One-Electron Reduction Potential and Ring Opening of the Succinimidyl Radical in Water

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Received: October 26, 1992

By means of pulse radiolysis in water, *N*-chlorosuccinimide (SCl) was reduced in a one-electron step to yield the succinimidyl radical, S•, via the intermediacy of the radical anion, SCl•⁻. The rate of ring opening of S• was measured to be 8×10^4 s^{-1}. By equilibration with Cl$_2$•$^-$/2Cl$^-$, the one-electron reduction potential of S• was determined to be 2.22 ± 0.02 V vs NHE. From this value and other data, the N–H bond strength in succinimide was calculated to be 118 ± 3 kcal/mol.

Introduction

The succinimidyl radical, S•, is an elusive species that has but once been observed directly. ESR measurements on X-ray irradiated single crystals of succinimide at 26 K showed S• to be a π radical in the ground state.[1] By reduction of imidyl triflates by Na at an *unspecified* temperature and subsequent trapping near 4 K, Kasai[2] observed by ESR the phthalimidyl radical and 1,8-naphthalimidyl radical, both having π ground states. Na atom reduction of succinimidyl triflate with the same method only yielded the β-(isocyanatocarbonyl)ethyl radical (PI•). PI• is known[3,4] to be formed from S• in reaction 1 (Scheme I).
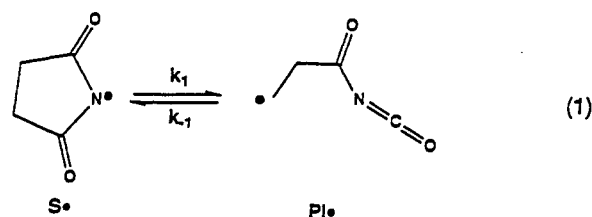
Three ab initio quantum chemical calculations[5–8] on S• identify its ground state as π. The most elaborate of them[5,6] places the first excited state, identified as $\Sigma(N)$, no more than 5.1 kcal/mol above the ground state. Quantum chemical considerations show that both PI• formed[9,10] in reaction 1 and the ground-state product of hydrogen abstraction[11] by S• correlate to the $\Sigma(N)$ state of S•.

Extensive end-product studies reveal the selectivity of S• in hydrogen-abstraction reactions to parallel that of Cl•, while in addition reactions to alkenes vs arenes, S• emulates the OH• radical.[12–14] From competition kinetics in CH$_2$Cl$_2$ solvent, the rate constant of hydrogen abstraction from cyclohexane by S• and k_1 were derived[15] to be $\approx 10^4$ M^{-1} s^{-1} and 10^3–10^4 s^{-1}, respectively. Furthermore, the rate of addition of S• to benzene was estimated[16] to be 8×10^4 M^{-1} s^{-1}. Pulse radiolysis experiments[17] place the reduction potential of S• in water above that of Br• (1.92 V).[18] From cyclic voltammetric measurements in acetonitrile,[19] a reduction potential > 1.84 V was found. These potentials refer to NHE. In this paper, we report on the rapid production in water of S• and the determination of its thermodynamic one-electron reduction potential as well as the rate of its ring opening.

Experimental Section

Pulse radiolysis was performed at room temperature utilizing doses of 0.3–15 Gy/pulse corresponding to 1.8×10^{-7}–9×10^{-6} M radicals. The 7-MeV microtron accelerator[20] and the computerized optical detection system[21] have been described elsewhere. Dosimetry was performed by means of an aerated 10^{-2} M KSCN solution taking[22] $G\epsilon = 2.23 \times 10^4$ and 100 eV^{-1} M^{-1} 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.[22] By mixing a stream from the sample in the γ-source with a 0.1 M

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SCHEME I

$$\text{S•} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{PI•} \tag{1}$$

KI solution or with a chemiluminescence reagent (pH 9.2, luminol 10^{-3} M, H$_2$O$_2$ 10^{-2} M), the amount of SCl was continuously monitored both by iodometry and by light detection. The conductivity of the irradiated sample was followed by an immersed Pt electrode, calibrated against HCl. All solutions were made up in Millipore-deionized water. To minimize any decomposition of SCl, the following precautions were taken: Immediately before each experiment, a weighed amount of SCl was dissolved in a solution containing all the other reagents. Sufficient SH was added so as to keep the ratio HOCl/SCl < 10^{-3}. SCl and SBr (Aldrich 99%) were 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. Throughout, the experiments were run at ambient temperature (23 ± 2 °C).

