

Kinetics of Radical-Initiated Chain Bromination of 2-Methyl-2-propanol by *N*-Bromosuccinimide in Water

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Abstract: The kinetics and product distribution of the radical chain bromination of 2-methyl-2-propanol (RH) by *N*-bromosuccinimide (SBr) in water have been studied by pulse-radiolytic and γ -radiolytic methods in order to obtain key data for the reactivity of the succinimidyl radical, S^{*}. The products of the reaction after γ -radiolysis are dependent on the concentration of RH, being essentially made up of equal amounts of (CH₃)₂C(OH)CH₂Br and succinimide at [RH] > 0.5 M, while the hydrolyzed ring-opened product, 3-bromopropionamide, increases at the expense of (CH₃)₂C(OH)CH₂Br when the RH concentration is lowered. The chain-propagating steps R^{*} + SBr → RBr + S^{*} (i) and S^{*} + RH → SH + R^{*} (ii) of the S^{*} mediated chain reaction had rate constants $k_i = (1.8 \pm 0.3) \times 10^8$ (determined in three ways) and $k_{ii} = (1 \pm 0.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (determined in four ways), respectively, whereas the corresponding rate constants for the Br^{*} mediated chain under the same conditions were 2.5×10^9 and $(5 \pm 3) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. Under pulsed conditions with initial radical concentrations around 10⁻⁴ M, the chain length is ≈ 10 . The ratio between k_{ii} and the rate constant for ring opening of S^{*}, k_{iii} (S^{*} → ^{*}CH₂CH₂CONCO), was determined to be 77 M⁻¹, significantly higher than the corresponding value with neopentane as substrate and with dichloromethane as solvent (0.10 M⁻¹). The k_{ii} value places S^{*} as having significantly lower reactivity than OH^{*} in hydrogen atom abstraction reactions, whereas a theoretical estimate based on electron affinities puts it in between Cl^{*} and OH^{*}, i.e. at higher reactivity than OH^{*}. This provides kinetic evidence for the II nature of ground state S^{*}. It was also established that Br^{*} complexes rather strongly to SBr according to SBr + Br^{*} → SBr₂^{*} (iv). As $k_{iv} = (4-7) \times 10^3 \text{ M}^{-1}$ and SBr₂^{*} is probably unreactive, the propagation rate of a bromine atom chain is expected to decrease with increasing SBr concentration.

Introduction

Extensive research^{1,2,3} during the past decades of alkane bromination by *N*-bromosuccinimide (SBr) has identified the succinimidyl radical, S^{*}, as the main chain carrier. Invariably, the investigations were carried out in organic solvents, such as CH₂Cl₂ or CH₃CN, and the reactions were initiated by light or thermally generated radicals. The problems encountered mainly reside in the fact that the contribution of a competing bromine atom chain has proved difficult to disentangle from that of the S^{*} chain. These efforts have been reviewed in the past, and we shall but briefly touch upon them. The measurement of product distribution was the almost exclusive means whereby to arrive at the properties of S^{*}, with very little direct kinetic information available. There seems to be consensus on the following points: (1) Thermal generation results in one single S^{*} species, characterized as a II radical. (2) S^{*} abstracts hydrogen from primary alkyl groups more readily than Br^{*}. (3) S^{*} ring-opens reversibly, to yield the β -(isocyanatocarbonyl)ethyl radical (PI^{*}). In addition, the following equilibration will remove the S^{*} radical even at low Br₂ concentration and may well introduce the additional radical

SBr₂^{*} into the system.



The main aim of the present work is to obtain direct kinetic data on the reactions of S^{*} and Br^{*} and to combine them with observed product yields. As the primary processes of radiation-induced radical production in water are well understood, we will employ the latter solvent in our pulse-radiolytic and γ -radiolytic studies. It is hoped that the results obtained may shed more light on the properties of S^{*}, both in water and in organic solvents.

Results

In order to facilitate reading of the text, the pertinent reactions and their rate or equilibrium constants have been compiled in Scheme I. As can be seen, the numbering of the reactions is the same as that of the constants, and this practice will be adhered to in the text to follow.

Hydrolysis Equilibria of SBr in Water. In the present work, it is important to have control over all potential bromine-containing species that may be formed in water from SBr. As there are no data in the literature, we determined equilibria 1 and 2. Note that in eqs 1 and 3 the activity of the pure water solvent is set to 1.



The absorbance of Br₃⁻ at 390 nm (where all the other species are essentially transparent) was measured while varying the concentrations of SBr (3×10^{-4} to 3×10^{-3} M), SH (0 to 5×10^{-3} M), and Br⁻ (10^{-2} to 3×10^{-1} M) and the pH (5.5 to 8). The equilibria were established within 1 min. By employing the well-known equilibrium constants⁴ $K_3 = 5 \times 10^{-9} \text{ M}^2$ and $K_4 = 17 \text{ M}^{-1}$,

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[†] Department of Nuclear Chemistry, Royal Institute.

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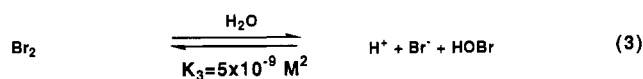
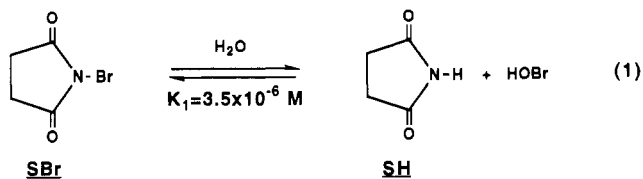
(1) (a) Skell, P. S.; Lüning, U.; McBain, D. S.; Tanko, J. M. *J. Am. Chem. Soc.* 1986, 108, 121. (b) Luning, U.; Skell, P. S. *Tetrahedron* 1985, 41, 4289. (c) Skell, P. S.; Seshadri, S. *J. Org. Chem.* 1984, 49, 1650. (d) Skell, P. S.; Tlumak, R. L.; Seshadri, S. *J. Am. Chem. Soc.* 1983, 105, 5125. (e) Skell, P. S.; Day, J. C. *Acc. Chem. Res.* 1978, 11, 381.

(2) (a) Tanner, D. D.; Reed, D. W.; Tan, S. L.; Meintzer, C. P.; Walling, C.; Sopchik, A. *J. Am. Chem. Soc.* 1985, 107, 6756. (b) Tanner, D. D.; Meintzer, C. P. *J. Am. Chem. Soc.* 1985, 107, 6584. (c) Tanner, D. D.; Meintzer, C. P. *J. Org. Chem.* 1985, 50, 1534. (d) Tanner, D. D.; Ruo, T. C.-S.; Takiguchi, H.; Guillaume, A.; Reed, D. W.; Setiloane, B. P.; Tan, S. L.; Meintzer, C. P. *J. Org. Chem.* 1983, 48, 2743.

