Scavenger and Time Dependences of Radicals and Molecular Products in the Electron Radiolysis of Water: Examination of Experiments and Models

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Laplace transform techniques have been used to compare the scavenger and the time dependences of \( e^{-} \), OH, \( H_{2} \), and \( H_{2}O_{2} \) produced following the electron radiolysis of water. A new empirical relationship for the variation of these yields on scavenger concentration is presented. Experimental data on the scavenging of \( e^{-} \), OH, \( H_{2} \), and \( H_{2}O_{2} \) have been fitted with the new function, and it is found that the inverse Laplace transform of the results for \( e^{-} \) and OH do not match the direct experimental measurements of the time dependences of these species. There is no apparent reason for this discrepancy. The accuracy of Laplace transform techniques in nonhomogeneous kinetics was determined by using a deterministic diffusion-kinetic model to calculate the time dependences of the yields of these species in pure water and the dependence of their yields on the concentration of a few selected scavengers. Numerical Laplace transforms of the time dependences of \( e^{-} \), OH, \( H_{2} \), and \( H_{2}O_{2} \) reproduced well the calculated scavenger concentration dependences. The inverse Laplace transform of the new function accurately reproduced the predicted time-dependent kinetics of diffusion-kinetic models even when very different initial distributions of \( e^{-} \) were used. This function is shown to be an improvement on previous functions, especially at matching the yields at high scavenger concentrations. The parameters derived in the analysis of the available experimental data can be used with the new function or its Laplace transform to easily determine the scavenger concentration dependence or time dependence of any of these species with other scavengers for which the scavenging rate constant is known. The influences of various parameters used in the diffusion-kinetic modeling of the radiation chemistry of water are discussed.

Introduction

One of the main goals in the study of the radiation chemistry of water is the determination of the yields and time dependences of the radicals and molecules produced by the irradiation. Each energy-transfer event of a fast electron in a liquid produces a cluster of reactive species, commonly known as a spur. Within a spur there exists a competition between the diffusion and the reaction of these species as the nonhomogeneous concentration gradients relax. Estimates of the yields of the radicals (\( e^{-} \), H, OH) that escape recombination within the spur and the associated products (\( H_{2} \), \( H_{2}O \), \( H_{2}O_{2} \)) are included in most of the standard compilations on the radiation chemistry of water. These yields are usually referred to as homogeneous or steady-state yields, and there are usually limitations associated with these techniques, and we were confined to the hydrated electron and the OH radical. In addition, there are numerous end product studies using radical scavengers that measure the dependence of the yields of the hydrated electron and the OH radical on scavenger concentration. Many of the early studies on the radiolysis of water showed that the yields of molecular products were dependent on the added solute concentration.

Indeed, it was this dependence on solute concentration that originally led to the suggestion of a nonhomogeneous spatial distribution for the reactants. The first complete deterministic treatments of the radiolysis of water addressed the variation of molecular yields with solute concentration specifically. The diffusion and recombination of a geminate pair of reactants are usually described by use of the Smoluchowski equation. Monchick used this approach to describe the reaction of such a pair in the presence of a homogeneously distributed solute. He related the probability of recombination in the presence of the solute to that in the solute's absence using a Laplace transform relationship. Monchick considered the recombination following photodissociation in aqueous solution in which only a single dissociation occurs. This condition is not necessarily valid in radiolysis and it is certainly not true in the radiolysis of water. Nevertheless, Hummel later reasoned that recombination of ions in hydrated hydrocarbons would also be pairwise. He followed the logic of Monchick and developed a phenomenological model for expressing the time dependence of the ion recombination in hydrocarbons as a function of the concentration of added scavengers. Hummel made use of several experimental studies that suggested a square root dependence of the scavenging reaction on the amount of scavenger at low concentrations and selected a simple expression for which the inverse Laplace transform was known. Warman et al. (WAS) developed an alternative set of formulas that matched the square root concentration dependence and that adequately fitted their experimental scavenger dependence studies of the electron in neat hydrocarbons. The theoretical foundations of the Hummel and WAS treatments have been discussed in detail by Mozumder.

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The Laplace transform methodology was first applied to the radiolysis of water to determine the yield of the hydrated electron.\(^\text{(25)}\) Subsequent studies have considered the kinetics of the OH radical.\(^\text{(26-28)}\) The significance of this type of treatment is that it can, in principle, provide information about other species that is inaccessible by direct means. Of course, the results for \(e_{\text{aq}}^-\) and OH radicals should agree and reinforce the time-dependent data obtained by direct techniques.

The use of the inverse Laplace transform method is strictly valid for spurs containing only one pair of radicals or ions, and the effect of the occurrence of multiple dissociations is not known. The relatively long range of the secondary electrons in the radiolysis of hydrocarbons is usually taken to imply that each spur contains only one pair of reactive species. The WAS and Hummel treatments, of course, rely on this assumption. Even in hydrocarbons, there is evidence which suggests that the scavenger concentration dependence does not follow the square root relation at low concentrations,\(^\text{(29)}\) and the single pair model is certainly not appropriate in the radiolysis of water.

The Hummel and the WAS formulas are based on observations of the dependence of ionic scavenging at low solute concentrations in hydrocarbons. Low scavenger concentrations are equivalent to long times in the lifetime of the spur, and there is considerable uncertainty in extending the empirical functions to high concentrations that are representative of the early stages of the development of a spur. Experimental tests of the different functions are limited by (i) the maximum scavenger concentration attainable, (ii) the scavenger's reactivity toward the reactive species, and (iii) problems arising from the radiolysis of the solute as well as the solvent at high concentrations. It is not immediately clear how accurately the time dependences obtained by using inverse Laplace transform methods will reproduce the true kinetics, especially at short times and high scavenger concentrations.

In the work presented in this paper, we have tested the validity of the WAS and the Hummel Laplace formalisms over an extended range of times and scavenger concentrations by applying them to data obtained from various deterministic calculations for the radiolysis of water. Particular attention was paid to the experimentally inaccessible short time and high concentration regime. Within the domain of the deterministic calculations all the scavenger and time dependences are known exactly. Although the WAS and Hummel formulas were found to work reasonably well, we propose a slightly different function that appears to give a more acceptable fit. This new function was applied to the available experimental data on the yields of \(e_{\text{aq}}^-\), OH, \(H_2\), and \(H_2O\) produced in the fast electron radiolysis of water. The inverse Laplace transforms of the fitted curves were compared to the measured time-dependent kinetic profiles of the hydrated electron and the OH radical. This study is the first in which a comparison of this type has been performed. A variety of factors that may influence the agreement between deterministic calculations and the observed yields of the radicals and the molecular products in the radiolysis of water are discussed.

