
$\mathrm{Br}^{\bullet} + \mathrm{OH}^-$	1.3×10^{10}	1.3×10^{10}[c]
$\mathrm{Br_2}^{\bullet-} + \mathrm{N_3}^-$	$1.8 \pm 0.2 \times 10^{8}$	4.0×10^{8}[d]
$\mathrm{Br_2}^{\bullet-} + \mathrm{HN_3}$	5×10^{8}	
$\mathrm{OH}^{\bullet} + \mathrm{Ag}^+$	9.7×10^{9}	1.4×10^{10}[e]

[a] The mean value of three measurements in ref 16. [b] The value is taken from ref 16. Values calculated from the equilibrium constant are 5×10^4 (ref 16) and 10^5 (ref 17). The first-order rate constants are expressed in s^{-1} unit. [c] Reference 16. [d] Reference 16, the literatue value was measured at an ionic strength of 0.2 M, while our measurements refer to $I = 0.01$ M. [e] Reference 18. [f] All units in $M^{-1}\,s^{-1}$ except where indicated otherwise.

to the suggestion of an $\mathrm{SBr}/\mathrm{Br}^{\bullet}$ adduct, the corresponding one-electron oxidation product. Likewise, the existence of *N*-bromoimide/imide anion complexes of the type $\mathrm{SBr}\cdots\mathrm{S}^-$ [14,15] and the fact that they show up as separate entities in the cyclic voltammograms of SBr[5] point to a certain stability of $\mathrm{SBr}\cdots\mathrm{S}^{\bullet}$ species.

The electrochemical reduction of SBr afforded S^-. However, due to the high concentration of reductants and since both $\mathrm{S}^{\bullet}$ and $\mathrm{Br}^{\bullet}$ are strong oxidants the primary events could not be ascertained. This difficulty does not apply to the pulse radiolytic technique, in which micromolar concentrations of electrons can be created instantaneously in solutions of a large excess of SBr. Thus it becomes possible to generate $\mathrm{SBr}^{\bullet-}$ and study its further reactions. We now provide evidence that $\mathrm{SBr}^{\bullet-}$ is cleaved to give S^- and $\mathrm{Br}^{\bullet}$. This fragmentation mode is unexpected, the opposite fragmentation into $\mathrm{S}^{\bullet}$ and Br^- having been taken for granted.[5]

Results and Discussion

One-Electron Reduction. In argon-saturated aqueous solutions containing 0.1 M *tert*-butyl alcohol (*t*-BuOH), the hydrated electron, e^-_{aq}, forms with a yield of 2.8×10^{-7} mol/J, while the $\mathrm{OH}^{\bullet}$ radical, produced with the same yield, is converted into rather unreactive $(\mathrm{CH_3})_2(\mathrm{OH})\mathrm{CCH_2}^{\bullet}$ radicals. Upon addition of 5×10^{-5} to 5×10^{-4} M of recrystallized SBr to such solutions e^-_{aq} disappears rapidly. By monitoring the strong characteristic absorbance of e^-_{aq} at 600–700 nm the rate constant of reaction 1 was determined (Table I). Searching the spectral region 300–700

$$\mathrm{SBr} + e^-_{aq} \rightarrow \mathrm{SBr}^{\bullet-} \tag{1}$$

nm for an absorbance buildup concomitant with reaction 1 proved futile. Thus it would seem that $\mathrm{SBr}^{\bullet-}$ either does not absorb in this spectral region or is too short-lived for observation. As will be shown below, the latter alternative obtains in this case. However, on a longer time scale an absorbance, with a spectral shape similar to that of $\mathrm{Br_2}^{\bullet-}$, was observed to build up. Its apparent extinction coefficient at 360 nm was less than 20% of that of the $\mathrm{Br_2}^{\bullet-}$ radical obtained in the presence of Br^- (see below). This clearly shows that an "invisible" intermediate is the precursor to this weakly colored species. Extensive recrystallization of SBr did not change the manner in which the sample responded to e^- beam irradiation.