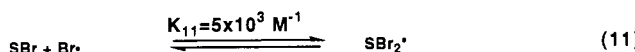
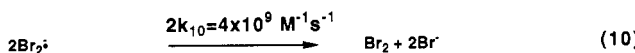
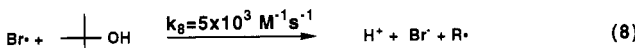
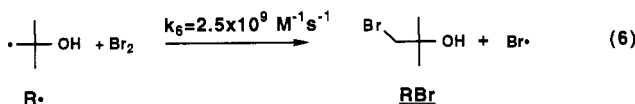
(3) Walling, C.; El-Taliawi, G. M.; Zhao, C. *J. Am. Chem. Soc.* 1983, 105, 5119.

Scheme I

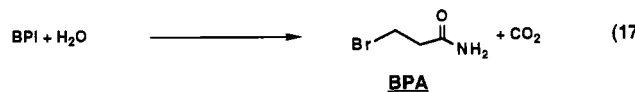
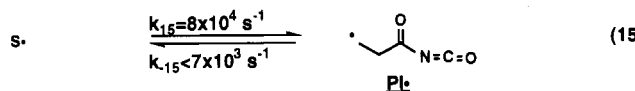
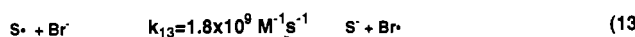
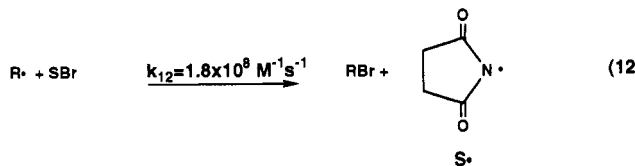
Hydrolysis equilibria



Bromine chain reactions



Succinimidyl chain reactions

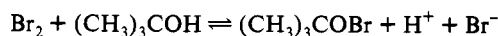


we calculated K_1 and K_2 for each combination of concentrations. These values were constant within a factor of ca. 2. $K_1 = (3.5 \pm 1.5) \times 10^{-6} \text{ M}$ and $K_2 = (7 \pm 3) \times 10^2 \text{ M}^{-1}$ were derived. Upon addition of 2-methyl-2-propanol (RH), some SBr may be

converted into alkyl hypobromite according to eq 5. As product

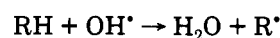
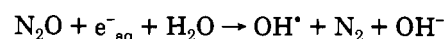
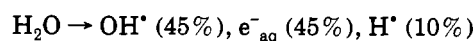


analysis will show (see below), the amount of $(\text{CH}_3)_3\text{COBr}$ is always sufficiently low not to compete with SBr for alkyl radicals. Furthermore, pulse-radiolytic reduction of SBr in the presence of 1 M RH quantitatively yielded $\text{Br}\cdot$. Had eq 5 been important, a substantial amount of e^-_{aq} would have reacted with $(\text{CH}_3)_3\text{COBr}$ to yield Br^- and $(\text{CH}_3)_3\text{CO}\cdot$, thus decreasing the yield of $\text{Br}\cdot$ atoms. By use of K_1 and the bond dissociation enthalpies of $(\text{CH}_3)_3\text{CO-H}$ (105 kcal/mol), HO-H (119 kcal/mol), HO-Br (56 kcal/mol), and $(\text{CH}_3)_3\text{CO-Br}$ (43.8 kcal/mol⁵) and assuming further S° and hydration free energies of the species to essentially cancel, we estimate K_5 to be $<10^{-5}$, in keeping with the apparent absence of $(\text{CH}_3)_3\text{COBr}$ in our experiments. In response to a reviewer's comment, the equilibrium constant of the following reaction was investigated and found to be $\leq 10^{-8} \text{ M}$.



This was done by measuring the Br_3^- absorbance at 390 nm in an aqueous 10^{-3} M Br_2 solution while varying the amount of added RH from 0 to 1 M. A slight increase in absorbance could be perceived through the scatter of the data. The upper limit of 10^{-8} M was derived from the largest increase measured (20% at 0.5 M RH). This yielded $K_5 \leq 7 \times 10^{-6}$, in excellent agreement with the above thermochemical estimate of $K_5 \leq 10^{-5}$.

The Reactivity of Br_2 and $\text{Br}\cdot$ in the Aqueous RH System. In order to clearly differentiate between the $\text{S}\cdot$ and $\text{Br}\cdot$ chains, we scrutinized the reactivity of the pure bromine species in some detail. First, we determined the rate constant for reaction 6 by means of pulse radiolysis. The experiment was performed as follows: N_2O -saturated solutions at pH ca. 4 containing 1 M RH, $1 \times 10^{-3} \text{ M}$ Br^- , and varying amounts of Br_2 (5×10^{-5} to $3 \times 10^{-4} \text{ M}$) were pulse irradiated, giving rise to the following reactions:



With $k_7 = 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and when 10^{-3} M Br^- is present, the last reaction occurs with a rate of 10^7 s^{-1} , and thus reaction 6 becomes the rate-determining step. The rate of the exponential buildup of $\text{Br}_2\cdot^-$ absorbance at 360 nm was found proportional to the concentration of added Br_2 . From this dependence, the rate constant $k_6 = 2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was determined. We note that this rate is practically the same as the rates of addition of O_2 to a number of alkyl radicals in water,⁶ and thus we believe it to be close to the diffusion-controlled limit. In order to determine k_8 , we γ -irradiated N_2O -saturated unbuffered RH solutions containing Br_2 . In this system, a chain reaction occurs with the propagation reactions 6 and 8, the latter being the rate-determining step. This was monitored by measuring the initial conductivity increase (due to the production of HBr) during irradiation. The measurements are complicated by HBr being buffered through eq 3. In fact, the initial HBr concentrations measured prior to irradiation are in good agreement with those calculated from eq 3 (see Table I). As can be seen from the data in Table I, the HBr production rate is proportional to $[\text{RH}]$ but does not change with varying $[\text{Br}_2]$. Addition of Br^- to the solution lowers the rate of HBr production. These findings clearly show that the chain

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Table I. k_8 Calculated from the Rate of HBr Production during γ -Radiolysis of Aqueous Solutions Containing RH and Br_2

added Br_2 , M	initial RH, M	measured ^a ($\text{H}^+ + \text{Br}^-$), M	calculated ^b ($\text{H}^+ + \text{Br}^-$), M	added Br^- , M	produced HBr, M/s	k_8 , $\text{M}^{-1} \text{s}^{-1}$
10^{-3}	0.1	1.8×10^{-4}	1.7×10^{-4}	0	2×10^{-8}	3×10^3
10^{-3}	1	1.9×10^{-4}	1.7×10^{-4}	0	2.8×10^{-7}	4.3×10^3
4×10^{-3}	1	2.8×10^{-4}	2.7×10^{-4}	0	2.5×10^{-7}	6.2×10^3
4×10^{-3}	2	2.9×10^{-4}	2.7×10^{-4}	0	4.7×10^{-7}	5.9×10^3
4×10^{-3}	1		^c	5×10^{-4}	1.1×10^{-7}	4.1×10^3

^a From the initial conductivity signal measured prior to irradiation. ^b Calculated using $K_3 = 5 \times 10^{-9} \text{ M}^2$. ^c $[\text{Br}^-]$ and $[\text{H}^+]$ are calculated to be 6.7×10^{-4} and $1.7 \times 10^{-4} \text{ M}$, respectively.