### Diffusion-Kinetic Methodology

The diffusion-kinetic model of the radiolysis of water used here is similar to the numeric deterministic model described in refs 30 and 31. A comparison of this method and a more sophisticated stochastic approach has shown that they predict similar results for the yields of radicals; however, the two methods do not agree as well on the yields of molecular products for the reasons discussed in ref 31. The present method uses a deterministic rate law to model the chemical reactions, and it considers a single "typical" spur representative of the whole system. The significance of this "typical" spur approximation is addressed later in this paper. The kinetics are described by a set of coupled differential equations. Each equation models the temporal and spatial evolution of one of the reactive species in the spur and has the form

\[ \frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i - \sum k_{ij} C_j + \sum \kappa_{in} C_n C_n \]  

(1)

where \(C_i\) and \(D_i\) are the spatially dependent concentration and the diffusion coefficient of species \(i\), respectively. In the present model, the spur is divided into concentric shells. The concentration of each species within a shell is assumed to be homogeneous, and diffusion occurs between adjacent shells. The differential equations are solved by use of the FACSIMILE code,\(^\text{(32)}\) which is based upon the Gear algorithm. The concentration profiles of all the spur species are usually assumed to be initially Gaussian,\(^\text{(33,34)}\) and this convention has been followed except for the hydrated electron. Three differential initial distributions for the hydrated electron were considered. Except where explicitly stated, a Gaussian distribution was employed, but an exponential distribution and a central minimum distribution similar to that of Trumbore and co-workers\(^\text{(35-37)}\) were also investigated.

The reaction scheme selected is similar to that of Schwarz\(^\text{(38)}\) and is listed in Table I. The rate constants were taken from the compilation of Buxton et al.,\(^\text{(39)}\) except for reaction 8 for which there is no direct experimental measurement.\(^\text{(40)}\) The rate coefficient given by Buxton et al. for reaction 8 is \(7.0 \times 10^{-10} \text{ M}^{-1} \text{ s}^{-1}\) and is taken from the work of Thomas.\(^\text{(39)}\) Detailed examination of Thomas' paper reveals this value to be a lower limit. An earlier study by Fricke and Thomas\(^\text{(41)}\) suggests a rate constant of \(3.2 \times 10^{-10} \text{ M}^{-1} \text{ s}^{-1}\), which value was used by Trumbore and co-workers.\(^\text{(35-37)}\) We have chosen \(k = 2.0 \times 10^{-10} \text{ M}^{-1} \text{ s}^{-1}\), which is approximately the average of the two experiments, and it is the same value estimated by Schwarz.\(^\text{(38)}\) The modeling of the scavenging of each water radiolysis species was performed by addition of a particular set of scavenger reactions to the scheme for pure water. These reaction sets are

### Table I: Scheme for the Radiolysis of Pure Water

<table>
<thead>
<tr>
<th>reaction</th>
<th>present work</th>
<th>ref 15</th>
<th>ref 33</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 (e_{\text{aq}}^- + e_{\text{aq}}^- \rightarrow H_2 + OH^- + OH^-)</td>
<td>(5.5 \times 10^6)</td>
<td>(5.5 \times 10^6)</td>
<td>(5.0 \times 10^6)</td>
</tr>
<tr>
<td>R2 (e_{\text{aq}}^- + H^+ \rightarrow H)</td>
<td>(2.3 \times 10^{10})</td>
<td>(1.7 \times 10^{10})</td>
<td>(2.3 \times 10^{10})</td>
</tr>
<tr>
<td>R3 (e_{\text{aq}}^- + H \rightarrow H_2 + OH^-)</td>
<td>(2.5 \times 10^{10})</td>
<td>(2.5 \times 10^{10})</td>
<td>(3.0 \times 10^{10})</td>
</tr>
<tr>
<td>R4 (e_{\text{aq}}^- + OH \rightarrow OH^-)</td>
<td>(3.0 \times 10^{10})</td>
<td>(2.5 \times 10^{10})</td>
<td>(3.0 \times 10^{10})</td>
</tr>
<tr>
<td>R5 (e_{\text{aq}}^- + H_2O \rightarrow OH^- + OH^-)</td>
<td>(1.1 \times 10^{10})</td>
<td>(1.3 \times 10^{10})</td>
<td>(1.2 \times 10^{10})</td>
</tr>
<tr>
<td>R6 (H^+ + OH^- \rightarrow H_2O)</td>
<td>(1.4 \times 10^{11})</td>
<td>(1.0 \times 10^{11})</td>
<td>(1.4 \times 10^{11})</td>
</tr>
<tr>
<td>R7 (H + H \rightarrow H_2)</td>
<td>(7.8 \times 10^8)</td>
<td>(1.0 \times 10^8)</td>
<td>(1.3 \times 10^8)</td>
</tr>
<tr>
<td>R8 (H + OH \rightarrow H_2O)</td>
<td>(2.0 \times 10^{10})</td>
<td>(2.0 \times 10^{10})</td>
<td>(3.2 \times 10^{10})</td>
</tr>
<tr>
<td>R9 (H + H_2O_2 \rightarrow H_2 + OH^-)</td>
<td>(9.0 \times 10^9)</td>
<td>(1.0 \times 10^9)</td>
<td>(1.6 \times 10^9)</td>
</tr>
<tr>
<td>R10 (OH^- + OH \rightarrow H_2O_2)</td>
<td>(5.5 \times 10^9)</td>
<td>(6.0 \times 10^9)</td>
<td>(5.0 \times 10^9)</td>
</tr>
<tr>
<td>R11 (e_{\text{aq}}^- + O_2 \rightarrow O_2^+)</td>
<td>(1.9 \times 10^8)</td>
<td>(1.0 \times 10^8)</td>
<td>(1.0 \times 10^8)</td>
</tr>
<tr>
<td>R12 (H + O_2 \rightarrow HO_2)</td>
<td>(2.1 \times 10^9)</td>
<td>(2.5 \times 10^9)</td>
<td>(3.0 \times 10^9)</td>
</tr>
<tr>
<td>R13 (H_2^+ \rightarrow O_2 + H_2O)</td>
<td>(3.8 \times 10^9)</td>
<td>(3.0 \times 10^9)</td>
<td>(3.0 \times 10^9)</td>
</tr>
</tbody>
</table>
shown in Table II along with the corresponding rate constants that were taken from the compilation of Buxton et al. Some of the H atom studies included reactions for which the rate constants are not included in the compilation of Buxton, and the values of those rate constants were taken to be the same as given in the original experimental study. All reactions with solutes were assumed to be pseudo first order, that is, no depletion of the solute was considered, and the rate constants were taken to be independent of time. The initial yields, radii, and diffusion coefficients employed in the calculations are given in Table III. The diffusion coefficients are the same as those used by Schwarz. The initial yields of the radicals and the molecular products were based on the observed scavenger yields and on the direct time-dependent studies as discussed below. Material balance was maintained. The initial radii were chosen so as to minimize the differences between the predicted yields and the experimentally observed yields of the hydrated electron and the OH radical at long times.