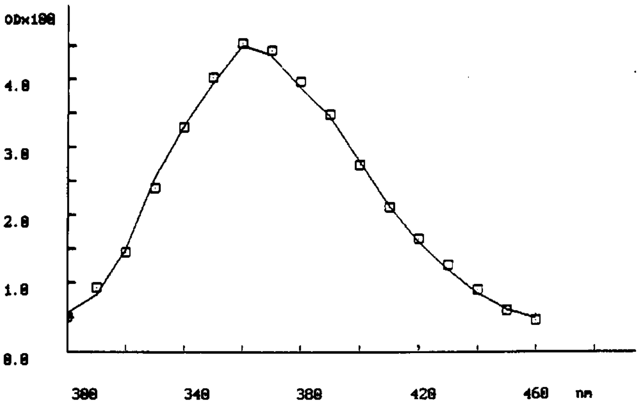

Figure 1. Transient spectra at maximum signal obtained by pulse radiolysis at 8.5 Gy/pulse of aqueous neutral solutions. Conditions: 5×10^{-4} M SBr; 5×10^{-3} M Br^-; 0.25 M 2-propanol, argon saturation and 10^{-2} M Br^-, $\mathrm{N_2O}$ saturation. The line was drawn through the experimental absorbances after scaling the latter by 1.12. This factor accounts for the fact that, contrary to case in the SBr solution ( ), the hydrogen atom does not produce $\mathrm{Br_2}^{\bullet-}$.

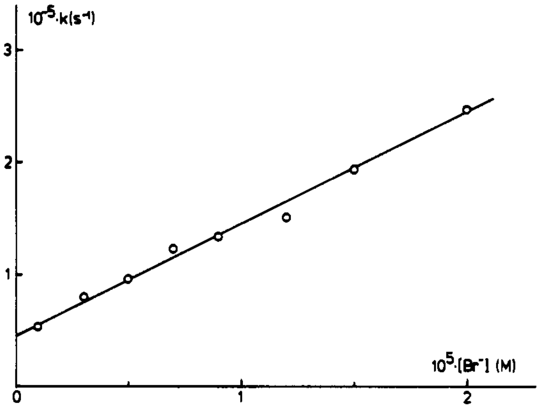

Figure 2. Rate constant of the buildup of the absorbance at 360 nm as a function of the Br^- concentration. Conditions: [SBr] 10^{-4} M, [*t*-BuOH] 0.05 M, argon saturation.

For reasons of comparison *N*-bromophthalimide (PBr) was also reduced by e^-_{aq}. In contrast to the case of SBr an absorbance centering around 325 nm ($\epsilon_{325} = 2500\ M^{-1}\,cm^{-1}$) appeared concomitant with the decay of e^-_{aq}. The 325-nm absorbance decayed slowly ($k < 10^5\ s^{-1}$) giving rise to the same 360-nm absorbance as was observed with SBr. We believe that the 325-nm absorbance is due to $\mathrm{PBr}^{\bullet-}$. Further investigation of a number of *N*-haloimides is envisaged in order to clarify this point.

Addition of Br^-. When the above-described SBr solution was pulse irradiated in the presence of added Br^- (5×10^{-5}–10^{-3} M), the decay of the e^-_{aq} absorbance was followed by a buildup of an absorption identical with that of $\mathrm{Br_2}^{\bullet-}$ (Figure 1). Further evidence for $\mathrm{Br_2}^{\bullet-}$ formation in the presence of added Br^- was as follows: (1) This species and authentic $\mathrm{Br_2}^{\bullet-}$ had the same rate of self-reaction, i.e., $2k/\epsilon_{360} = 4.5 \times 10^3$ m/s. (2) Both species oxidized $\mathrm{N_3}^-$ (at an ionic strength of 10^{-2} M) and $\mathrm{HN_3}$ with identical rates (for the rates see Table I).

The rate of formation of $\mathrm{Br_2}^{\bullet-}$ was proportional to the concentration of Br^-. However, the rate also depended slightly on the concentration of SBr. Below ca. 5×10^{-4} M Br^- the rate constants (Figure 2) were in agreement with the well-established equilibrium 2. The slope and intercept of the line in Figure 2

$$\mathrm{Br}^{\bullet} + \mathrm{Br}^- \rightarrow (\mathrm{Br_2})^{\bullet-} \tag{2}$$

yielded k_2 and k_{-2}, respectively. Hence K_2 is $2.2 \times 10^5\ M^{-1}$.

