Diffusion−Kinetic Modeling of the γ-Radiolysis of Liquid Cycloalkanes

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A deterministic diffusion−kinetic model has been successfully applied to the radiation chemistry occurring in a typical spur produced in the γ-radiolysis of liquid cyclopentane, cyclohexane, and cyclooctane. The predictions of the yields of the cycloalkenes, bicycloalkyls, and the cycloalkyl iodides in solutions of iodine are in excellent agreement with experimental data. The major adjustable parameters in the model are the characteristic radii of the initial Gaussian spatial distributions of the reactive species. Values for these radii were found to be 0.5, 1.1, and 0.55 nm in cyclopentane, cyclohexane, and cyclooctane, respectively. The results suggest that the spurs of cyclopentane and cyclooctane are very small, ca. one molecular diameter, with resulting large local concentrations of reactants. With cyclohexane, the spur size is twice as large and the initial local concentrations are an order of magnitude smaller. The experimentally observed temporal invariance of the cyclohexyl radical can be explained by competing effects in the spur evolution. Details and implications of the spur model are discussed.

Introduction

A considerable amount of knowledge of the radiation chemistry of hydrocarbons has been obtained from studies examining the end products formed[1,2] and the short time chemistry of the transient ions, excited states, and radicals.[3] However, only a few deterministic diffusion−kinetic[4−6] and stochastic Monte Carlo simulations[7−9] of the radiolysis of hydrocarbons have been made. These calculations have been hindered by uncertainties of the chemical processes and the lack of information about the physical aspects of the energy deposition by ionizing particles. Several advances in the field now permit the construction of diffusion−kinetic models that are suitable for predicting absolute radiation chemical yields in hydrocarbons. This information has been used to construct the deterministic model presented here for cyclic hydrocarbons irradiated with fast electrons or γ-rays.

The physical structure of the track produced by the passage of a fast electron can be described if one has fundamental data on the energy loss processes. Recent calculations of the energy loss distributions produced by electrons in hydrocarbons have given a considerable amount of information including the average energy involved per energy deposition event.[10] With fast electrons, these events are essentially well separated, and the chemistry occurring in a spur can be considered to be isolated from the others.[11] Therefore, it is possible to develop a deterministic diffusion−kinetic model based on a typical or track averaged spur. In the strictest sense, a deterministic model is inappropriate because it ignores stochastic effects, but this type of treatment has proven to be very useful in understanding the radiolysis of water and aqueous solutions.[12] A deterministic model for hydrocarbons is desireable for predicting the chemistry in poorly characterized systems, for examining the physicochemical track processes, and to aid the construction of more detailed Monte Carlo track codes.

Cyclic hydrocarbons are in many respects the simplest liquid hydrocarbons to study because they have only a few decomposition modes leading to the formation of the H atom, the cycloalkyl radical, H_2 molecule, and the cycloalkene.[1,2] With only a few reactive species, the variety of products is reduced, and radical scavenging techniques can readily give information on the temporal evolution of the spur. Recently, a number of studies were combined to give a rather complete mechanism for the radiolytic decomposition of cyclopentane, cyclohexane, and cyclooctane.[13] That work offered estimates of the yields of transients produced, but many of complexities of the nonhomogeneous kinetics were not examined. Application of a diffusion−kinetic model allows for a detailed examination of the chemistry occurring in the spur as well as estimates of physical parameters such as the spatial distributions of intermediates.

In the next section, the deterministic diffusion−kinetic model is presented. A general reaction mechanism and appropriate parameters are given for the fast electron or γ-radiolysis of cyclopentane, cyclohexane, and cyclooctane. The results and discussion section compares the predictions of the model with experimental data and explains how the unknown parameters were obtained. This section also shows the spatial distributions and temporal variations of radical species consistent with the model. Examination of the results expected for different radiolytic conditions or for various kinetic coefficients are also presented. The final section of the paper contains a summary of the significant conclusions.

Methodology

Diffusion−Kinetic Model. The diffusion−kinetic model used here follows the same numeric deterministic approach used in previous studies on the radiolysis of water, and many of the details of the methodology can be found there.[14,15] Briefly, the model uses a deterministic rate law to describe the chemical reactions and a single typical or track-averaged spur representative of the whole system. In this treatment the spur is considered

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to be spherically symmetric, and the volume under consideration is divided into a series of concentric shells. The initial overall concentration profile of each reactive species produced is assumed to be Gaussian. Shell sizes are sufficiently small that the concentration of each species can be considered to be constant within it. A set of coupled differential equations is constructed to describe the kinetics of the reactive species in each shell. Diffusion occurs between adjacent shells following Fick's law. The differential equations are solved by the use of the FACSIMILE code which is based on the Gear algorithm.[16]

Reaction Mechanism. The initial absorption of energy in radiolysis mainly leads to the ionization of the molecular medium. Fast combination reactions of the cations and electrons then produce excited triplet and singlet states. It is not feasible to model ionic reactions correctly using deterministic rate laws because these reactions are strongly influenced by long-range Coulombic forces. Fortunately, the ion recombination reactions are very rapid, taking place on the picosecond time scale.[7,8] For this reason, the kinetic scheme has been defined so that the lowest excited singlet and triplet states are the initial reactive species considered, and only their yields following neutralization reactions are required.