For comparison purposes, the models of Burns and co-workers and Trumbore and co-workers were considered with the same reaction scheme as the present model. The rate constants, initial yields, radii, and diffusion coefficients used in these two models were the same as in the original works. Except where otherwise stated, all the modeling calculations refer to a typical spur of the yields of the radicals and the molecular products resulting from the radiolysis of water by high-energy electrons were fitted with three different functions, using the nonlinear least-squares methodology outlined by Bevington. The general form of the empirical formula used to describe the influence of scavenger reaction is as follows:

\[ G(S) = G_{\text{isc}} + (G^{0} - G_{\text{isc}})F(S) \]

The quantity \( G(S) \) is the observed scavenged radiation chemical yield of a radical or molecular product with respect to a given concentration of scavenger \( S \). In pure water \( F(S) = 0 \) and the observed radiation chemical yield is equal to \( G_{\text{isc}} \), which in the case of radical species represents the yield of radicals that survive recombination reactions in the spur. For molecular products \( G_{\text{isc}} \) is the steady-state or homogeneous yield. The initial yield of a particular species is \( G^{0} \), and the quantity \( (G^{0} - G_{\text{isc}}) \) is that portion of the species that reacts or is produced in the spur in the absence of added solutes.

The function \( F(S) \) describes the scavenger concentration dependence of \( G(S) \). Hummel suggested the form

\[ F_{H}(S) = 1 - \exp(-(a[S])^{1/2}) \]

where \( a \) is a constant that is related to the rate constant for a particular scavenging reaction. At low scavenger concentrations this function approaches the square root dependence found in most experimental studies. Warman used a different function

\[ F_{\text{WAS}}(S) = (a[S])^{1/2}/(1 + (a[S])^{1/2}) \]

This function has the same limiting low-concentration scavenger dependence as the Hummel function. Both the Hummel and WAS functions are members of the family

\[ F(S) = \sum_{i=1}^{n} \frac{(a[S])^{i/2}}{i!} / \sum_{i=0}^{\infty} \frac{(a[S])^{i/2}}{i!} \]

where the former is the limit \( n = \infty \) and the latter results when \( n = 1 \). We have also considered an intermediate function with \( n = 2 \)

\[ F_{\text{LP}}(S) = ((a[S])^{1/2} + a[S]/2)/(1 + (a[S])^{1/2} + a[S]/2) \]

As discussed below, it was found that this function gives a more acceptable fit to the results obtained from deterministic diffusion-kinetic calculations. Equation 6 was used in all the studies involving experimental data. The results with different scavengers can be compared directly with the appropriate scaling, \( G(S) = G(S_{0}k_{S}/k_{a}) \). Here, \( G(S_{0}) \) is the scavenged yield of the radical or molecule with added scavenger \( x \) and a corresponding scavenging rate constant of \( k_{a} \). For each species under study one scavenger system was chosen, and all other systems were normalized to it. For the scavenging of molecular products it is actually the precursors to these products which are scavenged. Since both \( H_{2} \) and \( H_{2}O \) are formed by the combination of similar radicals, the rate constants used in the Laplace transforms are multiplied by 2.

The methodology of the inverse Laplace transform method was developed for a single ion pair. In this limit the ion pair recombines or one member of the pair is scavenged. The model is equally valid for a radical pair if only one of the radicals can be scavenged. It is additionally assumed that the scavenging rate constant is pseudo first order and independent of time. These assumptions are found to be acceptable in the present study, but they are not generally true and they will be addressed in a future publication.

The complete development of the Laplace transform technique for describing scavenger kinetics is rigorously detailed in refs 21 and 22, and only a brief description is given here.

The lifetime of a pair of reactants, in the absence of scavengers, has a distribution function \( f(t) \) such that \( f(t) \) \( dt \) describes the fraction of pairs that will react in the time period of \( t \) to \( t + dt \). In the presence of scavenger \( S \), of concentration [S], the probability that an isolated reactant will be scavenged at time \( t \) is \( 1 - \exp(-k_{S}[S]t) \), where \( k_{S} \) is the rate constant for the scavenging
reaction. The fraction of pairs that would normally have undergone reactions in the spur in pure water but are scavenged is then given by

\[ F(S) = 1 - \int_0^\infty \exp(-k_fS \tau)f(\tau) \, d\tau \]  

(7)

The distribution function \( f(\tau) \) is equal to the inverse Laplace transform of \( 1 - F(S) \). The fraction of pairs that exist after time \( t \), in the absence of scavenger, is given by

\[ F(t) = \int_0^t \frac{f(\tau)}{\tau} \, d\tau \]  

(8)

so the time dependence of reactive species in the absence of scavengers can then be obtained from the inverse Laplace transform of the observed dependences of scavenging reactions on scavenger concentration. Numerical determinations of inverse Laplace transforms are quite problematical since they require a complete description of \( f(S) \). It is more practical to use empirical relations for the scavenger dependences that have analytic inverse Laplace transforms. The inverse Laplace transforms of eqs 9, 4, and 6 are respectively

\[ F_{\text{H}}(t) = 1 - \text{erfc} \left( \frac{\lambda}{2} \sqrt{\frac{t}{\lambda}} \right) \]  

(9)

\[ F_{\text{WAS}}(t) = \exp(\lambda t) \text{erfc} \left( \sqrt{\frac{\lambda t}{2}} \right) \]  

(10)

and

\[ F_{\text{LP}}(t) = 2F \left( \frac{4\lambda t}{\pi} \right)^{1/2} \]  

(11)

Here, \( \text{erfc} \) is the complementary error function, \( F \) is the auxiliary function for the Fresnel integrals,\(^42 \) and \( \lambda \) is equal to \( k_f / \alpha \). Algorithms for \( \exp(x^2) \text{erfc}(x) \), \( \text{erfc}(x) \), and \( F(x) \) can be found in ref 42.