propagator is the free Br^\bullet atom through reaction 8 and that the slowdown in the propagation upon Br^- addition is due to reaction 7, $\text{Br}_2^{\bullet-}$ being essentially unreactive toward RH. To calculate k_8 , we use, in conjunction with the radical production rate of $1.8 \times 10^{-7} \text{ M/s}$ and the equilibrium constant⁷ $K_7 = 2 \times 10^5 \text{ M}^{-1}$, the rate constant of chain termination $2k_{10} = 4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (mean value of the data in ref 7). Furthermore, we allow for the buffering of HBr by eq 3. Since at all times $[\text{Br}^-] \gg K_7^{-1}$, it follows that $[\text{Br}_2^{\bullet-}] \gg [\text{Br}^\bullet]$ and thus chain termination is governed by reaction 10 to the virtual exclusion of reaction 9. From the mean value



in Table I, $k_8 = (5 \pm 3) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ is calculated, the large error margin reflecting the cumulative uncertainty in K_3 and K_7 . It is seen that, in water, the rate constant of hydrogen abstraction (calculated per equivalent of hydrogen atoms) by Br^\bullet from a primary alkyl group is ca. $500 \text{ M}^{-1} \text{ s}^{-1}$.

Does SBr Complex Br^\bullet Atoms? In a recent publication,⁸ we clearly demonstrated that, upon one-electron reduction of SBr, a Br^\bullet atom is rapidly expelled. The pertinent experiments were conducted in dilute aqueous solutions of SBr (5×10^{-5} to $2 \times 10^{-4} \text{ M}$) in the presence of RH by varying the amount of added Br^- and observing the kinetics of $\text{Br}_2^{\bullet-}$ production. Another set of experiments in the same work aimed at investigating the possible equilibrium 11. Here, a high concentration of SBr (10^{-2} M) was used and the Br^- concentration was varied from 5×10^{-5} to 10^{-2} M while 2-propanol was employed to convert the OH^\bullet radical into the reducing α -hydroxyalkyl radical. Under these conditions, we found no indication for the formation of $\text{SBr}_2^{\bullet-}$. During the present work, we discovered that 2-propanol is rather reactive toward SBr and the reaction is heavily catalyzed even by small amounts of the analyzing light. Thus, unawares, we may have had substantial amounts of Br^- in the solution, which may invalidate our conclusion concerning eq 11. In the present work, we utilized the rather less reactive methanol to produce the reductive $^\bullet\text{CH}_2\text{OH}$ radical and added small amounts of Ag^+ (2–10% of SBr) to keep the solution free of Br^- (the solubility product of $\text{AgBr}(s)$ is $7.7 \times 10^{-13} \text{ M}^2$ at 25°C). Furthermore, we added succinimide (the same amount as SBr) to suppress the production of HOBr. In view of eq 1, this precaution should keep the concentration of the latter species around $3.5 \times 10^{-6} \text{ M}$.

Figure 1 shows the transient spectrum obtained upon pulse radiolysis of an N_2O -purged solution containing 0.1 M methanol, $5 \times 10^{-3} \text{ M}$ SBr, $5 \times 10^{-3} \text{ M}$ SH, and 10^{-4} M Ag^+ . In order to ensure that the spectra were not distorted by some transient silver species, we varied the Ag^+ concentration and found the spectrum unaffected until $[\text{Ag}^+]$ exceeded ca. $5 \times 10^{-4} \text{ M}$. As seen from the figure, a peak around 360 nm is observed. Its spectral shape is very similar to that of $\text{Br}_2^{\bullet-}$ but has only ca. 25% of the latter's extinction coefficient. As we have $<10^{-8} \text{ M}$ Br^- present, we must ascribe this spectrum to $\text{SBr}_2^{\bullet-}$. In this assignment, we feel heartened by recent pulse-radiolytic findings⁹ where the Br^\bullet atom was shown to complex to a number of organic bromides, all of

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(8) Lind, J.; Shen, X.; Eriksen, T. E.; Merényi, G.; Ebersson, L. *J. Am. Chem. Soc.* **1991**, *113*, 4629.

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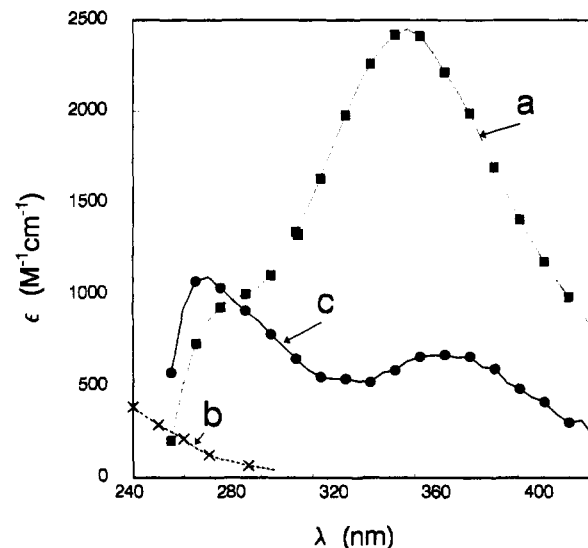


Figure 1. Transient spectra of radical species: \blacksquare $\text{SBr}_2^{\bullet-}$, \times $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2^\bullet$, \bullet S^\bullet . For experimental conditions, see text.

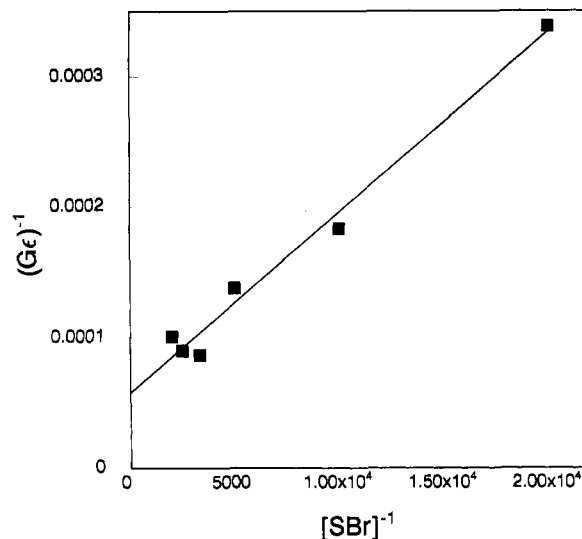


Figure 2. The inverse dose normalized yield of $\text{SBr}_2^{\bullet-}$ measured at 360 nm as a function of the reciprocal of $[\text{SBr}]$.

these complexes absorbing around 360 nm. Varying the SBr concentration was found to change the size but not the shape of the 360-nm absorbance. On the assumptions that only $\text{SBr}_2^{\bullet-}$ absorbs at 360 nm and that eq 11 operates, the size of the signal should be given by

$$\text{OD}^{-1} = (\text{OD}^\circ)^{-1} (1 + (K_{11}[\text{SBr}])^{-1})$$

where OD° is the full signal with eq 11 driven completely to the right. Accordingly, a plot of OD^{-1} versus $[\text{SBr}]^{-1}$ (Figure 2) yielded a straight line. From the slope/intercept, $K_{11} = 4 \times 10^3 \text{ M}^{-1}$ is calculated. Similarly, as $k_{\text{obs}} = k_{-11} + k_{11}[\text{SBr}]$, we estimate from the variation of the rate of absorbance buildup with SBr concentration k_{11} and k_{-11} to be $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and 1.5×10^5