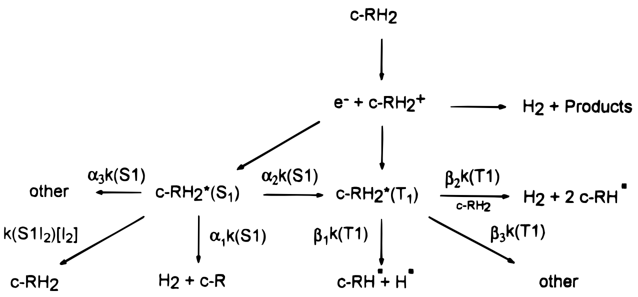
$$\text{c-RH}_2 \rightsquigarrow \text{c-RH}_2^*(\text{S1}) \qquad G(\text{singlet})$$

$$\rightsquigarrow \text{c-RH}_2^*(\text{T1}) \qquad G(\text{triplet})$$

$$\rightsquigarrow \text{H}_2 + \text{product} \qquad G(\text{excess H}_2)$$

In all experimental studies of the cyclic hydrocarbons, an excess of molecular hydrogen was found when compared to the total dehydrogenation product yields. A reaction to account for this excess yield has been added to the initial decomposition scheme for material balance only. It has no other effect on the nonhomogeneous kinetics.

The excited states of the cyclic hydrocarbons have lifetimes of less than 1 ns and decay to give molecular and radical products. These reactions may be summarized according to the following scheme.



The excited singlet state, $\text{c-RH}_2^*(\text{S1})$, decays to produce molecular hydrogen and the cycloalkene, c-R, or intersystem crosses to the triplet state, $\text{c-RH}_2^*(\text{T1})$. In the case of cyclooctane, the excited singlet state may also produce molecular hydrogen and pentalane, a cross-bridged product. On the other hand, the excited triplet state will give cycloalkyl radicals with molecular or atomic hydrogen. In the case of cyclopentane, 1-pentene may also be produced from the triplet excited state. Both excited states decay with pseudorates (k(S1) or k(T1)) which are equal to the inverse of the lifetimes of the respective states. The α and β coefficients express the fraction of the respective decomposition which leads to particular products ($\alpha_1 + \alpha_2 + \alpha_3 = 1$ and $\beta_1 + \beta_2 + \beta_3 = 1$). The inclusion of pentalane or 1-pentene production, when appropriate, is for the purpose of completeness as these products are not considered to react further. Also included in this reaction scheme is the quenching of the excited singlet state by iodine. The products of this reaction are assumed to be the ground state cycloalkane and some form of iodine that does not interfere with the subsequent chemistry.

TABLE 1: Parameters Used in the Diffusion−Kinetic Model

	C_5H_{10}	C_6H_{12}	C_8H_{16}	reference
$2k^a$(R+R)	2.52×10^9	2.02×10^9	0.86×10^9	17
k_d/k_c	0.97	0.94	0.73	13, 18, 19
k(R+H)	9.1×10^9	5.5×10^9	2.3×10^9	scaled
k_d'/k_c'	0	0	0	assumed
$2k$(H+H)	3.26×10^{10}	1.52×10^{10}	0.61×10^{10}	scaled
k(H+RH)	3.5×10^7	1.0×10^7	2.5×10^7	this work
$k(I_2+R)$	1.49×10^{10}	1.21×10^{10}	0.57×10^{10}	17
$k(I_2+H)$	7.4×10^{10}	3.4×10^{10}	1.4×10^{10}	scaled
G^b(singlet)	2.25	1.75	2.80	13
G(triplet)	3.15	3.40	3.50	this work
$G(\text{excess } H_2)$	0.85	0.75	0.15	13
k(S1), s^{-1}	1.0×10^{10}	1.0×10^9	1.0×10^{10}	23
α_1(H2 + ene)	0.9	0.85	0.66	13
α_2(triplet)	0.1	0.15	0.10	13
α_3(other)	0.0	0.0	0.24	13
$k(S1+I_2)$	5.0×10^{10}	5.0×10^{10}	0.0	this work
k(T1), s^{-1}	1.0×10^{13}	1.0×10^{13}	1.0×10^{13}	assumed
β_1(R+H)	0.45	0.48	0.75	13
β_2(2R+H2)	0.35	0.52	0.25	13
β_3(other)	0.20	0.00	0.00	13
D^c(R), cm^2/s	8.6×10^{-6}	4.0×10^{-6}	1.6×10^{-6}	scaled
D(H), cm^2/s	1.5×10^{-4}	6.9×10^{-5}	2.8×10^{-5}	scaled
$D(I_2)$, cm^2/s	3.2×10^{-5}	1.8×10^{-5}	9.1×10^{-6}	17
R^d(R), nm	0.50	1.10	0.55	this work
$[M]^e$	10.7	9.3	7.5	
η^f	0.423	0.905	2.263	25
spur,^{g} eV	47	47	47	10

[a] Rate coefficients (M^{-1} s^{-1} unless stated otherwise). [b] G values (molecules/100 eV). [c] Diffusion coefficients (cm^2/s). [d] Spur radius (nm). [e] Medium molarity. [f] Medium viscosity (mPa s). [g] Spur energy (eV).