Results and Discussion

Generation of S•. As the reduction potential of the sulfate radical, SO$_4$•$^-$, is as high as 2.43 V,[23] we attempted to oxidize S$^-$ with it in a one-electron process. However, this reaction occurred with a low rate constant, $k(\text{SO}_4$•$^- + \text{S}^-) = 5.7 \times 10^5$ M^{-1} s^{-1}, so that the properties of the S• radical could not be studied at leisure. In a previous publication,[17] one-electron reduction of *N*-bromosuccinimide (SBr) was shown to result in rapid expulsion ($k > 2 \times 10^7$ s^{-1}) of a bromine atom. It occurred to us that a corresponding one-electron reduction of *N*-chlorosuccinimide (SCl) might engender, after explusion of Cl$^-$, the succinimidyl radical.

Rapid one-electron reduction at pH 7 of SCl by the hydrated electron with a rate constant $k(\text{e}^-_{aq} + \text{SCl}) = 1.6 \times 10^{10}$ M^{-1} s^{-1} gave rise to a species absorbing around 320 nm (see Figure 1a). The spectrum decayed exponentially within ca. 2 μs to a new absorbance as shown in Figure 1b. The presence of 10^{-4} M protons had no effect on the size or decay rate of the absorbance. Addition of small amounts of Cl$^-$ (up to ca. 10^{-4} M) altered neither the initial nor the final absorbance and also did not affect the decay kinetics.
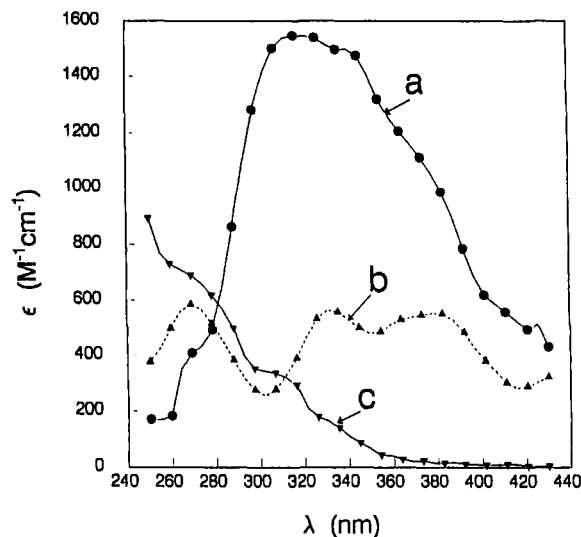
Figure 1. Spectra of intermediate radicals produced upon one-electron reduction of SCl in Ar-saturated solutions. Spectra were constructed in the following way: Transients were recorded both in Ar- and N_2O-saturated unbuffered solutions containing 10^{-3} M each SCl and SH. In order to remove the contribution of the $OH^•$ radical, the transient in the N_2O-purged solution was scaled to 45% and subtracted from the corresponding transient in the Ar-saturated solution. The absolute spectra were obtained after division with the radiation chemical yield of e^-_{aq} + $H^•$ = 3.3 × 10^{-7} M/J. (a) Spectrum immediately after 6-Gy (60 ns) pulses. (b) Spectrum 3 μs after the pulse. (c) Spectrum 40 μs after the pulse.