Consistent with eq 2 the yield of $\mathrm{Br_2}^{\bullet-}$ as a function of $[\mathrm{Br}^-]$ is described by $[\mathrm{Br_2}^{\bullet-}]^{-1} = [\mathrm{Br_2}^{\bullet-}]_0^{-1} \times (1 + (K_2[\mathrm{Br}^-])^{-1})$, where $[\mathrm{Br_2}^{\bullet-}]_0$ denotes the sum of $[\mathrm{Br_2}^{\bullet-}] + [\mathrm{Br}^{\bullet}]$. This was tested by

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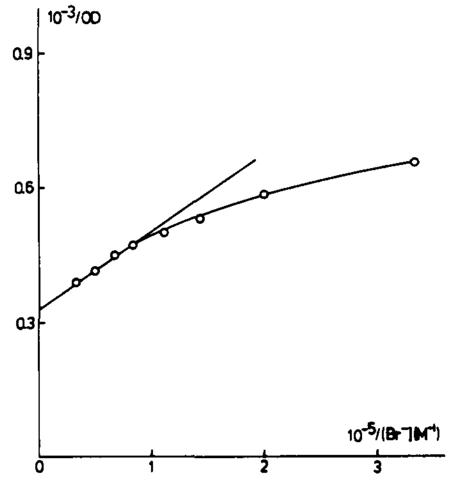

Figure 3. $OD_{(360nm)}^{-1}$ as a function of $[Br^-]^{-1}$. Conditions: same as in Figure 2.

measuring the absorbance at 360 nm at different Br^- concentrations. The formation of $Br_2^{\bullet -}$ in the absence of added bromide is not incorporated into the equation and therefore a curvature at low $[Br^-]$ is to be expected. As Figure 3 shows, a linear relationship is obtained at sufficiently high $[Br^-]$. From the straight line in the figure, K_2 is determined to be 2.2×10^5 M^{-1}. The determined rate constants and the equilibrium constant are in excellent agreement with published values,[16,17] which proves that $SBr^{\bullet -}$ yields $Br^{\bullet}$ in a nonrate-determining step according to reaction 3.

$$SBr^{\bullet -} \rightarrow Br^{\bullet} + S^- \qquad (3)$$

Two other observations confirm the expulsion of $Br^{\bullet}$: (1) At 275 nm where, according to ref 19, $Br^{\bullet}$ absorbs, we observed a slight absorbance immediately after the pulse which then decayed concomitantly with the buildup of $Br_2^{\bullet -}$. Due to the small size of this absorbance ($\epsilon_{275} \approx 1000$–$1500$ M^{-1} cm^{-1}) no quantitative data could be extracted from its decay pattern. (2) Added OH^- quenched[20] the formation of $Br_2^{\bullet -}$ through reaction 4. The k_4 determined from competition kinetics with Br^- (Table I) is in excellent agreement with the literature value.

$$Br^{\bullet} + OH^- \rightarrow BrOH^{\bullet -} \qquad (4)$$

In Table II the yield of $Br_2^{\bullet -}$ at various concentrations of Br^- and SBr is presented. As emerges from the values in the table the yield of $Br_2^{\bullet -}$ varies no more than required by equilibrium 2. Actually, the lowering of the $Br_2^{\bullet -}$ yield at 5×10^{-5} M Br^- is less than equilibrium 2 prescribes. This could be due to the formation of some Br^- in the reagent solution prior to e-beam irradiation (see Experimental Section). The result is that the actual Br^- concentration is higher than the added 5×10^{-5} M. Within experimental accuracy, which is better than 5%, we can state that the yield of $Br_2^{\bullet -}$ is not reduced beyond what is dictated by eq 2.