The radicals produced by the decomposition of the excited triplet states undergo reactions with themselves or with added iodine scavenger according to the following scheme.

$$\text{c-RH}^\bullet + \text{c-RH}^\bullet \rightarrow \text{c-R} + \text{c-RH}_2 \qquad p_1k(\text{R+R}) \qquad (1)$$

$$\rightarrow (\text{c-RH})_2 \qquad (1 - p_1)k(\text{R+R}) \qquad (2)$$

$$\text{c-RH}^\bullet + \text{H}^\bullet \rightarrow \text{c-R} + \text{H}_2 \qquad p_2k(\text{R+H}) \qquad (3)$$

$$\rightarrow \text{c-RH}_2 \qquad (1 - p_2)k(\text{R+H}) \qquad (4)$$

$$\text{H}^\bullet + \text{H}^\bullet \rightarrow \text{H}_2 \qquad k(\text{H+H}) \qquad (5)$$

$$\text{c-RH}^\bullet + \text{I}_2 \rightarrow \text{c-RHI} + \text{I}^\bullet \qquad k(\text{R+I}_2) \qquad (6)$$

$$\text{H}^\bullet + \text{I}_2 \rightarrow \text{HI} + \text{I}^\bullet \qquad k(\text{H+I}_2) \qquad (7)$$

The sum of the rate coefficients for radical−radical disproportionation (1) and combination (2) reactions is given by k(R+R), while the ratio of these rates is given by k_d/k_c ($=p_1/(1 - p_1)$). Similarly, the sum of the rate coefficients for radical−H atom disproportionation (3) and combination (4) reactions is given by k(R+H) while the ratio of these rates is given by k_d'/k_c' ($=p_2/(1 - p_2)$). The H atom combination reaction (5) and the iodine scavenging reactions for the cycloalkyl radical (6) and the H atom (7) complete the reaction scheme.

Model Parameters. Table 1 gives the parameters used in the diffusion−kinetic modeling. The rate coefficients for the radical−radical reactions and radical−iodine scavenging reactions were as previously measured.[17] Experimental values for cycloalkyl radical disproportionation/combination ratios were also used.[13,18,19] No experimental values for the rate coefficients for H atom−H atom combination or for H atom scavenging by iodine are available in hydrocarbon liquids. Since these reactions are nearly diffusion limited, the appropriate value in each of the cycloalkanes was obtained by a viscosity scaling of the rate coefficients in water.[20] The rate coefficient for the cross combination reactions of cycloalkyl radicals with H atoms was obtained from the relationship $k(\mathrm{R{+}H}) = 2[k(\mathrm{R{+}R})\,k(\mathrm{H{+}H})]^{1/2}$.[4−6] Hydrogen atom reactions with the molecular medium are the only reactions in which there is considerable uncertainty in the rate coefficients. The coefficients for cyclopentane and cyclohexane were determined to be 3×10^7 $\mathrm{M^{-1}\,s^{-1}}$ using ESR techniques.[21] Pulse radiolysis experiments estimated the coefficient in cyclohexane to be 4×10^7 $\mathrm{M^{-1}\,s^{-1}}$.[22] However, the predicted dependence of the cycloalkyl iodide yields with iodine concentration were found to be very dependent on the values chosen. Therefore, the rate coefficients were initially set at 3×10^7 $\mathrm{M^{-1}\,s^{-1}}$ but were allowed to vary slightly to achieve the best fit to the scavenging data. The resulting values, given in Table 1, are not very different than those measured.

The initial radiation chemical yields (*G* values, in units of molecules/100 eV energy absorbed) for the excited singlet state and the excess molecular hydrogen were taken to be the same as found in the scavenging experiments.[13] Because that study did not take into account H atom reactions with cycloalkyl radicals, the yields of the excited triplet states were increased slightly to give the same total dehydrogenation product yields as measured experimentally. The branching ratios for the decomposition of each excited state were taken to be the same as found previously.[13] For each cycloalkane, the overall rate of decay of the singlet state was assumed to be the inverse of the measured or estimated lifetime.[23] The decay of the triplet state is known to be very fast, and the value of 10^{13} $\mathrm{s^{-1}}$ was assumed, so that the decay is essentially instantaneous.

Iodine is believed to quench the singlet excited states of both cyclopentane and cyclohexane.[13,18] No rate coefficient for this reaction is available. However, the quenching of the excited singlet state is quite noticeable in the different dependences of cycloalkenes and bicycloalkyls on iodine concentration. It was straightforward to chose a value for the rate coefficient of this reaction so that the calculations fit the iodine concentration dependence of the cycloalkene.