From these findings, we conclude that the species initially produced is not the chlorine atom, as it would rapidly have reacted with Cl^- {k = (6.5–8 × 10^9 M^{-1} s^{-1}; refs. 24 and 25} to yield the strongly absorbing $Cl_2^{•-}$ species (ϵ = 9000 M^{-1} cm^{-1} at 360 nm). Rather, it would seem that Figure 1a represents the radical anion $SCl^{•-}$. The latter subsequently expels Cl^- to yield the succinimidyl radical, to which we assign spectrum 1b. The rate of Cl^- expulsion was measured to be (8 ± 2) × 10^5 s^{-1}. The $^•CH_2OH$ radical, produced as a result of hydrogen abstraction from methanol by the $OH^•$ radical, was also found to reduce SCl with a rate constant $k(^•CH_2OH + SCl)$ = 6 × 10^8 M^{-1} s^{-1} according to

$$SCl + {}^•CH_2OH \rightarrow SCl^{•-} + CH_2O + H^+$$
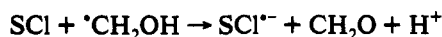
Ring-Opening Reaction of $S^•$. Irrespective of the pH (2.7–9.5), the yield of $S^•$ was found to be the same. In this pH interval, the $S^•$ radical disappeared with a pH-independent first-order rate of ca. 8 × 10^4 s^{-1}, to give rise to a species possessing spectrum 1c. A typical trace is shown in Figure 2 where the drawn line is a calculated exponential with k_1 = 8 × 10^4 s^{-1}. Due to the small absorbances, the signals are rather weak. In order to confirm the rate constant of $S^•$ disappearance, we carried out competition kinetic measurements in the presence of tris(2,2'-bipyridyl)-ruthenium(II) chloride (Ru(II)). The measurements were contingent on the fact that $S^•$ oxidizes Ru(II) to Ru(III), while the product of its first-order rearrangement does not. We determined the amount and kinetics of the spectral change at 450 nm, due to bleaching of Ru(II)

$$S^• \rightleftharpoons PI^• \tag{1}$$

$$S^• + Ru(II) \rightarrow S^- + Ru(III) \tag{2}$$

Denoting by A and A^0 the measured and maximum bleaching at 450 nm and by k_1 and k_2 the rate constants of reactions 1 and 2, respectively, we derive the following relationships:
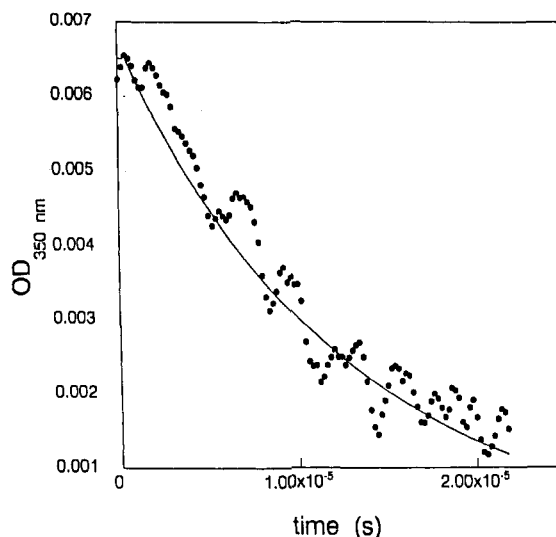

Figure 2. Transient at 350 nm showing the conversion of spectrum b into c. Conditions as in Figure 1, except the dose is 15 Gy/pulse. The full line is a calculated exponential with k = 8 × 10^4 s^{-1}.