It has been suggested that in addition to $Br^{\bullet}$ and $S^{\bullet}$ a third chain carrier may operate during bromination of alkanes by SBr. This carrier was assumed to be an adduct between SBr and $Br^{\bullet}$, $SBrBr^{\bullet}$, according to equilibrium 5. Setting the maximum decrease in

$$SBrBr^{\bullet} \rightarrow SBr + Br^{\bullet} \qquad (5)$$

$Br_2^{\bullet -}$ due to equilibrium 6 equal to the experimental accuracy we calculate the lower limit of K_6 to be 8×10^3. Combining K_6 with

$$SBrBr^{\bullet} + Br^- \rightarrow Br_2^{\bullet -} + SBr \qquad (6)$$

K_2 we obtain $K_5 > 4 \times 10^{-2}$ M. K_5 is not expected to vary much with solvent polarity, describing neutral species. It has been inferred[4b,c] that in CH_2Cl_2 a weakly complexed intermediate, $SBrBr^{\bullet}$, may participate in the equilibrium. From our estimate of K_5 it transpires that, in water at least, the concentration of $SBrBr^{\bullet}$ is negligible at $[SBr] < 10^{-2}$ M.

Table II. The Amount of $Br_2^{\bullet -}$ Produced by a Radiation Dose of 4.5 Gy and Measured as the Optical Density at 360 nm, Observed in Ar-Saturated Aqueous Solutions Containing 0.2 M 2-propanol and Varying Amounts of SBr and Br^-

[SBr], M	$[Br^-]$, M	$OD_{(360nm)}$
10^{-2}	5×10^{-5}	0.0236
10^{-2}	7×10^{-5}	0.0224
10^{-2}	1×10^{-4}	0.0234
10^{-2}	2×10^{-4}	0.0240
10^{-2}	3×10^{-4}	0.0238
10^{-2}	6×10^{-4}	0.0240
10^{-2}	1×10^{-3}	0.0243
1×10^{-3}	5×10^{-5}	0.0206
2×10^{-3}	5×10^{-5}	0.0233
3×10^{-3}	5×10^{-5}	0.0232
5×10^{-3}	5×10^{-5}	0.0225
2×10^{-2}	5×10^{-5}	0.0230

$$S^{\bullet} + Br_2 \rightarrow SBrBr^{\bullet} \xrightarrow{K_5} SBr + Br^{\bullet}$$

Reduction by Alcohol Radicals. The $(CH_3)_2C^{\bullet}(OH)$ Radical. With sufficient Br^- present (10^{-3} M or so) the attainment of equilibrium 2 can be made more rapid than the reduction of SBr, hence $Br_2^{\bullet -}$ will operate as a monitor.

In an N_2O saturated solution containing SBr and 2-propanol essentially all radicals are converted into the reducing $(CH_3)_2C^{\bullet}OH$ radical through the following reactions:

$$e_{aq}^- + N_2O + H_2O \rightarrow OH^{\bullet} + N_2 + OH^- \qquad (7a)$$

$$OH^{\bullet} + (CH_3)_2(OH)CH \rightarrow (CH_3)_2(OH)C^{\bullet} + H_2O \qquad (7b)$$

The rate of reduction of SBr by the α-2-OH-propyl radical is given in Table I.

In an initially Br^- free solution only a minor amount of $Br_2^{\bullet -}$ was formed (less than 30%). The size of the $Br_2^{\bullet -}$ absorbance increased dramatically upon delivery of a second pulse to the same solution. The total yield of e^-_{aq} in one pulse is 1–2×10^{-6} M which is less than 5% of [SBr] in the solution. Therefore, the extreme sensitivity of the solution toward the delivery of a single pulse would seem to implicate a chain reaction. γ-Radiolysis of SBr in the presence of methanol or 2-propanol and N_2O gave rise to chain reactions as was evidenced by the rapid increase of the conductivity during irradiation. By calibration it was found that the conductivity corresponded to one HBr produced for each SBr consumed. The time for complete SBr consumption decreased with increasing alcohol concentration and increased with added Br^-. More to the point, the initial rate of HBr production varied inversely with added Br^-. The chain length varied with the square root of the dose when the latter was reduced from 0.33 to 0.03 Gy s^{-1}. Thus, the termination reaction is radical/radical combination.

These observations agree with the following mechanism, where (9) is the rate-determining step in the propagation, and $R^{\bullet}$ denotes the alkyl moiety.