In our application of the Laplace formalism to water radiolysis, it was assumed that the time dependences of the yields of the radicals, and of the molecular products, can be obtained from equations similar to eq 2, that is

\[ G(t) = G_{\text{rad}} + (G^* - G_{\text{ele}})F(t) \]  

(12)

where \( F(t) \) is chosen from one of the eqs 9–11. Equation 12 gives the time dependence of the radicals or the molecular products in the radiolysis of pure water. In all the following calculations \( k_f \) was assumed to be independent of time, however, when a time-dependent rate coefficient rather than a rate constant is considered a scaling of \( F(t) \) results. The use of a time-dependent rate coefficient requires that the time \( t \) is replaced by \( \tau = \left( 1/k_f \right) \int_0^t f(\tau) \, d\tau \) in the eqs 9–11.\(^41 \)

### Results and Discussion

In order to check the validity of the Laplace transform technique for water, it was applied to the predictions obtained using a diffusion-kinetic model. With such a model both the time dependences and scavenger concentration dependences of radical and molecular products can be determined. The calculation is accurate, within the limitations of the diffusion-kinetic model, and the precision of these calculations is much greater than that achieved experimentally. Furthermore, model calculations can be extended to wide ranges of scavenger concentration or over long periods of time. Many other problems such as dosimetry and competition effects that can readily affect experimental studies do not arise with kinetic models. Therefore, the results obtained with a diffusion-kinetic treatment are ideal for determining the accuracy of the Laplace transform technique.

Based on available experimental studies, a chemical system was chosen for each species as a typical scavenger for that species or its precursors. The choice of such systems is arbitrary, but those with relatively well understood and simple chemistry were selected. The scavenging reactions lead to final products which are stable and for which there are several experiments that can be compared to the model. In the case of \( \text{e}^{-} \) and OH radical, the product yields are equal to the radical yields while in the case of molecular species such as \( \text{H}_2 \) and \( \text{H}_2 \text{O}_2 \), it is the precursors to these molecules which are being scavenged. Of course, most scavengers react with several radicals which makes interpretation of the experiments difficult. Some experiments also contained several additional scavengers to eliminate competition effects. The diffusion-kinetic model easily separates reacting pairs, which are especially prevalent at high scavenger concentrations.

Methyl chloride was chosen as the scavenger for \( \text{e}^- \) and formic acid for OH radicals. The molecular product \( \text{H}_2 \text{O}_2 \) was studied by the addition of bromide to scavenge OH radicals while \( \text{H}_2 \) was studied by the addition of nitrite to scavenge \( \text{e}^- \) and H atoms. Table II gives a complete listing of the chemical reactions appropriate to each scavenging system. The calculated scavenging yields of \( \text{e}^- \), OH, \( \text{H}_2 \), and \( \text{H}_2 \text{O}_2 \) are shown as a function of scavenger concentration in Figures 1a-4a, respectively, while the calculated time dependences of the species are shown in Figures 1b-4b, respectively. The Laplace transforms of the time dependences of these yields are also shown in Figures 1a-4a. Figures 1a-4a show that the agreement between the scavenger and time dependence calculations is good. The discrepancy is smallest for \( \text{e}^- \) and largest for OH and \( \text{H}_2 \). The general trend is for the Laplace transform of the time dependence to underestimate the yields of scavenger studies, with the exception of \( \text{H}_2 \text{O}_2 \) for which the yield is overestimated. The extensive scavenger concentration range and the long time period ensure that the results agree at very high and low scavenger concentrations.

Even though the Laplace transform technique strictly applies only to single-pair spurs, it appears to be very good at predicting yields with scavengers in the radiolysis of water. The maximum difference found between the scavenger yields and the Laplace transform of the time dependence is never greater than 5% for any of the species. This difference is less than the errors associated with the majority of experiments. It is seen in Figures 1–4 that the largest discrepancy occurs as the scavenger concentration increases through the region of the inflection. This region corresponds to the time where most spur reactions are occurring, and the kinetics in a water radiolysis spur are not expected to be similar to those of a single pair. Spur reactions with multiple pairs can have combination reactions between like species which are impossible in isolated spurs with a single pair of reactants. The combination of like species in water radiolysis is much less likely to occur than reaction with different species. This fact is apparent when one considers the rate constants and yields of molecular products. Each

\(^{42}\) Abramowitz, M.; Stegun, I. A. Handbook of Mathematical Functions; Dover: New York, 1970.
dependence and the scavenger concentration dependence of the species increases. Subsequent reactions will have a higher probability for scavenging reactions over recombination reactions. The increase in spur size gives a greater probability for recombination as compared to the initial conditions. However, the spur is constantly expanding as the concentration gradients relax. The increase in spur size gives a greater probability for scavenging reactions over recombination reactions. The Laplace transform techniques show the best agreement for \( \text{aq}^- \) which is initially formed with a wide distribution as compared to the other species. Even though the OH radicals, H atoms, and \( \text{H}_2 \) molecules have the same initial distribution in our calculation, local concentrations change rapidly in time because of the differences in diffusion coefficients.

The calculations presented here are the first in which a Laplace transform analysis has been applied to the formation of molecular products. Figures 3 and 4 demonstrate that the technique can be used successfully to describe the production of \( \text{H}_2 \) and of \( \text{H}_2\text{O}_2 \) in the radiolysis of water. Although some of the yield of \( \text{H}_2 \) is due to unimolecular processes, as discussed later, most of its production is due to reactions in multiple-pair spurs. The use of a deterministic rate law to describe the kinetics means that the transform technique is equally valid for describing the formation of molecular products from identical reactants as it is for the decrease in the yields of the reactants. Preliminary calculations using the stochastic technique described in ref 31 also support the use of a Laplace transform approach to the analysis of the time dependence and the scavenger concentration dependence of the formation of molecular products.