$$A^{-1} = (A^0)^{-1}(1 + k_1/(k_2[Ru(II)]))$$

$$k_{exp} = k_1 + k_2[Ru(II)]$$

These two types of measurements are presented in Figures 3 and 4. The ratio of k_2/k_1 extracted from Figures 3 or 4 agreed within 15%. The values of k_1 = (7.8 ± 1.2) × 10^4 s^{-1} and k_2 = (1.3 ± 0.2) × 10^9 M^{-1} s^{-1}1 were obtained. It is seen that the directly and indirectly determined k_1 values are in excellent agreement. Furthermore, this value is unchanged when the SCl concentration is varied from 5 × 10^{-4} to 10^{-2} M. This is evidence that k_1 represents a true first-order process, and we ascribe it to ring opening of the succinimidyl radical to yield $PI^•$ (spectrum 1c). The latter is essentially transparent above 350 nm but absorbs somewhat more strongly than $S^•$ below 300 nm. It is well established[26–28] that reaction 1 is reversible, and thus, the final absorbance should be a measure of the remaining fraction of $S^•$ at equilibrium. The absorbance above 350 nm of spectrum 1c is <10% of that of spectrum 1b. Thus, K_1 > 10, and hence, k_{-1} < 7 × 10^3 s^{-1}. Any residual absorbance of $PI^•$ above 350 nm will obviously raise K_1. The maximum value of k_{-1} is lower, by more than 2 orders of magnitude, than k_{-1} in cyclohexane obtained by competition kinetics at 55 °C in ref 28. This suggests that k_{-1} may be strongly solvent dependent.[29] As k_1 was unaffected by [SCl] up to 10^{-2} M, we conclude that k_3, the rate constant of the reaction between SCl and $PI^•$, must be smaller than ca. 10^6 M^{-1} s^{-1}. During γ-radiolysis of Ar-saturated SCl solutions, the initial rate of SCl consumption was found to increase with increasing SCl concentration, this rate being in excess of the rate of initiation. This implies the operation of a chain reaction, whose rate-determining propagation step is reaction 3, the reaction of $PI^•$

$$PI^• + SCl \rightarrow products^{30} \tag{3}$$

with SCl. While the mechanism of this chain reaction is still under study, the results put a lower limit of ca. 10^4 M^{-1} s^{-1} to k_3.

This can be seen as follows. The experimental chain lengths in the presence of 10^{-3} and 10^{-2} M SCl were found to be 1 and 10, respectively. Then, with a radical production rate of 1.7 × 10^{-7} M s^{-1} and assuming radical combination to be the termination reaction with a rate of 10^9 M^{-1} s^{-1}, we calculate a lower limit of 10^4 M^{-1} s^{-1} to k_3. Of course, $PI^•$ could have hydrolyzed prior to reacting with SCl, but we believe that $PI^•$ and its hydrolyzed form should have similar reactivities toward SCl.

Redox Properties of the $S^•$ Radical. With a lifetime of 13 μs, $S^•$ is sufficiently long-lived for its thermodynamic one-electron
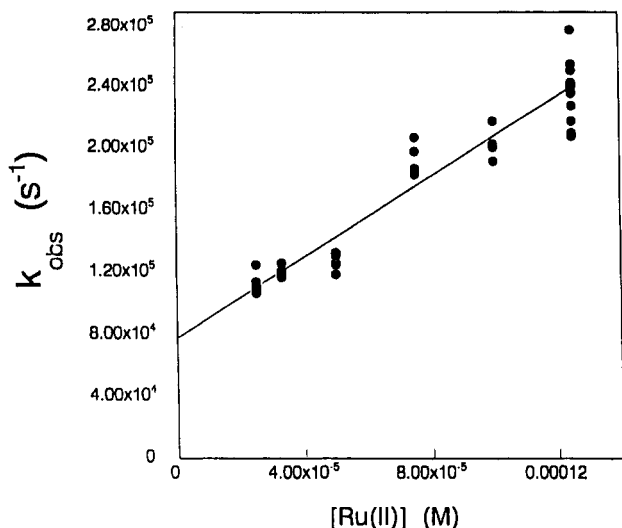
Figure 3. Measured rate of bleaching at 450 nm as a function of Ru(II) concentration. Conditions: 10^{-2} M SCl, 10^{-3} M SH, 2×10^{-2} M MeOH, neutral pH, N_2O saturation, dose/pulse 0.3 Gy.
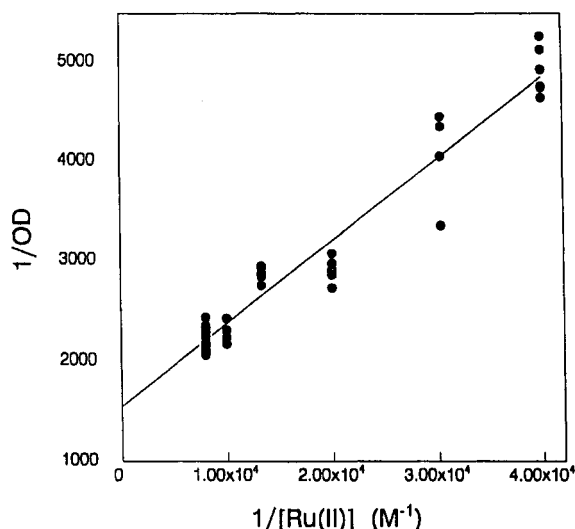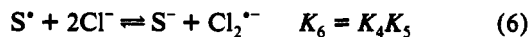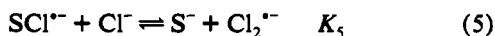