Only a few other parameters are needed for the diffusion−kinetic model. The diffusion coefficient for the cyclohexyl radical has been estimated to be 4.0×10^{-6} $\mathrm{cm^2/s}$.[24] The values for the other cycloalkyl radicals were obtained by a viscosity scaling. Diffusion coefficients for iodine were taken to be the same as used in a previous work,[13] while those for H atoms were viscosity scaled to the accepted value in water.[20] Values for the viscosity coefficients were taken from ref 25, and the energy deposited per spur was assumed to be the same as the average energy deposition in solids.[10] The characteristic radii for the initial Gaussian distributions of singlet and triplet excited states were assumed to be the same. Values for these radii were obtained by fitting the iodine scavenger concentration dependence of the product yields as explained in the following section.

Results and Discussion

Product Yields. The predictions of the diffusion−kinetic model for the various product yields are shown as a function of iodine scavenger concentration in Figures 1−3 for cyclopentane, cyclohexane, and cyclooctane, respectively. Also shown in these figures are the measured yields of the cycloalkenes, bicycloalkyls, and cycloalkyl iodides obtained using γ-radiolysis.[13,17,18] The experiments showed that a very large fraction of the cycloalkyl radicals produced in the radiolysis survive to times well beyond the lifetime of the spur. That is, much of the chemistry of the cycloalkyl radicals occurs while they have a homogeneous spatial distribution. It would be impossible to model these systems using data only for the neat solutions because there is no benchmark as to how much chemistry occurred within the spur. Any choice of radii for the initial spatial distributions would suffice to give the observed product yields, assuming the initial yields are correct. Scavenging experiments are invaluable for modeling the nonhomogeneous chemistry because in essence they give fixed reference points in the temporal evolution of the spur.

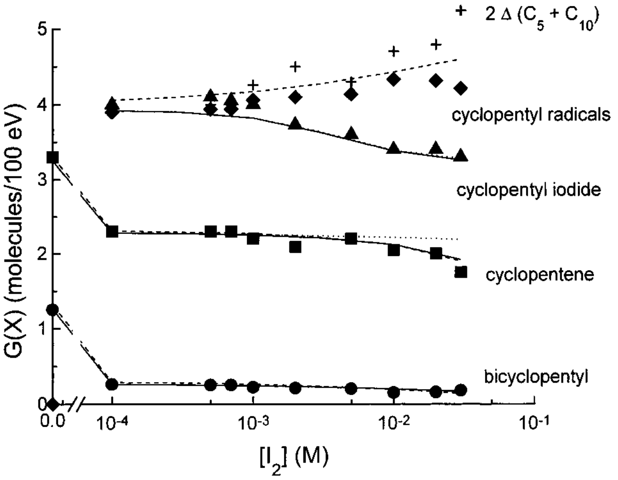


Figure 1. Predictions of the model for the γ-radiolysis of cyclopentane, solid lines, as a function of iodine concentration. Experimental points, ref 13, are (■) cyclopentene, (●) bicyclopentyl, (▲) cyclopentyl iodide, (+) $2\Delta(\mathrm{C_5 + C_{10}})$ (twice the net change in yields of cyclopentene and bicyclopentyl), (◆) cyclopentyl radical yields calculated from k_d/k_c and the change in yield of bicyclopentyl. Model predictions for complete conversion of H atoms to cyclopentyl radicals are denoted by the dashed line and for no iodine quenching of the excited singlet state by the dotted line.

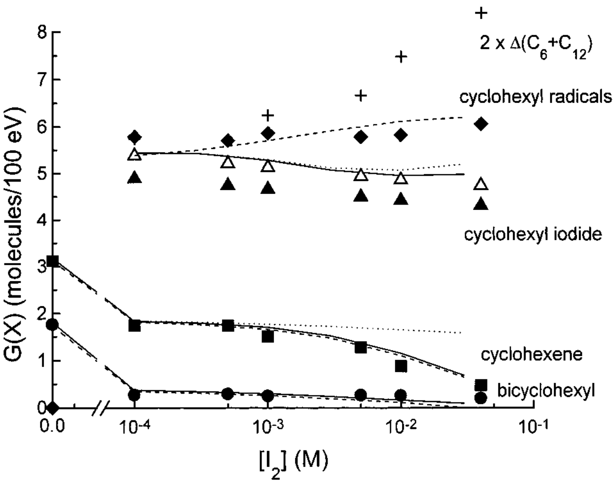


Figure 2. Predictions of the model for the γ-radiolysis of cyclohexane, solid lines, as a function of iodine concentration. Experimental points, ref 18, are (■) cyclohexene, (●) bicyclohexyl, (▲) cyclohexyl iodide, (△) 1.1 × cyclohexyl iodide, (+) $2\Delta(\mathrm{C_6 + C_{12}})$ (twice the net change in yields of cyclohexene and bicyclohexyl), (◆) cyclohexyl radical yields calculated from k_d/k_c and the change in yield of bicyclohexyl. Model predictions for complete conversion of H atoms to cyclohexyl radicals are denoted by the dashed line and for no iodine quenching of the excited singlet state by the dotted line.