Initiation

$$RH(OH) \rightarrow R^{\bullet}(OH)$$

Propagation

$$R^{\bullet}(OH) + SBr \rightarrow Br^{\bullet} + S^- + H^+ + R{=}O \qquad (8)$$

$$Br^{\bullet} + RH(OH) \rightarrow R^{\bullet}(OH) + Br^- + H^+ \qquad (9)$$

Termination

$$Br^{\bullet} + Br^- \rightarrow (Br)_2^{\bullet -} \qquad (2)$$

$$2(Br)_2^{\bullet -} \rightarrow Br_2 + 2Br^- \qquad (10)$$

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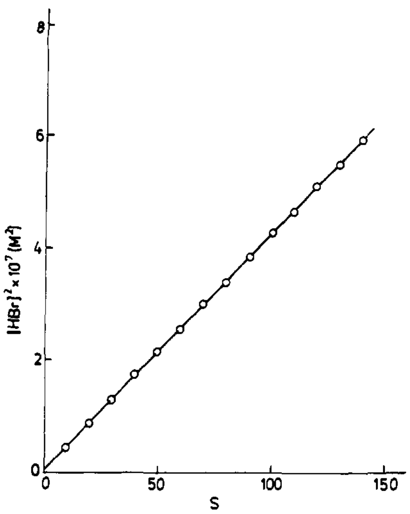

Figure 4. The square of the concentration of produced HBr as a function of time during γ-radiolysis. Conditions: [SBr] 10^{-3} M, [2-propanol] 0.13 M, N_2O saturation, dose rate 0.33 Gy/s.

Applying steady-state treatment to the above scheme, the following time dependence of Br^- production is dictated.

$$d[Br^-]/dt = k_9[RH(OH)][Br^\bullet]$$

After less than a second $[Br^-] \gg K_2^{-1}$, whence $[Br_2^{\bullet-}] \gg [Br^\bullet]$. Therefore,

$$[Br^\bullet] = K_2^{-1}[Br_2^{\bullet-}]/[Br^-]$$

Denoting the production rate in the γ-source by P we have

$$[Br_2^{\bullet-}] = (P/2k_{10})^{1/2}$$

Insertion into the above rate equation yields

$$d[Br^-]/dt = K_2^{-1}k_9[RH(OH)](P/2k_{10})^{1/2}[Br^-]^{-1}$$

By integration we obtain

$$[Br^-]^2 = K_2^{-1}2k_9[RH(OH)](P/2k_{10})^{1/2}t$$

Inserting the appropriate values with RH(OH) being 2-propanol we calculate from the slope of $[Br^-]^2$ vs t in Figure 4 $k_9 = 4.5 \times 10^5$ M^{-1} s^{-1}.

The linearity between $[Br^-]^2$ and t persisted upon substituting 2-propanol for methanol, and from a similar plot $k_{11} = 5 \times 10^4$ M^{-1} s^{-1} was calculated for the reaction

$$Br^\bullet + CH_3OH \rightarrow {}^\bullet CH_2OH + Br^- + H^+ \qquad (11)$$

By use of this technique the rate of $Br^\bullet$ reaction with ethanol, formaldehyde, and acetaldehyde, all of them giving a chain reaction in the presence of SBr, has been studied. The rates were found to decrease monotonously with increasing C–H bond strength.[21]

When γ-irradiation of SBr was carried out in the presence of t-BuOH and N_2O (see reaction 7), we again observed a chain reaction as was evidenced by the consumption of more than 15 SBr molecules per initial radical produced at [t-BuOH] above 0.1 M. However, at these t-BuOH concentrations, the production of HBr, reflected by the conductivity change with time, was merely 1.3 times that of the initial radical production. In this case the lack of agreement between HBr production and SBr consumption rules out $Br^\bullet$ as the main chain propagator. Another radical is involved which we, in accordance with refs 1a, 3, and 22, take to be $S^\bullet$ produced in reaction 12. Pulse radiolysis of the system

$$(CH_3)_2C(OH)CH_2^\bullet + SBr \rightarrow S^\bullet + (CH_3)_2C(OH)CH_2Br \qquad (12)$$