Figure 4. Double-inverse plot depicting the size of bleaching at 450 nm as a function of [Ru(II)]. Conditions as in Figure 3.

redox potential to be measurable, provided the equilibration with a reference couple is fast enough. This was found to be the case with the $Cl_2^{\cdot-}/2Cl^-$ couple. In a N_2O-purged aqueous solution containing 2×10^{-3} M SCl and CH_3OH, pulse irradiation resulted in the rapid formation of $SCl^{\cdot-}$ and $S^{\cdot}$. In the presence of Cl^- and S^-, the following equilibria were established in less than 3 μs:

$$S^{\cdot} + Cl^- \rightleftharpoons SCl^{\cdot-} \qquad K_4 \qquad (4)$$

$$SCl^{\cdot-} + Cl^- \rightleftharpoons S^- + Cl_2^{\cdot-} \qquad K_5 \qquad (5)$$

$$S^{\cdot} + 2Cl^- \rightleftharpoons S^- + Cl_2^{\cdot-} \qquad K_6 = K_4 K_5 \qquad (6)$$

The measurements were done at pH 9.5, the pK_a of SH, by adding varying amounts of equimolar mixtures of SH and S^- and the same amount of methanol to the solution and also varying the concentration of Cl^-, while determining the final absorbance at 350 nm, the spectral maximum of the $Cl_2^{\cdot-}$ radical. At this wavelength, $SCl^{\cdot-}$ absorbs only one-fifth as strongly as $Cl_2^{\cdot-}$, whereas the absorbance of $S^{\cdot}$ is merely 6% of that of $Cl_2^{\cdot-}$. Qualitatively, therefore, the increase of the 350-nm absorbance mainly reflects the increase in $Cl_2^{\cdot-}$ concentration. In accordance with equilibrium 6, the 350-nm absorbance increased with
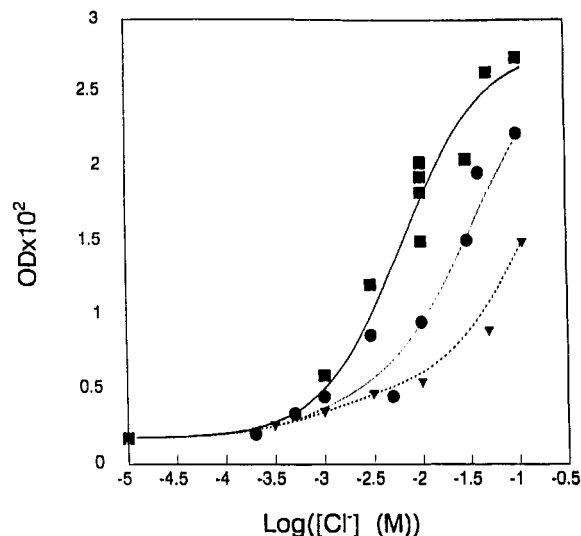