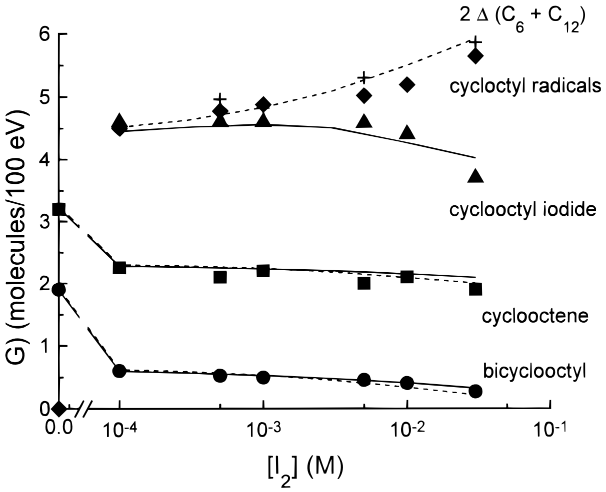


Figure 3. Predictions of the model for the γ-radiolysis of cyclooctane, solid lines, as a function of iodine concentration. Experimental points, ref 19, are (■) cyclooctene, (●) bicyclooctyl, (▲) cyclooctyl iodide, (+) $2\Delta(C_8 + C_{16})$ (twice the net change in yields of cyclooctene and bicyclooctyl), (◆) cyclooctyl radical yields calculated from k_d/k_c and the change in yield of bicyclooctyl. Model predictions for complete conversion of H atoms to cyclooctyl radicals are denoted by the dashed line.

At 0.1 mM iodine concentration the lifetime of the cycloalkyl radical is about 1 μs, at which time much of the spur chemistry is complete; see below. Model calculation using radii of 0.5, 1.1, and 0.55 nm for cyclopentane, cyclohexane, and cyclooctane, respectively, gave good agreements with the decrease in yields of the cycloalkenes and bicycloalkyls and with the formation of the cycloalkyl iodide. The one apparent exception was in the case of cyclohexane where there is a discrepancy in the experimental data; the loss of cyclohexyl radicals does not compare to their scavenged yield. There is no reason for the disagreement between the experimental data except that possibly the calibration of the cyclohexyl iodide was incorrect in that study.[18] For consistency in the comparisons of the calculations with experiments, the measured yields of cyclohexyl iodide were increased by 10%. The only major effect of this procedure is to increase the radius of the initial spatial distribution.

There is no obvious dependence of the radii of the spatial distributions on the molecular properties of the media. For both cyclopentane and cyclooctane the radii are about the same as the molecular diameters whereas in cyclohexane it is twice as large. Several explanations for this results are feasible: the excited states of cyclohexane may partially involve excimer formation or some other higher order molecular entity, the thermalization of the energetic fragments produced may have different efficiencies, or the mobility of the initial cations may be different. A very mobile cation in the case of cyclohexane could migrate substantially from the site of initial ionization on the time scales of the neutralization reactions and manifest itself as an increase in the spatial distribution of excited states. Such a mobile cation has long been proposed and verified in cyclohexane.[26,27] At 0.1 mM iodine concentration, the radii increase with increasing cycloalkyl iodide yields. Such a correlation is expected since larger radii would permit more radicals to escape track reactions and therefore be available to be scavenged. Of course, the relationship between the cycloalkyl iodide yields and the radii is not linear because of the high-order kinetics involved and variation in the radical diffusion coefficients. The physical property responsible for defining the radii is unknown.

Figures 1−3 show that the yields of the cycloalkenes and bicycloalkyls decrease with increasing iodine concentration. However, in a given medium the rate of decrease is not necessarily the same for both compounds. It is assumed that the bicycloalkyls are entirely and the cycloalkenes are partially produced from the reaction of two cycloalkyl radicals. If the addition of iodine leads only to the scavenging of radicals, twice the difference between the sum of the cycloalkene and bicycloalkyl yields at a given iodine concentration and the sum of the cycloalkene and bicycloalkyl yields found in neat solutions should be equal to the cycloalkyl iodide yield (i.e., $2\Delta(C_n + C_{2n})$). Since the disproportionation to combination ratios are known, an alternative method of calculating the amount of cycloalkyl radicals scavenged is by the expression $2(1 + k_d/k_c)\Delta C_{2n}$. Both methods give the same results for cyclooctane, while there is a large discrepancy for cyclopentane at above about 5 mM iodine concentration and for cyclohexane at above 0.5 mM iodine. In these two media, the iodine is believed to be quenching the singlet excited state.[13] The lifetime of the excited state of cyclohexane is estimated to be an order of magnitude greater than that of the excited state of cyclopentane.[23] Furthermore, it can be observed that the quenching in cyclopentane occurs at almost an order of magnitude higher iodine concentration than in the cyclohexane, so the quenching rate coefficients are approximately the same. The choice of 5×10^{10} M^{-1} s^{-1} for the rate coefficient of the quenching reaction was found to match the experimental data well. This rate coefficient may seem to be high, but a similar value of 6.9×10^{10} M^{-1} s^{-1} was found for the rate coefficient of the cyclohexane excited state quenching by O_2.[28] The effect of ignoring the quenching reaction (i.e., setting $k(S1 + I_2) = 0$) is shown as dotted lines in Figures 1 and 2. As expected, the major effect of omitting this reaction is on the yield of the cycloalkene.