Different initial distributions for \( \text{aq}^- \) were used to check if the agreement between Laplace transform techniques and scavenger studies was a consequence of using Gaussian distributions. A central minimum distribution similar to that of Trumbore and co-workers\(^\text{33-35}\) and an exponential distribution were considered. As shown in Figure 1, the agreement is equally good for all three distributions. Clearly, within reasonable limits, the initial distribution has little effect on use of the Laplace transform technique. This result is significant since there is considerable disagreement as to the initial spatial distributions of the species in a water radiolysis spur.\(^\text{14,15,30,31,33-35}\)

Another criticism of the use of Laplace transform techniques for predicting nonhomogeneous kinetics is the time dependence of rate constants. The largest effect of the time dependence of rate constants should be at very short times. Kinetic modeling of the spur kinetics in the radiolysis of water using a stochastic model with both time-independent rate coefficients and time-dependent rate coefficients for scavenging showed only small differences in the predictions at short times.\(^\text{41}\) The dependence of rate coefficients on time is not expected to have a large effect on the use of Laplace transform techniques in the radiolysis of water. As mentioned previously, any time dependence of the scavenging rate coefficient will merely result in a nonlinear scaling of the time dependences obtained from scavenger experiments. It should be noted that this shift will be to shorter times. Calculations for the hydrated electron using a time-dependent rate coefficient in the inverse Laplace transform give results essentially identical with those presented.

There are many more radiation chemistry studies using scavengers than there are time-resolved studies\(^\text{2-5}\). In addition, there

are no time-dependent studies for the molecular products H₂ and H₂O₂. For practical reasons, it is very desirable to be able to convert scavenger concentration studies to time dependences. Most scavenger studies are performed at low concentrations which correspond to the later stages of the chemistry in the spur. Low reactivity or solubility usually hinders studies at high concentrations. Scavengers in high concentrations will directly absorb some of the incident particle energy, leading to dosimetry problems of the yields and its numerical Laplace transform are shown as solid lines. The fits to the scavenger data and their appropriate Laplace transforms are shown with the same line types as in Figure 1.

Figures 1a-4a. The deviations of the Hummel and WAS functions from the expected kinetics are much more apparent in the time dependences than in the scavenger concentration studies, especially at short times. Equation 11 seems to give the best overall agreement with the modeled time dependences. Figures 1-4 show that a reliable set of data for the production of e⁻, OH, H₂, or H₂O₂ can be fit with eq 6 to give a set of values of a and λ for each species. These coefficients can be used with eq 11 to give the time dependence of that species in pure water. The rest of the analysis of experimental data presented in this paper was performed in this manner.

The study of the scavenger and time dependences using Laplace transforms has been limited to e⁻, OH, H₂, and H₂O₂. The species HO₂ was not considered because its yield is very small with electron radiolysis, although it should be included in any study with heavy ions. The production of H atoms was also not included in this study. The Laplace transform method appears to work equally well for radical decay or molecular product production, but the change must be monotonic in time or scavenger concentration over the regime studied. Most diffusion-kinetic models, as shown in Table III, assume an initial yield of H atoms. Reaction R2 produces additional H atoms so the yield of this species initially rises for a few nanoseconds. Following the completion of reaction R2 the yield of H atoms decreases due to reactions R8-R10. The formalisms given here cannot follow the variation in yields as exhibited by the H atom. A more complete

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Analytic formulas for the inverse Laplace transforms of eqs 3, 4, and 6 are given by eqs 9-11, respectively. The curves obtained from these equations, using the same values of a and λ as found in the scavenger concentration fitting of the previous section, are shown in Figures 1b-4b. The deviations of the Hummel and WAS functions from the expected kinetics are much more apparent in the time dependences than in the scavenger concentration studies, especially at short times. Equation 11 seems to give the best overall agreement with the modeled time dependences. Figures 1-4 show that a reliable set of data for the production of e⁻, OH, H₂, or H₂O₂ can be fit with eq 6 to give a set of values of a and λ for each species. These coefficients can be used with eq 11 to give the time dependence of that species in pure water. The rest of the analysis of experimental data presented in this paper was performed in this manner.

The study of the scavenger and time dependences using Laplace transforms has been limited to e⁻, OH, H₂, and H₂O₂. The species HO₂ was not considered because its yield is very small with electron radiolysis, although it should be included in any study with heavy ions. The production of H atoms was also not included in this study. The Laplace transform method appears to work equally well for radical decay or molecular product production, but the change must be monotonic in time or scavenger concentration over the regime studied. Most diffusion-kinetic models, as shown in Table III, assume an initial yield of H atoms. Reaction R2 produces additional H atoms so the yield of this species initially rises for a few nanoseconds. Following the completion of reaction R2 the yield of H atoms decreases due to reactions R8-R10. The formalisms given here cannot follow the variation in yields as exhibited by the H atom. A more complete

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study of the yield of H atoms in the radiolysis of water is in progress. The only modeling of H atom yields in this work is to examine the initial yields for water radiolysis; see below.

The yield of the hydrated electron has been measured with scavengers\(^\text{45-48}\) and by direct observation.\(^\text{27-29}\) In this work, the scavenging of \(e_{aq}^-\) by methyl chloride has been taken as the primary system to be examined. The data from the studies with other scavengers were normalized relative to the results with methyl chloride and fit by using eq 6. It was found that the initial yield of \(e_{aq}^-\) was 4.3 molecules/100 eV when no restrictions were placed on the fitting parameters. In view of the considerable data on the time dependence of the yield of \(e_{aq}^-\), this value is probably a little too low and reflects the lack of data at very high scavenger concentrations. The time dependent studies strongly suggest an initial yield of \(e_{aq}^-\) of about 4.8 molecules/100 eV, and this value was chosen. The difference between the two values is only about 10%, and they give equally good fits to the data obtained in studies with scavengers. The resultant parameters are given in Table IV, and the fit through the data is shown as the solid line in Figure 5. One data point of Balkas et al.\(^\text{49}\) at about 1 M was quite different from the rest of the data. That experiment contained no added methanol to suppress the reactions of OH radicals, and that data point was ignored in the fitting of the data. It can be seen in Figure 5 that the rest of the data are well represented by the fit. The inverse Laplace transform of Figure 5a is shown in Figure 5b. There is a large discrepancy between the Laplace transformed data and the directly observed yields in the region 0.1–100 ns. It has been suggested that the data of Fanning\(^\text{50}\) are certainly too low because of residual oxygen in the system.\(^\text{31}\) The differences in the yields predicted by the two techniques are as much as 20% which, as discussed above, is much greater than the error expected to arise from the use of Laplace transform techniques. Furthermore, the discrepancy is in the opposite direction from any error arising from the use of a time-independent rate constant rather than a time-dependent coefficient. Also shown in Figure 5b are the modeled kinetics for \(e_{aq}^-\) using the parameters (see Table III) of Burns et al.,\(^\text{\text{50}}\) which were optimized to scavenging data, and those of Trumbore et al.,\(^\text{\text{33-35}}\) which were optimized to the time-dependent studies. The numerical Laplace transforms of the Burns and Trumbore models are shown in Figure 5a. It is apparent that each model is fairly good at reproducing the data it was designed to match, but each gives a very poor fit in the other domain. The differences in the two sets of experimental data are beyond their respective errors.