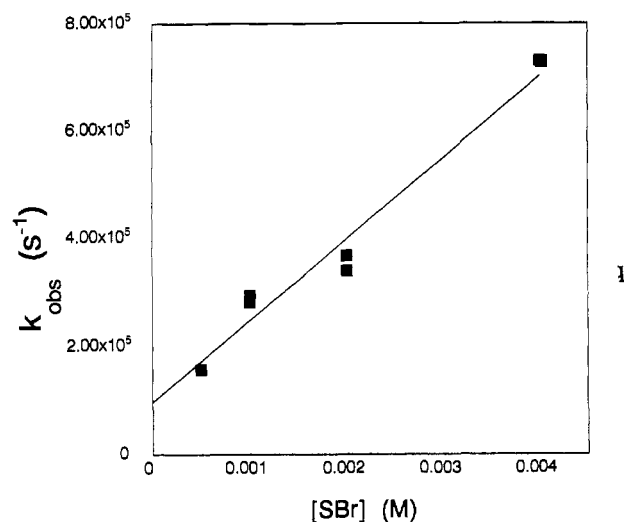


Figure 3. The rate of S^{\bullet} formation measured at 270 nm versus $[SBr]$.

s^{-1} , which yields $K_{11} = 7 \times 10^3 M^{-1}$. Thus, SBr_2^{\bullet} appears to be a rather strong complex in water, only about 40 times weaker than the well-known $Br_2^{\bullet-}$ (equilibrium 7). This suggests that, in organic systems where high SBr concentrations (0.1 M or so) are employed, the bulk of Br^{\bullet} is very likely in the SBr_2^{\bullet} form. We lack information on the reactivity of SBr_2^{\bullet} , but we shall assume, in analogy to the case with $Br_2^{\bullet-}$, that only the fraction of free Br^{\bullet} present will participate in hydrogen abstraction reactions.

Spectral and Kinetic Properties of the Succinimidyl Radical, S^{\bullet} . An N_2O -saturated aqueous solution containing $10^{-2} M$ RH, $5 \times 10^{-3} M$ SBr, and $10^{-4} M$ Ag^+ to remove Br^- ions was pulse-irradiated. In this solution, the OH^{\bullet} radicals produce a primary alkyl radical, which in turn reacts with SBr according to reaction 12. Spectrum b in Figure 1 displays the absorbance observed immediately after the pulse, it being identical to that of the R^{\bullet} radical recorded in SBr-free solutions. Within a few μs , the absorbance increases to a new spectrum. As ca. 10% of all initial radicals are H^{\bullet} atoms which reduce SBr to Br^{\bullet} and the last two should form SBr_2^{\bullet} , we subtract ca. 10% of spectrum a in Figure 1 from the raw spectrum to obtain spectrum c. Allowing for errors inherent in measuring transient absorbances below 10^{-2} , the last spectrum is in satisfactory agreement with that of the succinimidyl radical, S^{\bullet} , recorded in ref 10. The buildup rate of spectrum c was found proportional to added SBr concentration, and the rate constant k_{12} was determined to be $1.5 \times 10^8 M^{-1} s^{-1}$ (Figure 3). As this rate constant is rather important, we have determined it in two additional ways. As will be shown in the sequel, S^{\bullet} reacts rapidly with Br^- , with a rate constant, $k_{13} = 2 \times 10^9 M^{-1} s^{-1}$, close to diffusion control. This reaction will be followed by the even more rapid reaction 7 to yield the strongly absorbing $Br_2^{\bullet-}$ species. Now, O_2 is known to react with R^{\bullet} to yield a peroxy radical with a rate constant⁶ of ca. $3 \times 10^9 M^{-1} s^{-1}$, and the latter is a poor oxidant. Therefore, the yield of the $Br_2^{\bullet-}$ radical as a function of the ratio $[O_2]/[SBr]$ reflects the competition of SBr and O_2 for R^{\bullet} . The ratio was varied from 0 to 0.25 by varying both $[O_2]$ (0–50% in N_2O) and $[SBr]$ (10^{-3} to $10^{-2} M$). From these experiments, k_{12} was determined to be $2 \times 10^8 M^{-1} s^{-1}$. The third method will be described in the next section.

When the concentration of RH is increased, the size of the S^{\bullet} absorbance decreases. As Figure 4 shows, there is a proportionality between the concentration of RH and the inverse of the absorbance. Formally, this behavior reflects an equilibrium between S^{\bullet} and R^{\bullet} . This can be rationalized by a rapid chain reaction creating steady-state concentrations of S^{\bullet} and R^{\bullet} within

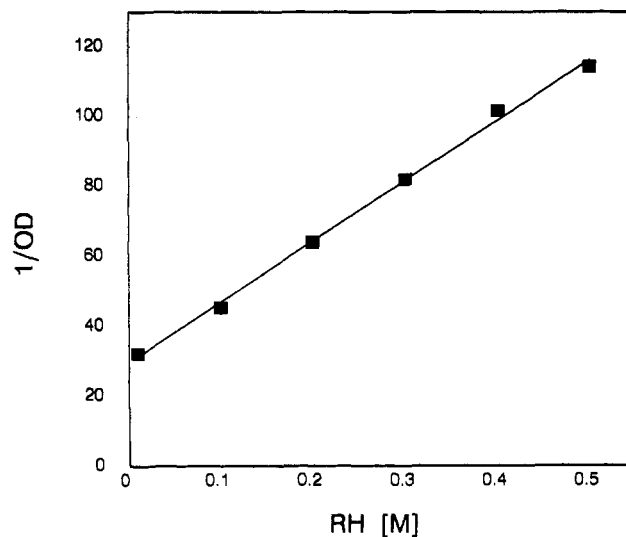


Figure 4. The inverse of the signal at 270 nm as a function of 2-methyl-2-propanol concentration.

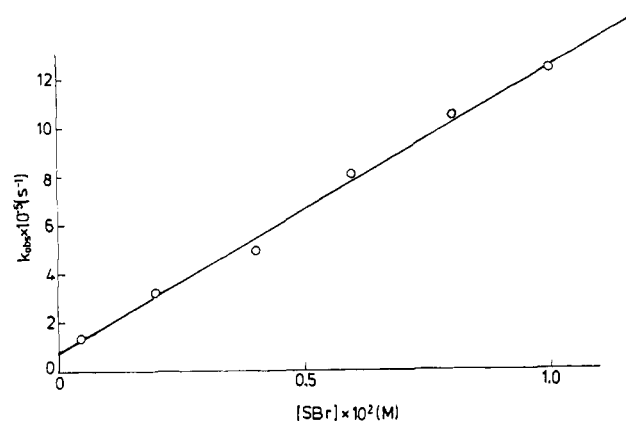


Figure 5. The measured rate of $Br_2^{\bullet-}$ formation as a function of $[SBr]$. Conditions: $[Br^-]$ 10 mM, $[RH]$ 1 M, N_2O saturation.

a few μs according to reactions 12 and 14. The slope divided by the intercept in Figure 4 is 5.8. In the sense of the model, this quantity is $k_{14}/(k_{12}[SBr])$, from which $k_{14}/k_{12} = 0.03$ is calculated.