If all cycloalkyl radicals were formed at very short times, the yields of cycloalkyl iodides would be expected to increase with increasing iodine concentrations until all of the cycloalkyl radicals were scavenged. However, H atoms abstract from the solvent medium to give molecular hydrogen and cycloalkyl radicals. This reaction is a major source of cycloalkyl radicals. On the other hand, H atoms can also be scavenged by the iodine. The net result is a decrease in cycloalkyl iodide yields with increasing iodine concentration. Unfortunately, H atom abstraction is not well characterized in hydrocarbon media. As mentioned earlier, literature values for the rate coefficient of this reaction are 3×10^7 M^{-1} s^{-1} for cyclopentane[21] and $(3-4) \times 10^7$ M^{-1} s^{-1} for cyclohexane.[21,22] It is obvious that such a slow reaction is not fully diffusion controlled so viscosity scaling of the rate coefficient is not appropriate. The model calculations reported here give the best agreement with experiment when values of 3.5×10^7, 1.0×10^7, and 2.5×10^7 M^{-1} s^{-1} are used for cyclopentane, cyclohexane, and cyclooctane, respectively. The rate coefficient for cyclohexane is smaller than the measured range of values, but it is of the same order of magnitude. The results for the other two media are in good agreement. Cyclohexane has a slightly smaller strain energy and more stable C−H bonds than the other two cyclic hydrocarbons so its rate coefficient might be expected to be smaller.[1]

The apparent yields of cycloalkyl radicals can be modeled by removing secondary sources of the radicals. This procedure is accomplished by setting the branching ratio of the triplet excited state to radical formation, β_1, to zero. The initial yield of the triplet state also has to be decreased slightly and the radius increased because H atoms are not lost in reactions with cycloalkyl radicals. It can be seen in Figures 1−3 that the predicted yields of cycloalkyl radicals agree well with the results

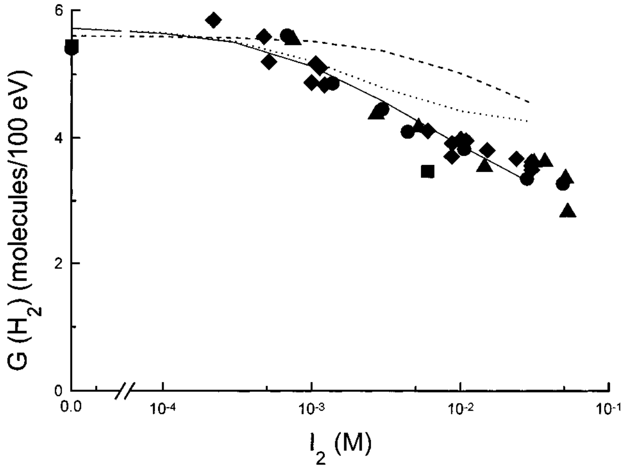


Figure 4. Production of molecular hydrogen in the γ-radiolysis of cyclohexane, solid lines, as a function of iodine concentration. Experimental points are (◆) ref 29, (●) and (▲) ref 30, (■) ref 31. Model predictions for complete conversion of H atoms to cyclohexyl radicals are denoted by the dashed line and for no iodine quenching of the excited singlet state by the dotted line.

obtained by the expression $2(1 + k_d/k_c)\Delta C_{2n}$. Such a good agreement reinforces the conclusion that the formation of the bicycloalkyls is due solely to combination reactions of cycloalkyl radicals. The observed effect of iodine on the yield of this product can be explained by cycloalkyl radical scavenging.

For every dehydrogenation product there should be an equivalent yield of molecular hydrogen. Consideration of the molecular hydrogen yields provides a check of material balance and shows that no additional chemistry occurs in the system because of the addition of iodine. Figure 4 shows the experimental yields of molecular hydrogen from cyclohexane as a function of iodine concentration.[29-31] The results predicted by the model agree very well with the experimental data. Removing the singlet state quenching reaction (dotted line, by setting $k(\mathrm{S1} + \mathrm{I_2}) = 0$) leads to a higher molecular hydrogen yield because this state is a precursor to molecular hydrogen. Similarly, if no hydrogen atoms were formed (dashed line, setting $\beta_1 = 0$), the predicted molecular hydrogen yields would be higher because iodine could not scavenge the H atom precursors.

Unfortunately, no experimental results are available for the production of molecular hydrogen in cyclooctane with added iodine, and only one measurement at 2 mM iodine has been made in cyclopentane.[29] This data point is about 30% lower than the model predicts, but the same study also found molecular hydrogen yields in cyclohexane that were lower than the other experimental studies by about the same amount. Therefore, the results of ref 29 may be questionable. Clearly, data on the production of molecular hydrogen in the radiolysis of liquid hydrocarbons under a variety of conditions would be of great value in understanding the radiation chemical processes.