The source of this discrepancy is not obvious. From Figure 5b it appears that the two sets of data are transposed in time by almost an order of magnitude. It is very unlikely that the scavenger rate constants, especially for several completely different systems, could be in error by this amount, but it is also unlikely that the time-resolved studies are shifted by such a large time interval. Clearly more experiments using both techniques are in order. The scavenger studies do show a considerable amount of scatter but not enough to account for the observed differences.

The yield of OH radicals has been measured with a variety of scavengers,\(^\text{28,30-31}\) and direct measurements have been made.\(^\text{11-12}\)

Table IV: Parameters in the Fitting of the Data

<table>
<thead>
<tr>
<th>species</th>
<th>(G_0)</th>
<th>(G_\infty)</th>
<th>(a_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(e_{aq}^-)</td>
<td>4.80</td>
<td>2.55</td>
<td>9.560 (\times) 10^{-1}</td>
</tr>
<tr>
<td>(H_2)</td>
<td>0.15</td>
<td>0.44</td>
<td>3.911</td>
</tr>
<tr>
<td>OH</td>
<td>5.50</td>
<td>2.66</td>
<td>3.358 (\times) 10^{-2}</td>
</tr>
<tr>
<td>(H_2O_2)</td>
<td>0.00</td>
<td>0.72</td>
<td>4.128</td>
</tr>
</tbody>
</table>

\(^{\text{a}}\) In molecules/100 eV. \(^{\text{b}}\) In M^{-1}.

The formic acid dosimeter was used as the primary scavenger system and all of the other scavenger systems were normalized to it. Hydroxyl radical yields as a function of scavenger concentration are shown in Figure 6a. Using eq 6 a best fit to the data was found, and the resulting parameters are given in Table IV. When no constraints were placed on the fitting parameters, the initial OH radical yield was found to be 4.4 molecules/100 eV, which is considerably lower than that found in the time-dependent studies. The time-dependent studies suggest an OH radical yield of about 5.9 molecules/100 eV at 0.2 ns,\(^\text{11}\) but the use of this value as a fitting parameter clearly does not reproduce the scavenger data. A value of 5.5 molecules/100 eV was chosen as the initial OH radical yield based mainly on material balance; see below. In the fitting of the data the highest yield of OH determined by Hart\(^\text{50}\) with a 1 M formic acid solution and the data of Burns and Sims\(^\text{32}\) at an effective concentration of 2.5 M were not used. It appears from Figure 6a that these two points are considerably different from the other points. Inclusion of these two data points, however, would not change the fitted curve enough to affect the following discussion. Also shown in Figure 6a are the Laplace transforms of the OH radical yields predicted by the Burns\(^\text{50}\) and Trumbore\(^\text{33-35}\) models. The Trumbore model predicts...
Electron Radiolysis of Water

The relative reactivities of formate and ferrocyanide to formic acid are determined by using the same parameters as above in the inverse Laplace transform, and their numerical Laplace transforms are shown with the same line type as in Figure 5.

The time dependence of the OH radical yield is shown in Figure 6. It is seen that the inverse Laplace transform of the scavenger data is considerably different from that found by direct measurements. The later experimental study did not give absolute yields so that data were normalized to the value of 5.9 molecules/100 eV at 0.2 ns as suggested in ref 11. This absolute value of the OH radical yield was used by Trumbore and co-workers to determine the parameters of their model. Figure 6b shows that model does match the experimental time-dependent data very well. It is also obvious from Figure 6a that the Laplace transform of the data from the Trumbore model does not even closely reproduce the data obtained with scavengers. Significant errors can be expected when the Trumbore model is used to describe end product measurements using scavengers. The discrepancy between the time dependence measurements and the yields of OH radicals determined with scavengers is much too large to be a result of errors in the Laplace transform method. There is clearly a fundamental error in one or more of the measurements. The direct measurement of OH radicals is very difficult because the absorption is at such a low wavelength and intensity that the dosimetry is difficult. The scavenger studies were performed with a variety of different systems in various laboratories, and with a few exceptions, all the data points agree well. As shown in Figure 6b, the direct measurements of Jonah and co-workers are fairly reproducible in a relative sense. It is most likely that the yield of OH radicals at 0.2 ns is not 5.9 but about 4.4 molecules/100 eV as suggested by the studies with scavengers.

There are no direct measurements of the time dependences of the molecular products $H_2$ and $H_2O$. The yields of these products have been determined by using scavengers for the radical precursors. The yield of $H_2$ has been determined with H atom and $e_{aq}$ scavengers while the yield of $H_2O$ has been determined with several OH radical scavengers. The nitrite system has been chosen as the primary scavenger of $H_2$ precursors and the normalized data are shown in Figure 7a, while the scavengers of $H_2O$ precursors were normalized to the bromide system and those data are given in Figure 8a. There is a considerable amount of scatter in the different sets of data. Fits of the two sets of data using eq 6 are shown in Figures 7a and 8a as solid lines. The parameters are listed in Table IV. No additional restrictions were placed on the fitting of the data. The best fit of the $H_2O$ data implies that at very high concentrations it can be completely

OH radical yields that are in some cases 50% greater than those found with scavengers. The model of Burns gives a much better representation of the data with scavengers, but it too shows considerable discrepancies.