Kinetic Studies Using $Br_2^{\bullet-}$ as a Spectral Monitor. With $E^{\circ}(S^{\bullet}/S^-) = 2.22 V$ vs NHE,¹⁰ S^{\bullet} is expected to rapidly one-electron oxidize Br^- to Br^{\bullet} (reaction 13) and the latter should form the strongly absorbing $Br_2^{\bullet-}$ through eq 7. Consequently, in order to better monitor the kinetics of the weakly absorbing S^{\bullet} radical, varying amounts of Br^- were added to N_2O -saturated SBr solutions containing SH and RH. In the presence of added Br^- , the formation of $Br_2^{\bullet-}$ was indeed 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 to depend on $[SBr]$, $[RH]$, and $[Br^-]$ in the following way: At constant $[RH]$ and $[Br^-]$, k_{obs} was proportional to $[SBr]$ (Figure 5). With $[RH]$ and $[SBr]$ held constant, k_{obs} varied linearly with $[Br^-]$ at small additions (Figure 6) but tended to a limiting value at sufficiently high $[Br^-]$ (Figure 7). As seen in Figure 6, k_{obs} decreases with increasing $[RH]$. These observations are consistent with a rapid chain propagation through reactions 12 and 14, as was proposed above. As long as $k_{13}[Br^-] \ll k_{12}[SBr]$ and $k_{14}[RH]$, we can consider R^{\bullet} and S^{\bullet} to be in rapid dynamic equilibrium through reactions 12 and 14. Then we obtain for the rate of buildup of $Br_2^{\bullet-}$:

$$k_{obs} \approx (k_{12}k_{13}[Br^-][SBr]) / (k_{12}[SBr] + k_{14}[RH])$$

By plotting in Figure 8, the inverse of the slopes, extracted

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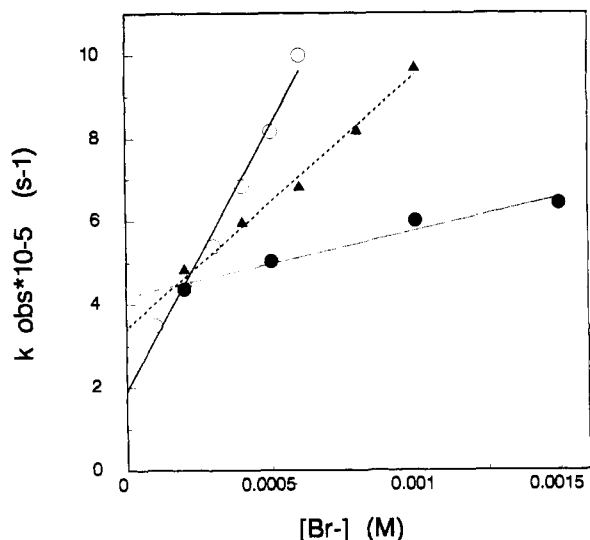


Figure 6. The measured rate of $\text{Br}_2^{\bullet-}$ production vs $[\text{Br}^-]$ at different RH concentrations: \circ [RH] 0.1 M, \blacktriangle [RH] 0.2 M, \bullet [RH] 1.0 M. Conditions: $[\text{SBr}]$ 12 mM, N_2O saturation.

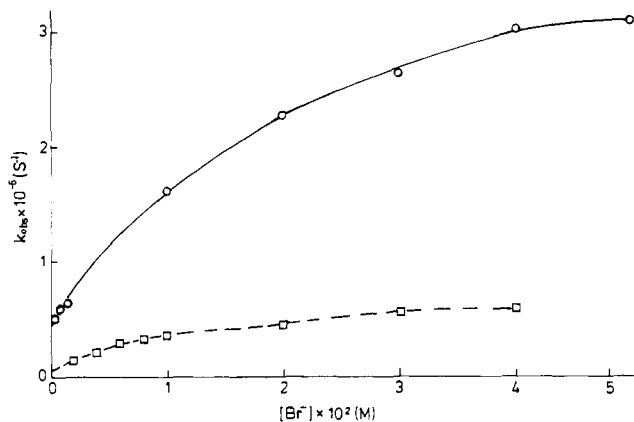


Figure 7. The measured rates of $\text{Br}_2^{\bullet-}$ formation vs $[\text{Br}^-]$: \square 2 mM SBr, \circ 12 mM SBr. Conditions: [RH] 1 M, N_2O saturation.

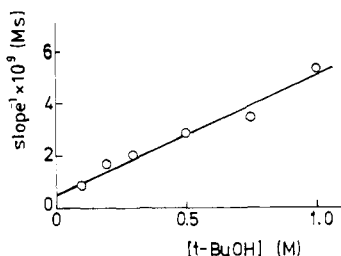


Figure 8. The inverse of the slopes extracted from Figure 6 and other experiments as a function of [RH].

previously from k_{obs} vs $[\text{Br}^-]$ plots in Figure 6, as a function of [RH], a straight line is obtained with the intercept and slope equal to $(k_{13})^{-1}$ and $k_{14}/(k_{12}k_{13}[\text{SBr}])$, respectively. From these data, $k_{13} = 1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{14}/k_{12} \approx 0.08$ are obtained. The leveling off at high Br^- concentrations in Figure 7 suggests that reaction 13 eventually becomes more rapid than reaction 14. As reaction 13 forms the nonpropagating $\text{Br}_2^{\bullet-}$ radical, the chain reaction ceases to operate. Now, the rate-limiting step becomes reaction 12 and its rate constant k_{12} comes out as $\approx 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

The Chain Length during Pulsed Irradiation. With the high rate constants k_{12} and k_{14} , we would expect consumption of SBr through a chain reaction to occur even at initial radical concentrations $> 10^{-4} \text{ M}$. Consequently, N_2O -saturated solutions containing 10^{-2} M SBr, 10^{-3} M SH, and 1 M RH were pulse-

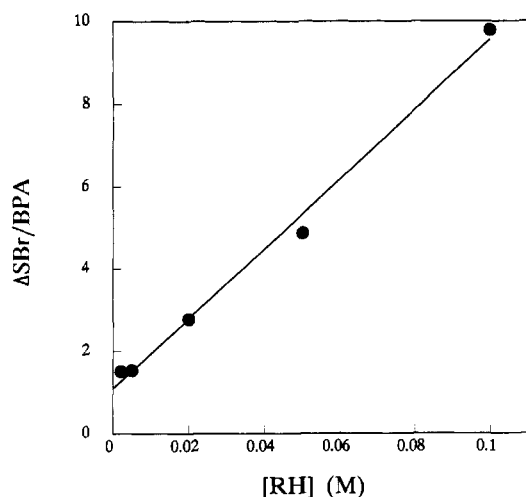
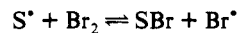