Figure 5. Absorbance measured at 350 nm as a function of $[Cl^-]$ and $[S^-]$. Conditions: 2×10^{-3} M SCl, $[SH] = [S^-]$, $[MeOH] = 2[S^-]$, N_2O saturation, dose/pulse 5.2 Gy. Experimental points: (■) 1×10^{-3} M S^-, (●) 5×10^{-3} M S^-, (▼) 2×10^{-2} M S^-. Calculated curves: (—) 1×10^{-3} M S^-, (- - -) 5×10^{-3} M S^-, (– –) 2×10^{-2} M S^-.

increasing Cl^- concentration, while it decreased when more S^- was added. In view of the fact that all three species, $Cl_2^{\cdot-}$, $SCl^{\cdot-}$, and $S^{\cdot}$ absorb, the 350-nm absorbance is a complex function of $[Cl^-]$ and $[S^-]$. Figure 5 presents three sets of measured absorbance values as a function of $[Cl^-]$ with $[S^-]$ as the parameter. Employing the steepest decent algorithm to the entire data set, the best fit was obtained with $K_4 = 1000 \pm 200$ M^{-1}, $K_5 = 0.14 \pm 0.02$, and $K_6 = 140 \pm 20$ M^{-1}. The error margins were estimated from the simulation. The drawn lines were calculated by use of the experimental extinction coefficients of the radical species at 350 nm and the above equilibrium constants. A value of ≈ 1000 M^{-1} for K_4 was qualitatively assessed through the finding that an increase of added Cl^- from 10^{-4} to 10^{-3} M resulted in an enhanced rate of $SCl^{\cdot-}$ decay with a concomitant reduction of the amount of decay. At 10^{-3} M Cl^- in the presence of 2×10^{-2} S^-, the signal change was about half of that in Cl^--free solutions. Utilizing $E^{\circ}(Cl_2^{\cdot-}/2Cl^-)^{18} = 2.09$ V and $K_6 = 140$ M^{-1}, we obtain the one-electron reduction potential of $S^{\cdot}$, $E^{\circ}(S^{\cdot}/S^-) = 2.22 \pm 0.02$ V vs NHE. In acetonitrile, the oxidation potential of S^-, measured from the irreversible wave by cyclic voltammetry (CV), was found to be 1.84 V vs NHE, in reasonable agreement with our thermodynamically measured one after allowing for transfer of S^- from acetonitrile to water. However, CV of S^- in dimethyl sulfoxide showed an irreversible wave[31] at 0.74 V vs NHE. This value would seem far too low for it to be related to the thermodynamic redox potential of $S^{\cdot}$.

One-Electron Reduction Potentials of SCl and SBr. From the data in ref 32, the equilibrium constant K_7 (eq 7) is calculated to be 5.0×10^{-5} M^{-1}. By utilizing $E^{\circ}(S^{\cdot}/S^-) = 2.22$ V, $pK_a(SH)^{33}$

$$SCl + H^+ + Cl^- \rightleftharpoons SH + Cl_2 \qquad (7)$$

$= 9.5$, and $^2E^{\circ}(Cl_2/2Cl^-) = 1.395$ V, we obtain $E^{\circ}(SCl/S^{\cdot},Cl^-) = -0.24$ V. Our simulation yielded $K_4 = 10^3$ M^{-1}. From these values, we calculate $E^{\circ}(SCl/SCl^{\cdot-}) = -0.07 \pm 0.03$ V. Since $k_{-4} \approx 10^6$ s^{-1}, k_4 is ca. 10^9 M^{-1} s^{-1}. Thus, the rate constant of addition of Cl^- to $S^{\cdot}$ is close to diffusion control. In this work, we determined by combined conductometric and absorbance techniques the equilibrium constant $K_8 = (7 \pm 3) \times 10^2$ M^{-1} in water.

$$SBr + H^+ + Br^- \rightleftharpoons SH + Br_2 \qquad (8)$$

Combination of K_8 with $pK_a(SH) = 9.5$, $^2E^{\circ}(Br_2/2Br^-) = 1.09$ V, and $E^{\circ}(Br^{\cdot}/Br^-) = 1.92$ V yields $E^{\circ}(SBr/S^-,Br^{\cdot}) = -0.13$ V. In a previous publication, we derived the lower limit to k_{-9} to be