SBr-t-BuOH-N_2O produced the $(CH_3)_2C(OH)CH_2^\bullet$ radical quantitatively. As mentioned before only a weak absorbance was seen around 360 nm. In the presence of added Br^- the formation of $Br_2^{\bullet-}$ was observed. In all cases the buildup of $Br_2^{\bullet-}$ was found to fit a single exponential without any lag phase. The extracted first-order rate constants, k_{obs}, of $Br_2^{\bullet-}$ formation were found proportional to [SBr] but inversely proportional to [t-BuOH]. The rate constants equally increased with Br^- concentration but they leveled off at sufficiently high $[Br^-]$. Lacking product analysis the observed data cannot be unambiguously interpreted, but it seems that $S^\bullet$ oxidizes Br^-.

Reduction of SBr by $O_2^{\bullet-}$. Oxygen-saturated aqueous solutions containing 0.5 M 2-propanol and 10^{-2} M Br^- at pH 9.3 were pulse irradiated in the presence of SBr with the concentration of the latter varying between 0.5×10^{-4} and 2×10^{-4} M. In these solutions the buildup rate of the 360-nm absorbance was dependent on SBr concentration only. Under these conditions essentially all radicals are converted to $O_2^{\bullet-}$ according to

$$e^-_{aq} + O_2 \rightarrow O_2^{\bullet-}$$

$$(CH_3)_2C^\bullet OH + O_2 + OH^- \rightarrow O_2^{\bullet-} + (CH_3)_2CO + H_2O$$

Therefore the kinetics of the observed buildup reflects reaction 17 yielding $k_{17} = 5 \times 10^8$ M^{-1} s^{-1}. Considering that $O_2^{\bullet-}$ is a

$$SBr + O_2^{\bullet-} \rightarrow SBr^- + O_2 \qquad (13)$$

mild reductant ($E^0 = -0.16$ V) the rapid rate of reaction 13 implicates SBr as a relatively powerful one-electron oxidant in water. In acetonitrile, Eberson et al.[23] estimated the one-electron reduction potential of SBr to be 0.17 ± 0.30 V. $E^0(SBr/SBr^{\bullet-})$ should be even more positive in water given the higher polarity of the latter as compared to acetonitrile.

The Reaction of the OH$^\bullet$ Radical with SBr. For a judicious design of solution composition it was necessary to determine the reaction rate between $OH^\bullet$ and SBr. This was performed by having Ag^+ compete with SBr for $OH^\bullet$, and the growth rate as well as the size of the $Ag(OH)^+$ absorbance at 320 nm monitored the reaction. The SBr concentration was held constant, and thus the intercept of the measured rate against $[Ag^+]$ yielded the rate constant 3.6×10^8 M^{-1} s^{-1} for $OH^\bullet$ + SBr, close to the corresponding rate of $OH^\bullet$ reacting with succinic acid.[18] This indicates that the $OH^\bullet$ reaction is a hydrogen abstraction from the backbone. The rate of $Ag^+ + OH^\bullet$ is in agreement with literature values.

The Stability of $SBr^{\bullet-}$. Although the one-electron reduction of SBr was shown to result in the formation of $Br^\bullet$, the process is most likely not a dissociative electron transfer, i.e., $SBr^{\bullet-}$ has a certain lifetime. There is both spectral and kinetic evidence for this assumption.

The $SBr^{\bullet-}$ radical, stable at 77 K, has been investigated by ESR.[24,25] The ESR spectrum revealed that the unpaired electron is equally distributed along the N–Br bond, i.e., $SBr^{\bullet-}$ is a three-electron-bonded species as opposed to an amide type radical. The UV spectra of a number of three-electron-bonded radicals such as $Br_2^{\bullet-}$, $I_2^{\bullet-}$, $(SCN)_2^{\bullet-}$, $N_6^{\bullet-}$, etc. have been recorded.[26] All of them were found to absorb rather strongly above 300 nm. As stated before, the pulse radiolytic one-electron reduction of PBr yielded a species absorbing around 325 nm which disappeared rather slowly. As this species is very likely $PBr^{\bullet-}$, the above observation is evidence that, if stabilized, three-electron-bonded

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N-bromo radical anions can have considerable stability even at room temperature.