Temporal Variation. The model described here considers the radiation chemical kinetics of the excited singlet and triplet states produced in the radiolysis of cycloalkanes, and it ignores the ultrafast combination reactions of electrons and parent cations from which these states are formed. Neutralization reactions occur in the picosecond regime, and a comparison of experiment with the model on this time scale would require a convolution of the results of the model with the ion combination kinetics.[7,8] However, for times longer than about 0.1 ns the ion combination kinetics can be considered to be complete, and a direct comparison of the model with experiment is possible.

Figure 5 shows the yields of H atoms and cycloalkyl radicals as a function of time in the three cyclic hydrocarbons. Each of the cycloalkyl radicals has a fairly constant yield over the course of the spur lifetime. After about 1 ns there should be substantial radical−radical combination reactions occurring in the spur which would decrease the cycloalkyl radical yields noticeably. However, this is also the time scale for the H atom abstraction reaction with the molecular medium which results in the formation of additional cycloalkyl radicals. Following completion of the latter reaction, the cycloalkyl radical yields decrease again because of the continuing spur reactions. The final decrease in cycloalkyl yields occurs until about 1 μs, beyond which the spatial distribution of the radicals is essentially homogeneous.

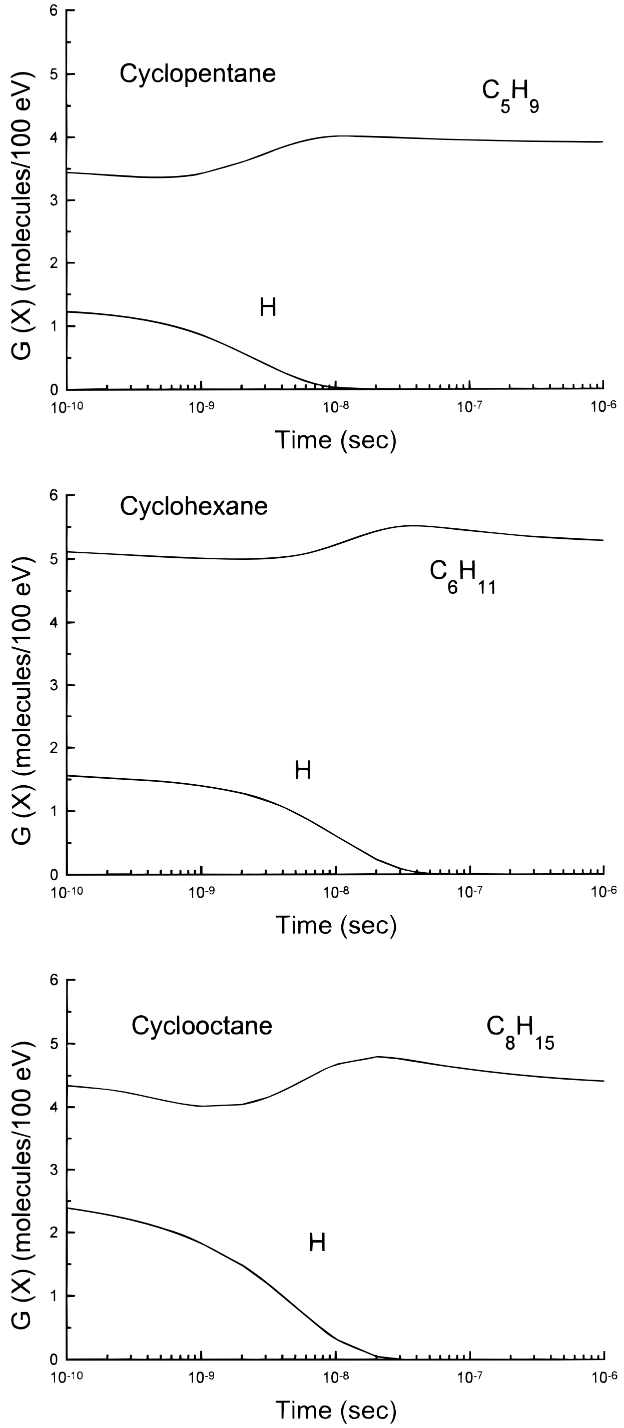


Figure 5. Temporal variation of the total yields of cyclopentyl, cyclohexyl, and cyclooctyl radicals and the respective H atom yields.

No experimental data for the temporal variation of cyclopentyl and cyclooctyl radicals exist. Measurements for the cyclohexane