Figure 9. The consumption of SBr divided by produced BPA as a function of [RH]. Conditions: γ -irradiation, $[\text{SBr}]$ 1 mM, N_2O saturation, total conversion $< 50\%$.

irradiated with several pulses, and afterward, the solutions were analyzed iodometrically with respect to remaining SBr. Each $4\text{-}\mu\text{s}$ electron pulse corresponded to the production of ca. $2 \times 10^{-4} \text{ M R}^{\bullet}$. The consumption of SBr was found to be $> 2 \times 10^{-3} \text{ M/pulse}$, but there was a large spread in the data. At the above dose, the lifetime of the radicals with respect to combination should be less than 10^{-5} s . The finding that, in spite of their short lifetime, the radicals manage to bring about a more than 10-fold SBr consumption as compared to their initial concentration confirms the existence of a rapid chain reaction. In order to quantify k_{14} , a first-order termination with a known rate was imposed on S^{\bullet} by repeating the above experiments in the presence of Br^- . Varying the latter from 10^{-4} M to 10^{-3} M caused the chain length to decrease from 6.2 to 2.7. From these data, $k_{13}/k_{14} = 220$ was obtained.

Product Formation during γ -Radiolysis. We have performed product analysis by means of GC/MS and HPLC. The almost exclusive products obtained after γ -irradiation of N_2O -purged solutions containing 1 M RH and $3 \times 10^{-3} \text{ M}$ SBr were about equal amounts of RBr and SH, with a very little trace of BPA. The product balance between RBr and SH implies that no significant amount of $(\text{CH}_3)_3\text{COBr}$ could have been present in the solution. Note that 1 M is the highest RH concentration used in this work, and when in more dilute RH solutions, alkyl hypobromite formation can be ruled out a fortiori. RBr and SH are formed in reactions 12 and 14, while BPA arises subsequent to ring opening of S^{\bullet} in reactions 15–17. Less RH present resulted in an increase of BPA. This titration should reflect the competition between the ring-opening reaction 15 and the hydrogen abstraction reaction 14. A plot of the inverse of BPA yield per consumed SBr versus [RH] yielded a straight line (Figure 9) from which the ratio $k_{14}/k_{15} = 77 \text{ M}^{-1}$ was obtained.

Thermodynamics demand¹⁰ the following equilibrium to be completely shifted to the right.



In order to find out whether the Br^{\bullet} atom or its SBr-complexed form (see eq 11) could cause any other complications, Ar-saturated solutions containing 10^{-3} M each of MeOH and SBr were irradiated. Since in these solutions all radicals are reducing ($\cdot\text{CH}_2\text{OH}$, H^{\bullet} , and $\text{e}_{\text{aq}}^{\bullet}$), Br^{\bullet} is formed quantitatively. Under these conditions BPA did not form. Furthermore, upon γ -irradiation of 10^{-3} M SBr solutions containing 10^{-2} M RH, the BPA yield was found to be about twice as high in N_2O -saturated solutions as in Ar-purged ones. As in the N_2O case, the initial yields of R^{\bullet} and Br^{\bullet} are 90% and 10%, respectively, whereas in the Ar case

Table II. Rates of SBr Consumption and HBr Production as a Function of the Concentrations of Added Substrates during γ -Irradiation at a Radical Production Rate of 1.8×10^{-7} M/s

RH, M	SBr, mM	Br ⁻ , mM	SH, mM	HBr, M/s	-SBr, M/s	purging gas
10 ⁻²	1	0	0	2.13×10^{-7}	6.0×10^{-7}	Ar
10 ⁻²	1	0	0	4.97×10^{-7}	1.65×10^{-6}	N ₂ O
2×10^{-3}	1	0	1	2.4×10^{-7}	1.2×10^{-6}	N ₂ O
5×10^{-3}	1	0	1	3.1×10^{-7}	2.9×10^{-6}	N ₂ O
2×10^{-2}	1	0	1	2.3×10^{-7}	3.8×10^{-6}	N ₂ O
0.1	1	0	1	1.6×10^{-7}	2.7×10^{-5}	N ₂ O
1	1	0	1	1.5×10^{-7}	1.2×10^{-4}	N ₂ O
0.1	1	0	0	2.41×10^{-7}	2.7×10^{-5}	N ₂ O
0.1	1	0.1	0	1.44×10^{-7}	2.7×10^{-6}	N ₂ O
0.1	3	0	0	2.8×10^{-7}	9.0×10^{-5}	N ₂ O
0.1	3	0.1	0	1.9×10^{-7}	1.1×10^{-6}	N ₂ O
1	1	0	0	1.43×10^{-7}	1.4×10^{-4}	N ₂ O
1	1	0.1	0	6.46×10^{-8}	1.4×10^{-5}	N ₂ O
1	3	0.1	0	3.36×10^{-7}	1.4×10^{-5}	N ₂ O
2×10^{-3}	1	0	0.2		1.2×10^{-6}	N ₂ O ^a
2×10^{-3}	0.3	0	0.2		5×10^{-7}	N ₂ O ^a

^a Buffered at pH 6.8.

these figures are 45% and 55%; it is clear that Br[•] atoms, free or complexed, do not cause BPA formation.

It is conceivable that S[•] or OH[•] radicals might abstract hydrogen from SBr. Irradiation of N₂O-purged RH-free solutions containing 10⁻³ M SBr resulted in the formation of BPA as well as of a second unidentified product (detected by HPLC). As the latter product was only observed in RH-free solutions, we must conclude that the rate of hydrogen abstraction from SBr (or from SH) by S[•] is at least 10 times slower than the rate of reaction 14 and hence this possibility need not be considered in the presence of RH.

The Chain Length in γ -Radiolysis. Table II presents the rate of SBr consumption in various conditions. In solutions containing 10⁻³ M SBr and 10⁻³ M SH, the chain length, Q , is around 8×10^2 in the presence of 1 M RH. Q diminishes with decreasing concentration of RH. At 2×10^{-3} M RH, $Q \approx 6$. Were PI[•] not to yield a chain reaction, one would observe a drop in Q from 77 at 1 M to 0.15 at 2×10^{-3} M RH, as can be calculated from $k_{14}/k_{15} = 77 \text{ M}^{-1}$. At 2×10^{-3} M [RH], the chain propagator with a $Q \approx 6$ is then obviously the PI[•] radical in reaction 16. We note also that Q decreases linearly with decreasing [SBr]. This is most noticeable at low RH concentrations. Due to the low value of k_8 , a Br[•] chain should only be observable at substantial RH contents. Such a chain may explain the difference at 1 M [RH] between the experimental $Q \approx 800$ and $77 \times 6 = 462$, the Q resulting from S[•] and PI[•] chains alone. An additional indication of a Br[•] chain operating in solutions containing 1 M RH and 10⁻³ M SBr is provided by the finding that, upon addition of Br⁻, Q decreases more than can be accounted for by reaction 13. For example, addition of 10⁻⁴ M Br⁻ reduces Q by a factor of 10 (see Table II), even though the breaking of the S[•] chain by reaction 13 would be expected to reduce Q merely by a factor of ≈ 3 . The chain length was found to be independent of the rate of initiation; thus termination should be a first-order process. At high RH contents, the total reaction time is sufficiently short (ca. 10 s) for small amounts of potential chain terminators, such as residual O₂, to survive. Therefore, the first-order termination is likely to be due to e.g. O₂ quenching. Indeed, deliberate addition of 10⁻⁴ M O₂ to the sample stops the chain reaction completely. At low RH (<0.1 M), we observe a lag phase of 10–20 s in the consumption dynamics of SBr, which we interpret as consumption of residual O₂. However, the chain length after the lag phase is still found to be dose-independent. A plausible first-order termination in the latter case could be the production of Br[•] atoms.