2×10^7 s^{-1} and estimated its upper limit as 2×10^9 s^{-1}.

$$S^- + Br^\bullet \rightleftharpoons SBr^- \qquad (9)$$

Judging by k_4, k_9 should be diffusion controlled, i.e., ca. 2×10^9 M^{-1}s^{-1}. Thus, we obtain $E^\circ(SBr/SBr^{\bullet-}) = -0.07 \pm 0.06$ V. This value can be compared to $E^\circ(SBr/SBr^{\bullet-}) = 0.17 \pm 0.3$, previously estimated[34] in acetonitrile. Within experimental error, SCl and SBr are seen to be equally strong one-electron oxidants.

Thermochemical Parameters of Succinimide and *N*-Halosuccinimides. Combining $E^\circ(S^\bullet/S^-) = 2.22$ V with pK_a(SH) = 9.5, we obtain $E^\circ(S^\bullet,H^+/SH) = 2.78 \pm 0.03$ V. In order to calculate BDE(N–H)$_g$, the gaseous N–H bond dissociation enthalpy at 298 K of SH, the following relation is employed:

$$BDE(N-H)_g = 23.06E^\circ(S^\bullet,H^+/SH) + \Delta G^\circ_f(H^\bullet)_g -$$
$$\Delta\Delta G^\circ(SH)_{aq-g} + 298(S^\circ(H^\bullet)_g + S^\circ(S^\bullet)_g - S^\circ(SH)_g)$$

In this expression, g and aq denote standard gaseous and aqueous states, respectively, $\Delta G^\circ_f(H^\bullet)_g$ signifies the standard gaseous free energy of formation of the hydrogen atom at 298 K, and S° is the gaseous entropy of the corresponding species. $\Delta\Delta G^\circ(SH)_{aq-g}$ $= \Delta G^\circ(SH)_{aq-g} - \Delta G^\circ(S^\bullet)_{aq-g}$ is the difference between the free energies of transfer from the aqueous to the gaseous phase of SH and S$^\bullet$, respectively. We assume $\Delta\Delta G^\circ_{aq-g}(SH) = 2$ kcal/mol, similar to the corresponding value for phenol. Also, $S^\circ(SH)_g - S^\circ_g(S^\bullet)_g$ should be ca. 1.5 eu, close to the phenol value.[35] The other parameters are well-known literature constants. Thus, the above expression simplifies to BDE(N–H) $= 23.06 \times 2.78 + 54.3$ $= 118 \pm 3$ kcal/mol. The error range incorporates the uncertainty in the redox measurement (0.7 kcal/mol), in $T(S^\circ(SH) - S^\circ(S^\bullet))$ (0.3 kcal/mol), and a generously estimated uncertainty of 2 kcal/mol in $\Delta\Delta G^\circ_{aq-g}(SH)$. With 118 kcal/mol, the N–H bond in SH is seen to be extremely strong, essentially equal to the O–H bond in water.

In ref 36, the bond strengths of N–Br in SBr and N–Cl in SCl relative to BDE(N–H) have been accurately determined to be

$$BDE(N-H) - BDE(N-Cl) = 47.16 + \Delta_1$$

$$BDE(N-H) - BDE(N-Br) = 54.73 + \Delta_2$$

Here, Δ_1 and Δ_2 are the differences, respectively, in the heats of sublimation between SCl or SBr and SH. Assuming with Tanner et al.[37] $\Delta_1 \approx \Delta_2 \approx -2$ kcal/mol with an uncertainty of ± 1 kcal/mol, we obtain BDE(N–Cl) $= 73 \pm 4$ kcal/mol and BDE(N–Br) $= 65 \pm 4$ kcal/mol. Within the estimated range, the latter value is the same as BDE(C–Br)[38] $= 68 \pm 2$ kcal/mol for primary alkyl bromides. Since BDE(N–Br) is larger by about 19 kcal/mol than BDE(Br–Br) in molecular bromine, any S$^\bullet$ formation via the suggested equilibrium SBr + Br$^\bullet \rightleftharpoons$ S$^\bullet$ + Br$_2$ can safely be ruled out in all chemically realistic situations. Indeed, assuming the rate of S$^\bullet$ reacting with Br$_2$ to be nearly diffusion controlled, small amounts of Br$_2$ in any solution should completely smother the S$^\bullet$ radical. Thus, the present determination bears out and amplifies the early surmise of Tanner et al.[37] that such may be the case, even in the presence of olefinic Br$_2$ scavengers.