Rapid cyclic voltammetry has shown that SBr^- decomposes with a rate exceeding[27] 2×10^6 s^{-1}. In the present work the rate of formation of $Br_2^{\bullet -}$ was found proportional to $[Br^-]$ up to 2×10^7 s^{-1}, the time resolution of the setup. This shows the monomolecular rate of expulsion of $Br^{\bullet}$ from $SBr^{\bullet -}$ to be higher than 2×10^7 s^{-1}.

As $SBr^{\bullet -}$ is stable enough for ESR investigation at 77 K, it implies that k_3 at this temperature is 10^{-3} s^{-1} or less. This value combined with the lower limit at room temperature predicates the minimum activation energy of reaction 3 to be 20 kJ/mol. Assuming the maximum frequency factor to be 10^{13} s^{-1}, this yields $k_3 < 2 \times 10^9$ s^{-1} at room temperature. Of course, we tacitly assume k_3 to be essentially independent of the solvent.

On the Redox Potential of the ($S^{\bullet}/S^-$) Couple. The finding that $SBr^{\bullet -}$ expels Br^- implies that $E^0(S^{\bullet}/S^-) > E^0(Br^{\bullet}/Br^-) = 1.94$ V.[28] From literature values an estimate of $E^0(S^{\bullet}/S^-)$ can be made. Cyclic voltammetry on $Bu_4N^+S^-$ in acetonitrile[5] showed an irreversible anode reaction with $E_{pa} = 1.6$ V vs SCE. With a conservative estimate that rapid chemical followup reactions cause E_{pa} to be 0.3 V lower than the E_{pa} value of the hypothetical reversible $S^{\bullet}/S^-$ couple, which in turn is assumed to display a peak-to-peak separation of 0.2 V, E_{rev} would come out at 1.8 V. Corrections for changing the reference electrode from SCE to NHE (0.24 V) and for the free energy change upon transfer of S^- from acetonitrile to water (0.5 V, similar to that of acetate ion) would then place $E_{rev}(H_2O)$ around 2.5 V vs NHE. We were unable to observe oxidation of S^- by $SO_4^{\bullet -}$ (i.e., $k_{(S^- + SO_4^{\bullet -})} < 10^6$ M^{-1} s^{-1}) although the redox potential of $SO_4^{\bullet -}$ is reported to be >2.5 V.[29] This may either reflect a redox potential in the vicinity of 2.5 V or an unusually high reorganization energy for the $S^{\bullet}/S^-$ couple. Although the precise value of the redox potential remains to be determined it is probably above 2 V.

Experimental Section

The pulse radiolysis equipment consists of a microtron accelerator[30] delivering 7 MeV electrons and a computerized optical detection system.[31] Unless noted otherwise doses of 1–2 Gy/pulse were delivered in order to keep the radical concentration below 10^{-6} M. For dosimetry air-saturated 10^{-2} M KSCN solutions were employed. The $G\epsilon$ value of the $(SCN)_2^{\bullet -}$ radical was taken to be 2.2×10^{-4} m^2/J at 500 nm.[32]

SBr oxidizes primary and secondary alcohols within hours, while it is fairly stable in the presence of *tert*-butyl alcohol.[33] To minimize any decomposition of SBr the following precautions were taken: For every experiment a fresh aqueous solution of SBr was prepared, while all other reagents were dissolved in a separate solution. These solutions were then mixed in a flow system just before being irradiated. The time elapsed between mixing of the solution and its exit from the cuvette was less than 2 s. HPLC on aqueous SBr solutions with or without *t*-BuOH revealed no (<1%) HOBr, Br_2, or *t*-BuOBr. Conductometric measurements on these solutions showed $[H^+]$ to be both constant over several hours and <1% of the SBr concentration. Addition of *t*-BuOH to such solutions did not increase the amount of H^+. Thus, less than 1% of other bromine-containing compounds are formed spontanously within hours.

The dose rate in the γ-source was 0.33 Gy s^{-1}, corresponding to a radical production rate of 2×10^{-7} M s^{-1}.

SBr (Aldrich 99%) was recrystallized from water, vacuum dried, and kept in the dark. All other chemicals were of the purest quality available (Aldrich or Merck) and were used as received.

Water was triple distilled in quartz.

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