The Yield of HBr during γ -Irradiation. The production rate of protons, measured as the initial slope of the conductivity buildup, was found to be close to, if slightly higher than, the rate of initiation. This transpires from Table II. Measurements with

a bromide-selective electrode showed that the main counterion (more than 70%) to H⁺ was Br⁻. As for the kinetics of HBr formation, at [RH] > 0.2 M, HBr increased linearly with time as long as there was SBr remaining. A final concentration of ca. 10⁻⁵ M HBr was reached. When [RH] was lowered to below 5×10^{-2} M, the conductivity passed through a maximum of ca. 5×10^{-5} M HBr and eventually decreased to a value of ca. 3×10^{-5} M HBr. This final level was reached simultaneously with the total consumption of SBr. The concentration of the latter was continuously monitored and was found to decrease linearly until less than 10% remained. The finding of a linear rather than an exponential time course of SBr consumption is surprising as Q was found to depend on the initial [SBr] present (see above). We suggest that SBr and adventitious Br₂ compete for carbon-centered radicals (R[•] and PI[•]) in a dynamic equilibrium. Analysis of Br₂ by continuous UV spectrophotometry showed the latter to pass through a maximum simultaneously with HBr. The measured yield of Br₂ was as required by eq 2 and [HBr]. The significant findings are that Br₂ forms subsequent to HBr, the rate of HBr production almost equals the initiation rate, and that the total amount of HBr correlates with the yield of BPA found. These facts strongly indicate that HBr is produced from PI[•] in a side reaction with SBr, presumably with the intermediacy of Br[•]. The formation of the latter species should then constitute the chain termination. A reasonable mechanism for HBr formation could be enolization of PI[•] according to reaction 18 to form a reducing α -hydroxyl radical.



When similar experiments were performed on *N*-chlorosuccinimide (SCI) instead of SBr, the rate of SCI consumption was found to almost equal that of HCl production, and both rates were characteristic of a chain reaction with the propagation rate being proportional to [SCI]. At the same time, HPLC analysis revealed ClCH₂CH₂C(O)NH₂ not to be a product of the reaction. These findings support the above proposal regarding the reaction mode of PI[•] with haloimides in water. The role of hydrolysis of PI[•] in the mechanism of HBr formation is not known. Clearly, resolution of the exact mechanism will have to await quantitative data on the hydrolysis rate of PI[•].

Discussion

Rate Constants of Br Abstraction by R[•] from Br₂ (k_6) and SBr (k_{12}). The determination of k_6 was straightforward, and the rate was found to be close to diffusion control. This is in keeping with the very favorable thermodynamics of the reaction and tallies

Table III. Parameters of the Hydrogen Abstraction Reaction $X^{\bullet} + RH \rightarrow XH + R^{\bullet}$ in Water

X^{\bullet}	BDE(X-H), kcal/mol	$E^{\circ}(X^{\bullet}/X^{-})_{aq}$, V vs NHE	k_H , $M^{-1} s^{-1}$
Cl $^{\bullet}$	103 ^a	2.41 ^b	2×10^9 ^c
OH $^{\bullet}$	119 ^a	1.89 ^b	6×10^8 ^d
S $^{\bullet}$	118 ^e	2.22 ^e	10^7
(CH ₃) ₃ CO $^{\bullet}$	105 ^a	≈ 1.2 ^f	$\approx 10^5$ ^g
Br $^{\bullet}$	87 ^a	1.92 ^b	5×10^3

^a Reference 12. ^b Reference 26. ^c Reference 27. ^d Reference 28. ^e Reference 10. ^f Reference 29. ^g Calculated from data in refs 20a, 30, and 31.

with the corresponding rate measured in organic solvents.¹¹ Rate constant k_{12} was measured in three different ways, yielding values of 1.5, 2.0, and $3 \times 10^8 M^{-1} s^{-1}$, respectively. The last value was determined in the presence of very high Br $^-$ concentrations. Given the unavoidable formation of Br₂ via eq 2 and the large k_6 , the last value, 3×10^8 , is probably spuriously high. Thus we assign to k_{12} the value $(1.8 \pm 0.3) \times 10^8 M^{-1} s^{-1}$. k_{12} is seen to be significantly lower than k_6 . The low rate of k_{12} would seem in apparent contradiction with the diffusion-controlled rate of bromine abstraction by the primary cyclopropylcarbonyl radical from 3,3-dimethyl-*N*-bromoglutarimide (NBG), as measured by Tanko et al.¹¹ in CCl₄ solvent. While it is always possible to invoke solvent effects in an ad hoc way, we believe the discrepancy in the two rates can be more plausibly explained as follows: In ref 10, the N-Br bond strength in SBr was shown to be 65 ± 4 kcal/mol, very close to BDE(C-Br) = 68 ± 2 kcal/mol in alkyl bromides,¹² implying essential thermoneutrality for bromine abstraction reactions with primary alkyl radicals. Thus, modification of the *N*-bromoimide and/or variation of the alkyl radical may easily change the energetics from slightly exothermic to slightly endothermic, which may account for a lowering of k_{12} , by a few orders of magnitude below the diffusion-controlled regime. A typical case in point may be reaction 16. From the selectivity ratio¹³ $k_{-15}/k_{16} = 0.035$ (in CH₂Cl₂) and the estimated¹⁴ $k_{-15} = 3.7 \times 10^6 s^{-1}$ (328 K in C₆H₁₂), $k_{16} \approx 10^8 M^{-1} s^{-1}$ is calculated, a value well below the diffusion-controlled limit.