![Figure 6](image1)

![Figure 7](image2)

**Figure 6.** (a) Scavenged yield of OH radical as a function of effective scavenger concentration relative to formic acid: (A) results of diffusion-kinetic calculations with formic acid; (F) formic acid, ref 50; (M) ref 51; (A) ref 53; (O) formate, ref 52; and (W) ferrocyanide, ref 28. The relative reactivities of formate and ferrocyanide to formic acid are 24.6 and 80.8, respectively. The solid line is a fit through the data using eq 6 and the parameters in Table IV. (b) The time dependence of OH radicals in pure water: (M) ref 11, (A) ref 12. The data of ref 12 were normalized to a value of 5.9 at 0.2 ns. The solid line was obtained by using the same parameters as above in the inverse Laplace transform, eq 11. The time dependences as obtained from the diffusion-kinetic models and their numerical Laplace transforms are shown with the same line type as in Figure 5.

**Figure 7.** (a) Scavenged yield of $H_2$ molecules as a function of effective scavenger concentration relative to nitrite: (A) results of diffusion-kinetic calculations with nitrite; (M) nitrite, (F) cupric, ref 13; (O) hydrogen peroxide, ref 54; and (W) nitrous oxide, ref 55. The relative reactivities of cupric, hydrogen peroxide, and nitrous oxide to nitrate are 8.0, 2.7, and 2.2, respectively. The solid line is a fit through the data using eq 6 and the parameters in Table IV. (b) The time dependence of $H_2$ molecules in pure water. The solid line was obtained by using the same parameters as above in the inverse Laplace transform, eq 11. The time dependences as obtained from the diffusion-kinetic models and their numerical Laplace transforms are shown with the same line type as in Figure 5.
The Trumbore model considerably underestimates the yield measurements which, as stated above, give yields of the OH radical means that less H2O2 is produced. The early experiments of Schwarz suggested that the yield of H2 could not be completely suppressed with scavengers. It has been assumed that a unimolecular or ionic process is responsible for its production.2

As shown in Figure 8, the scavenged yield of H2O2 molecules as a function of effective scavenger concentration relative to that of bromide; (a) results of diffusion-kinetic calculations with bromide; (●) bromide, ref 60; (+) ref 61; (●) ref 58; (●) ethanol, ref 56; (+) propanol, (●) ethanol, (●) ethanol and acetone, ref 57; and (●) chloride, ref 59. The relative reactivities of ethanol, propanol, and chloride to bromide are 0.17, 0.25, and 0.39, respectively. The solid line is a fit through the data using eq 6 and the parameters in Table IV. (b) The time dependence of H2O2 molecules in pure water. The solid line was obtained by using the same parameters as above in the inverse Laplace transform, eq 11. The time dependences as obtained from the diffusion-kinetic models, and their numerical Laplace transforms are shown with the same line type as in Figure 5.

Material balance of the oxidizing species, therefore, also suggests that the yield of OH radicals at 0.2 ns is not 5.9 molecules/100 eV but a value somewhat lower.

No kinetic modeling of the radiolysis of water can be expected to be completely correct using a single, typical spur. The effects of entities such as blobs and short tracks on the chemistry can be considerable. The inclusion of different track entities in modeling is usually called linear energy transfer (LET) effects, and these types of calculations have been performed. However, it is much more common to use an average spur in modeling calculations. The determination of the parameters of such a spur was attempted. Initial yields for eaqH, OH, H2, and H2O2 were taken from the parametric fit of the scavenger data of Figures 5–8, as given in Table IV. Because of the scatter of the experimental data, there are some uncertainties in the initial yields, especially for eaqH and OH radicals. Scavenger studies and direct observation experiments seem to agree that the initial yield of eaqH is about 4.8 molecules/100 eV, and this value was used here. Given the available experimental data it was thought that the initial yield of OH radicals is too uncertain, and so material balance was used to give more confidence to its value. As discussed above, the initial yields of H2 and H2O2 are taken to be 0.15 and 0.0 molecule/100 eV. The last species for which the initial yields must be determined is the H atom.

Most studies on the yields of H atoms in the radiolysis of water determine the sum of the reducing species. There are only a few studies that attempted to determine the yield of H atoms as a function of scavenger concentration. Measurement of the H atom yield is quite complicated because of the many competing reactions. During the lifetime of the spur H atoms are both formed and lost by reaction. No experimental study has been able to determine its initial yield. For modeling purposes, the initial yields of eaqH, H2, and H2O2 were held constant as the OH radical and H atom yields varied while maintaining material balance. The experimental data for OH radicals shown in Figure 6 give some bounds on the range of possible OH radical yields.

The diffusion-kinetic model requires the initial yields of radicals and molecules, their initial radii, and the average energy per spur. It was assumed here that the energy of a "typical" spur is 62.5 eV, similar to the other kinetic models. This value is not the average energy deposited per energy loss event along an electron track, which is about 40 eV. The use of a spur with a slightly higher energy content is a crude attempt to compensate for LET effects. The effect of energy content of the spurs on product yields will be discussed below.

The initial radii of the species and initial yields of OH and H atoms were varied in a systematic manner until the calculated yields of eaqH and OH radicals at long times gave the best agreement with experiments. The final parameters thus obtained are given in Table III, and the kinetic calculations using these parameters are shown as solid lines in Figures 5–8. It can be seen that the model reproduces well the yields of eaqH and OH radicals as determined by using scavenging experiments. The results of the model do not agree as well with the molecular yields. Molecular yields are much more sensitive to stochastic effects. It is probably impossible to get a better representation of the experimental data using a simplistic spur and a deterministic model.

The modeling of H atom experimental studies with scavengers is shown in Figure 9. The chemistry of the H atom is quite complicated, and each experimental study has to be modeled separately. Figure 9 shows the results of three such scavenger studies, and it can be seen that the agreement is reasonably good.
Figure 9. H atom yields (molecules/100 eV) as determined by the change in the yields of molecular hydrogen with the scavengers (●) hydroxide; (●) phosphate, ref 65; and (●) nitrate, ref 67. The actual scavenger concentrations are plotted. The open symbols are the results of the diffusion-kinetic model, and they are connected with straight lines to aid the eye.

Figure 10. Dependence of the yield of e− (molecules/100 eV) on the energy content of the spur as a function of relative scavenger concentration (a) and as a function of time in pure water (b). The dashed lines show the calculated variation in yields for spurs of 20, 40, 62.5, 80, and 100 eV. The solid points and lines are the same as described in Figure 5.