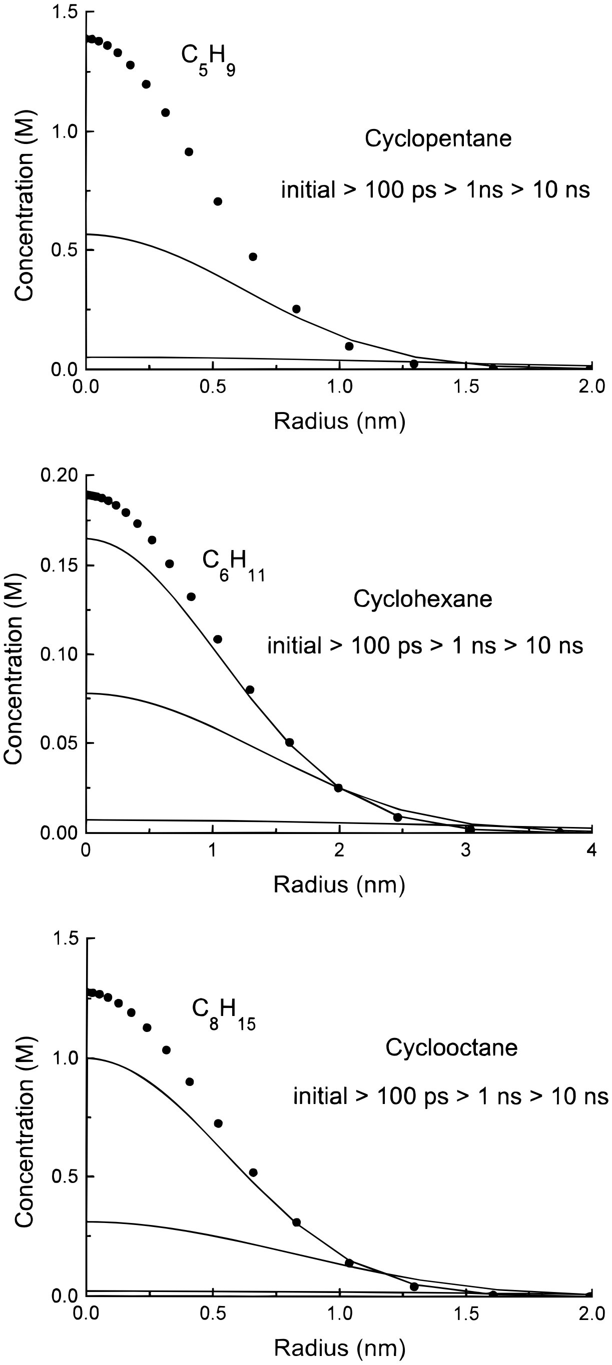


Figure 6. Temporal evolution of the spatial distributions of the cyclopentyl, cyclohexyl, and cyclooctyl radicals in the spur. Initial spatial distributions are dotted lines and solid lines are for 0.1, 1.0, and 10 ns, respectively.

system have probed to the picosecond domain where no variation in cyclohexyl radical yields was observed.[32] It was concluded from this work that formation of cyclohexyl radicals was complete within 20 ps of the deposition of energy. The model calculations suggest that cycloalkyl radicals are produced in the nanosecond time region, and these radicals almost exactly replace the cycloalkyl radicals consumed in spur processes. It is apparent in Figure 5 that at no time in the lifetime of the spur does the cyclohexyl radical yield vary by more than 10%. Only extremely accurate measurements could detect such small variations. Of course, the apparent consistency of the cyclohexyl radical yields reflects many competing factors.

Spatial Distributions. The diffusion−kinetic model used here assumes an initial Gaussian spatial distribution for each of the excited states comprising the spur. However, the nature of the model lets the spatial distributions relax in a nonprescribed manner; cf. the prescribed diffusion treatment frequently used to model spur kinetics.[4−6] At later times in the evolution of the spur, a non-Gaussian profile is possible for the spatial distribution of reactive species. Figure 6 shows the temporal variation of the spatial distributions for cyclopentyl, cyclohexyl, and cyclooctyl radicals in their respective media. Throughout the course of the spur chemistry the distributions decrease monotonically as the distance from the center of the spur increases. Within tens of nanoseconds the distributions are very broad and have increased in size to radii of many nanometers.

It is difficult to estimate the nonhomogeneous radical concentrations in the spurs from experimental measurements. Only a crude average can be obtained. The concentration profiles of Figure 6 suggest that for cyclopentane and cyclooctane the initial concentrations at the center of the spur may be on the order of 1 M. These values are very high and would suggest that almost 10% of the medium molecules are affected. With cyclohexane the radius is about twice as large, and the maximum concentration is almost an order of magnitude lower. Obviously, the actual spatial distributions of molecules within a spur are not continuous and more complete Monte Carlo track codes are necessary to recognize the discrete nature of the reactants. Experience with the diffusion−kinetic code applied to water has shown that this approach is a very good predictor of radiation chemical yields.[12] For the sake of estimating the outcome of a particular experiment, the model presented here may be used with confidence.

Conclusions

A deterministic diffusion−kinetic model has been successfully applied to the radiation chemistry occurring in the γ-radiolysis of liquid cyclopentane, cyclohexane, and cyclooctane. The predictions of the yields of the cycloalkenes, bicycloalkyls, and the cycloalkyl iodides in solutions of iodine are in excellent agreement with experimental data. Within the inherent limitations of a deterministic model, it provides considerable insight into the evolution of the spatial distributions of cycloalkyl radicals in a typical spur produced in γ-radiolysis. Many of the uncertainties in the formation and decay of cycloalkyl radicals have been explained. The model contains very few adjustable parameters that cannot be ascertained by other methods. Therefore, there is a great deal of confidence that the model is giving a complete and coherent analysis of the radical chemistry of liquid cyclic hydrocarbons.

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