The Rate Constant of Hydrogen Abstraction by S $^{\bullet}$, k_{14} . Like k_{12} , k_{14} was determined in several ways, the calculated rates being $5.4 \times 10^6 M^{-1} s^{-1}$ (from $k_{14}/k_{12} = 0.03$ and $k_{12} = 1.8 \times 10^8 M^{-1} s^{-1}$), $1.5 \times 10^7 M^{-1} s^{-1}$ (from $k_{14}/k_{12} = 0.081$), $8.2 \times 10^6 M^{-1} s^{-1}$ (from $k_{13}/k_{14} = 220$ and $k_{13} = 1.8 \times 10^9 M^{-1} s^{-1}$) and $6 \times 10^6 M^{-1} s^{-1}$ (from $k_{14}/k_{15} = 77 M^{-1}$ and $k_{15}^{10} = 7.8 \times 10^4 s^{-1}$). These values are very close and yield the safe value of $k_{14} = (1 \pm 0.5) \times 10^7 M^{-1} s^{-1}$. As it is for the first time that the absolute rate constant of hydrogen abstraction from a primary alkane by S $^{\bullet}$ has been measured, it is interesting to compare it to other rates. Table III presents parameters for the hydrogen abstraction reaction by radicals X $^{\bullet}$ from the common substrate 2-methyl-2-propanol (RH) in water. As the C-H bond strength in R-H is ca. 100 kcal/mol, all reactions except with Br $^{\bullet}$ are exothermic. k_H for the latter reaction (k_8 in this work) is satisfactorily reproduced with the assumption of a typical preexponential factor of $10^{11} M^{-1} s^{-1}$ and the activation energy being close to the gas phase ΔH° . Note that in the gas phase¹⁵ the preexponential factors of the hydrogen abstraction reactions by Br $^{\bullet}$ from methane, ethane, and isobutane were all found to be close to $10^{11} M^{-1} s^{-1}$. In ref 16, a good correlation between the rate of hydrogen

abstraction and the ionization potential of the substrate was found. A recent theoretical paper¹⁷ comparing the hydrogen abstraction reactivities of H $^{\bullet}$, CH₃ $^{\bullet}$, and Cl $^{\bullet}$ demonstrated that the electron affinity of the radical is a factor of overriding importance in determining the rate constant, provided the reaction is thermodynamically favorable. It is readily seen from Table III that, in the sense of this analysis, k_H with S $^{\bullet}$ should have been in between Cl $^{\bullet}$ and OH $^{\bullet}$. The finding that it is significantly below the OH $^{\bullet}$ value is strong kinetic evidence for the ground state of S $^{\bullet}$ to be a Π radical. Clearly, hydrogen abstraction by S $^{\bullet}$ can occur thanks to in-mixing of a relatively low-lying Σ excited state, but this process entails a barrier.

Comparison of Our Results to Those in Organic Solvents. It would be instructive to compare the aqueous rate constants of hydrogen abstraction (k_H) by or ring opening (k_{15}) of S $^{\bullet}$ with those in organic solvents. The ratio k_H/k_{15} in CH₂Cl₂ solvent (0.10 M $^{-1}$ with neopentane as the substrate¹⁸) and our determined $k_{14}/k_{15} = 77 M^{-1}$ differ by ca. 10^3 . We recall that k_{-15} in water has been shown¹⁰ to be below $7 \times 10^3 s^{-1}$, to be compared to $3.7 \times 10^6 s^{-1}$ as estimated¹⁴ in cyclohexane. In the case of alkoxy radicals, Walling and Wagner¹⁹ have suggested that solvent polarity may dramatically influence the rate of β -scission while leaving the rate of hydrogen abstraction virtually unaffected. Direct measurements²⁰ support this suggestion. The ring opening of S $^{\bullet}$ being a β -scission, it is very probable that the variation of k_H/k_{15} between water and CH₂Cl₂ is mainly ascribable to the variation of k_{15} . If so, both k_{15} and k_{-15} appear to be lowered by a factor of ca. 10^3 in water as compared to nonprotic and nonpolar organic solvents. This could be rationalized by assuming that both PI $^{\bullet}$ and S $^{\bullet}$ are stabilized by hydrogen bonding to the solvent while the transition state is not. A consequence of this model is that k_H should be around 10^7 also in CH₂Cl₂, which appears to contradict published values.^{3,21} However, the uncertainties inherent in the derivation of rate data from γ -radiolysis results in this work may also bedevil the continuous radical production data on which Walling et al.³ base their rate estimates. An ultimate transformation of the S $^{\bullet}$ chain into a Br $^{\bullet}$ chain may not much affect the end product composition, but it could turn the Br $^{\bullet}$ atom into the main determinant of the chain length during SBr consumption. Consequently, the calculated propagation rate (assuming the termination to be radical combination) could be the hydrogen abstraction rate by the Br $^{\bullet}$ atom. We note that the estimated³ value of $k_H \approx 590 M^{-1} s^{-1}$ (assumed to be $k_H(S^{\bullet} + C(CH_3)_4)$) is close to our $k_8 = (5 \pm 3) \times 10^3 M^{-1} s^{-1}$ and is also in between the hydrogen abstraction rates by Br $^{\bullet}$ from ethane and isobutane, respectively, in the gas phase.¹⁵ In the literature, a direct flash photolytic measurement is reported²¹ on the hydrogen abstraction reaction between the glutarimidyl radical and cyclohexane, yielding a rate constant on the order of $10^3 M^{-1} s^{-1}$. However, given the rapid bromine abstraction of the cyclohexyl radical from *N*-bromoglutarimide, the authors could only have observed the rate of chain termination. Thus, although a definitive measurement in some organic solvent is still lacking, the above considerations taken together suggest a $k_{15} \approx 10^8 s^{-1}$ and a $k_H \approx 10^6 M^{-1} s^{-1}$ per primary H atom in organic solvents.

Experimental Section

Pulse radiolysis was performed at room temperature utilizing doses of 0.3–15 Gy/pulse corresponding to 1.8×10^{-7} to 9×10^{-6} M solutions

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of radicals. The 7-MeV microtron accelerator²² and the computerized optical detection system²³ have been described elsewhere. Dosimetry was performed by means of an aerated 10^{-2} M KSCN solution taking²⁴ $G_{\epsilon} = 2.23 \times 10^4 \text{ heV}^{-1} \text{ M}^{-1} \text{ cm}^{-1}$ at 500 nm. γ -Radiolysis was carried out in a ^{60}Co γ -source at a dose rate of 0.27 Gy/s, as determined by the Fricke dosimeter.²⁴ By mixing a stream from the sample in the γ -source with a 0.1 M KI solution or with a chemiluminescent reagent (pH 9.2, 10^{-3} M luminol, 10^{-2} M H_2O_2), the amount of SBr was continuously monitored both iodometrically and by light detection. The conductivity of the irradiated sample was followed by an immersed Pt electrode, calibrated against HBr. All solutions were made up in Millipore-deionized water. To minimize any decomposition of SBr, the following precautions were taken: Immediately before each experiment, a weighed amount of SBr was dissolved in a solution containing all the other reagents. SBr (Aldrich 99%) was recrystallized from water, vacuum dried, and kept in the dark. 1-bromo-2-methyl-2-propanol (RBr) was prepared according to procedures in ref 25.

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3-Bromopropionamide was synthesized by bubbling NH_3 into an ether solution of 3-bromopropionyl chloride and collecting the precipitate. Both of these products, BPA and RBr, were identified by means of MS and NMR. All other chemicals were of the purest quality available (Aldrich or Merck) and were used as received. Throughout, the experiments were run at ambient temperature (23 ± 2 °C). Quantitative analysis was performed by means of GC/MS (RBr) and reversed-phase HPLC (BPA and SH) by comparison to reference substances.

Acknowledgment. We are grateful to the Swedish Natural Science Research Council for its financial support.

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