Many of the experimental studies used ionic scavengers for the e− for which rate constants are not well known. In addition, at high OH− concentrations, the chemistry is no longer represented by the reaction scheme used in this study. The most confidence in the model is in the long time, small scavenger concentration, limit where it reproduces the experimental studies well. It was found that the initial yield of H atoms needed to be of the order of 0.42 molecule/100 eV. This result suggests a value of 5.5 molecules/100 eV for the initial yield of OH radicals. As shown in Table III, these yields are somewhat lower than commonly used in kinetic modeling studies of water.

The kinetic model calculations assumed a spur of 62.5 eV. It is possible to obtain similar long time yields by use of different spur energies and initial radii. A series of calculations were performed for spurs of 20, 40, 62.5, 80, and 100 eV in which the radii were varied so as to optimize the agreement between the calculated and observed e− and OH radical yields. The results are shown in Figures 10 and 11, respectively. Similar results, but inverted, were found for the molecular products and are not shown. It can be seen that there are any number of combinations of spur energies and radii that will give similar long time yields. The figures show that it is the time dependence of the radicals that is most affected by changing the energy of the spur. As the energy of the spur increases, radical recombination processes occur at longer times. The radii used in these calculations are shown in Table V. It was found that the radii vary almost linearly with spur energy. The average spur energy density, assuming a homogeneous distribution, is also shown in Table V. The lower energy spurs are more dense than the high energy spurs. This increase in density is the predominant reason for the faster recombination of radicals. Similar results are expected when higher LET components of the electron track are included with the simple
spur. It can be seen from Figures 10 and 11, and similar figures for the molecular products, that the use of a 62.5-eV spur seems to give the best overall fit to the experimental data obtained with scavengers when a "typical" spur is modeled. It is expected that when LET effects are correctly included in the model the average spur will be closer to 40 eV as predicted by calculations of the energy loss of fast electrons. 8

Conclusions
The Laplace transform technique was found to be quite satisfactory in interconverting scavenger concentration dependence and time dependence studies on the radical and the molecular product yields in the radiolysis of water. Complications due to multiple dissociations appear to be unimportant. New formulas are presented which when properly parametrized to the experimental data on the scavenger concentration studies give time dependences accurate to within a few percent. The parameters for $e_{aq}^-$, OH, H, and H$^+$ were determined from existing experimental studies. These parameters can be used as guides in further modeling efforts. They can also be used to predict the kinetics for scavengers other than the ones modeled here if the appropriate rate constants are known. For most simple aqueous systems, the use of the Laplace formalism should give as good results as complicated diffusion-kinetic models. Of course, diffusion-kinetic models give greater insight into the radiation chemistry and the reaction mechanisms in particular. Further experimental effort in both scavenger concentration studies and time-dependent studies of the radical and the molecular products of the radiolysis of water are needed. It is clear that there is still considerable uncertainty in the yields and kinetics for this medium of crucial importance in radiation chemistry and biology.

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Registry No. H$_2$O, 7732-18-5; CH$_3$Cl, 74-87-3; HCOOH, 64-18-6; OH, 3352-57-6; H$_2$, 1333-74-0; H$_2$O$_2$, 7722-84-1; H, 12385-13-6.

Low-Temperature Photochemistry and Spectroscopy of the Photoadducts of Tetracene with Anthracene and with 9-Bromoanthracene

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The low-temperature photochemistry and spectroscopy of the photoadduct of anthracene and tetracene (AT) and the photoadduct of 9-bromoanthracene and tetracene (BrAT) are reported. Included are the fluorescence and phosphorescence spectra and the associated excited-state lifetimes of these molecules. Heavy-atom effects due to the bromine substitution in BrAT are apparent in these results. The low-temperature photochemical decomposition mechanism for both molecules is investigated by photochemical hole burning (PHB) as well as emission spectroscopy. Satellite holes in the PHB spectra of AT give excited-state vibronic energy levels. The predominant low-temperature photochemical decomposition mechanism occurs following absorption of a photon by the excited triplet state. These conclusions are supported by experiments in which both fluorescence and phosphorescence intensities are observed under conditions of one- and two-color excitation. Action spectra for two-color PHB are similar to triplet–triplet absorption spectra, also supporting this conclusion. Finally, a quantitative model of PHB hole depth vs burn intensity supports the triplet–triplet absorption photochemical decomposition mechanism.

1. Introduction
Over the past few years we have been studying the low-temperature spectroscopy of a series of polycene photoadducts. Our studies include work on dianthracene $^1$ (A$_2$), the anthracene–tetracene photoadduct $^2$–$^4$ (AT), ditetracene $^5$ and dipenta–tetracene. $^6$ One of the principal techniques used in these investigations was photochemical hole burning (PHB). $^7$ In the present paper we discuss further the low-temperature spectroscopy and photochemistry of AT as well as new results on the photoadduct of 9-bromoanthracene with tetracene (BrAT).

The photochemistry and photophysics of A$_2$, bis(9-methylanthracene), and AT have been investigated by Yamamoto and Grellmann. $^8$ $^5$ The photochemical and photophysical schemes deduced in these cases involve excited singlet and triplet states of the photoadduct as well as those of the product excimer or exciplex. These authors describe three distinct decomposition channels: thermally activated, mainly adiabatic decomposition from the S$_2$ state; decomposition from an upper triplet state, T$_2$; direct decomposition from an upper singlet state, S$_1$. Specifically, $^8$ for AT, molecules in the S$_2$ state can undergo decomposition over a relatively high energy barrier. Therefore, decomposition through the lowest energy excited singlet state competes with fluorescence only at temperatures greater than about 200 K. From higher singlet states, prepared by exciting from S$_0$ with light of $\lambda$ < 280 nm, decomposition can occur directly at low temperatures without the intervention of a triplet state. The effect of this process is apparent when the fluorescence excitation and the absorption spectra of this molecule are compared. $^8$ Photodecomposition may also possibly occur from the lowest energy singlet state at low temperature following an S$_0$ – S$_1$ absorption process. Intersystem crossing (isc) from the S$_1$ state of AT was reported to occur with a yield $^9$ of 0.53 at 293 K, assuming that the

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(1) Iannonet, M. A.; Scott, G. W. Unpublished results.