Reactivity of the Succinimidyl Radical. The well-known controversy about the π vs Σ character of S$^\bullet$ has been resolved, in that S$^\bullet$ was acknowledged to act as one single species in all chemical situations.[14] The high electron affinity of S$^\bullet$ and the strong N–H bond in SH determined in this work are in keeping with the Cl$^\bullet$-like selectivity of S$^\bullet$ in hydrogen-abstraction reactions as well as its OH$^\bullet$-like addition pattern.

In view of the above, it is interesting that the rates[15] of, e.g., hydrogen-abstraction reactions are so low. In our opinion, this is strong kinetic evidence for the π character of the S$^\bullet$ ground state. For reaction to occur at all, this symmetry-forbidden[9-11] state has to be assisted by a low-lying Σ state. Such an in-mixing

creates a barrier to the reaction, but the details of its dynamics may be extremely complex. Below, we shall present a drastically simplified model, which, however, provides a qualitative rationale.

We neglect the mixing of states and assume the unmixed π state to be completely unreactive. On the assumption that the most accurate quantum chemical calculation[5,6] to date is anywhere near reality, the energy of the $\Sigma(N)$ state (E_Σ) may be close to 5 kcal/mol, say 3–8 kcal/mol above that of the π ground state (E_π). Then, as in the sense of statistical mechanics, the Boltzmann factor $\exp(-(E_\Sigma - E_\pi)/RT)$ is the fraction of the lowest excited state present at all times; the latter should be somewhere between 10^{-2} and 10^{-6} at room temperature. Furthermore, this fraction may vary somewhat with the solvent. For instance, the fraction of $\Sigma(N)$ in water might deviate significantly from that in non-hydroxylic solvents at the same temperature, due to hydrogen bonding to the N atom. Note that, contrary to previous discussions, where one was arguing about the lifetime of the lowest excited state, we assume *the dynamic equilibration between the electronic states to be much more rapid than any chemical reaction of S$^\bullet$*. Given the absence of symmetry restrictions in the $\Sigma(N)$ state and since its BDE(N–H) is above 120 kcal/mol while its E° is close to $E^\circ(Cl^\bullet/Cl^-) = 2.41$ V,[18] both its hydrogen-abstraction and -addition reactions should occur with very high rates, presumably close to diffusion control. Similarly, the allowed ring opening may have a very high rate (10^9 s^{-1} or so) and may perhaps be solvent dependent as well. In conclusion, while the *gross properties of S$^\bullet$* (*such as spectroscopic and thermodynamic*) *reflect the predominant* (*more than 99%*) π *state, its reactivity may be that of the lowest excited Σ state attenuated by the Boltzmann factor*.

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(29) The k_{-1} value in ref 28 was based on the assumption of equal hydrogen-abstraction reactivities toward Et$_3$GeH of PI• and the primary hex-5-enyl radical. A substantially higher value of k_{-1} was obtained by assuming that PI• and the cyclopropylmethyl radical abstract bromine from SBr at the same rate (Tanko, J. M.; Skell, P. S.; Seshadri, S. *J. Am. Chem. Soc.* **1988**, *110*, 3221). In view of the above, it is possible that, for a primary alkyl radical, the PI• radical may be an especially unreactive hydrogen abstractor, due to the electron-withdrawing properties of its CH$_2$C(O)NCO group.

(30) In reaction 3, HCl is formed almost quantitatively. Until we succeed in identifying the degradation product of the PI• radical, the coproduct of HCl, we defer further discussion of reaction 3.

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