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Radiolysis of Cyclooctane with γ-Rays and Helium Ions

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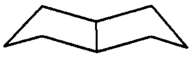
Iodine scavenging techniques have been used to examine the role of the cyclooctyl radical in the radiolysis of cyclooctane with γ-rays and with 5–20-MeV helium ions. In γ-radiolysis about 70% of the total yield of 6.6 cyclooctyl radicals/100 eV are scavenged with 10^{-4} M iodine, which agrees well with other studies on cycloalkanes that show most of the radicals produced in these systems react in the bulk medium at times longer than 1 μs. However, it is found that 2.5 radicals/100 eV (38%) are produced by H atom precursors as compared to a value of 1.5 cyclohexyl radicals/100 eV (25%) in cyclohexane. With 10-MeV helium ions (average LET of 106 eV/nm), only 8% of the cyclooctyl radicals survive longer than a few microseconds due to the increased initial radical concentration in the helium ion track. The yield of the cross-bridged product bicyclo[3.3.0]octane (pentalane) was found to be independent of iodine concentration up to 0.03 M with both types of radiation. However, the pentalane yield found with 10-MeV helium ions was only one-third of that found in γ-radiolysis. The most likely reason for this result is the decreased yield of singlet-state formation due to the enhanced probability of cross combination reactions of electron–cation pairs in the high-density region of the helium ion track.

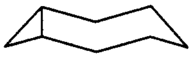
Introduction

Although the radiolysis of cyclohexane has attracted much attention, and that of cyclopentane to a slightly lesser extent, the radiolytic processes taking place in other cycloalkanes have hardly been investigated.[1] Cycloalkanes are especially suitable for studying the effects of linear energy transfer (LET, equal to the stopping power, $-dE/dx$) and particle track structure on product yields in hydrocarbons because of the relatively few final products formed. Only Foldiak and co-workers have published results on the radiolytic yields from larger cycloalkanes.[2,3] The γ-radiolysis of these cycloalkanes, including cyclooctane, is in many respects similar to that of cyclohexane where the yield of carbon–carbon decomposition is low ($G \sim 0.45$ molecule/100 eV)[4] and the basic radiolytic process is the production of hydrogen ($G(H_2) = 5.9$). Cyclooctyl radicals have been identified in solid cyclooctane by ESR measurements,[5–7] and they should also be formed in the liquid by an initial hydrogen atom detachment and in the subsequent abstraction reaction of the hydrogen atom with cyclooctane. The formation of bicyclooctyl probably occurs entirely through radical combination reactions while that of cyclooctene in both radical disproportionation reactions and unimolecular H_2 elimination.

There is at least one major difference in the radiolysis of cyclooctane as compared to the radiolysis of cyclohexane. In the radiolysis,[1] as well as the 7.1- and 7.6-eV photolyses,[8–9] of larger cycloalkanes, an additional dehydrogenation process with cross-bridge formation in the ring is observed. This process in cyclooctane leads to the production of bicyclo[3.3.0]octane (pentalane) with a G value of 0.5–0.6 in γ-radiolysis and a quantum yield of $\Phi = 0.33$ in photolyses at 7.1 and 7.6 eV. Another cross-bridged product, bicyclo[5.1.0]octane, is formed with a yield of about 10% of the pentalane. The cross-bridged products were shown to originate from the carbene produced by the elimination of molecular hydrogen from parent molecules excited to the S_1 singlet state.[8–9] Since the bicycloalkanes are formed only in this unimolecular process, their yields can be used to monitor the production of singlet excited states in various particle tracks. In heavy particle tracks, the formation of these molecular excited states is very sensitive to the initial physical conditions; however, their yields are normally experimentally difficult to observe because of their very short lifetimes.



bicyclo[3.3.0]octane
(pentalane)



bicyclo[5.1.0]octane

In the present work, the radiolyses of cyclooctane and its solutions with iodine are studied with γ-radiation and with helium ions of 5–20-MeV initial energy. In order to avoid secondary reactions, the production of cyclooctene, bicyclooctyl, pentalane, and cyclooctyl iodide is measured with very low total doses. Variations of the product yields with particle LET and iodine concentration are used to examine the effects of track structure on the competition between radical reactions within the track with radical diffusion out of the track. This type of information is very useful for estimating average densities of reactive species in the particle track and for subsequent modeling studies. Also, by measurement of the pentalane yield, it is possible to determine whether all of the observed track effects are due to radical competition, as was stated in the earlier works for alkanes,[10] or to changes in the yields of primary decomposition with particle LET.

Experimental Section

Irradiations with γ-rays were made using two ^{60}Co γ-sources having dose rates of 12.5 and 157 rad/s. The sample cell was made from a quartz cuvette and contained about 3 mL of sample. The sample was purged with nitrogen and the cell sealed with a rubber septum just before the radiolysis. Dosimetry was made in the same sample cell with the Fricke dosimeter.[11] The absorbed dose in the cyclooctane was assumed to be proportional to its electron density relative to that of the Fricke dosimeter. Total doses were varied from 25 to 1000 krad.

Helium ion irradiations were carried out with the 9-MV FN Tandem Van de Graaff accelerator of the Notre Dame Nuclear Structure Laboratory. The details of the accelerator facility, window assembly, and radiolysis procedure have been described elsewhere.[12,13] The sample cells had mica windows (4–6 mg/cm^2) and magnetically driven internal stirrers. Dissolved air was

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removed from the sample by passing a nitrogen stream saturated with cyclooctane from a prebubbler through the cell throughout the irradiations. Particle energy incident to the window assembly was determined magnetically to within 0.1%. Energy loss to the windows was obtained using standard stopping power tables.[14] The total dose was determined from the particle energy and the charge collected from the sample cell. Energy deposited in the sample was typically 5×10^{19} eV in 20 mL of sample (total dose ~ 50 krad).

Product analyses were carried out with an EXTREL Model ELQ-400-1 gas chromatograph–mass spectrometer operating in the selective ion monitoring mode. Pentalane and cyclooctene were detected at mass 67 while cyclooctyl iodide and bicyclooctyl were detected at mass 111. Chromatographic separations were made with a 30-m Chrompack CP-Sil-5-CB apolar type capillary column. Splitless mode injection of a 0.2-μL solution was used. The initial column temperature was maintained at 112 °C for 14 min. Pentalane, cyclooctene, and cyclooctane were eluted in this order. The temperature was then raised to 240 °C at a rate of 30 °C/min and held 2 min at this temperature while cyclooctyl iodide eluted. The column was then heated at 30 °C/min to 250 °C to elute bicyclooctyl. A typical chromatogram took about 30 min.

Cyclooctane was purchased from Fluka and had a purity of about 99% with the main impurity being cyclooctene. The purity was rather crucial from the point of view of the present experiments since pentalane and bicyclooctyl in the presence of iodine were detected at a level of 10–20 μM ($(1.3–2.6) \times 10^{-4}$%) and cyclooctene and cyclooctyl iodide at a level of 50–100 μM. Therefore thorough purification was started with sulfuric acid washing followed by multiple washing with water. The cyclooctane was then vacuum distilled in a grease-free automatic spinning band still Model 36 100A made by B/R Instrument Corp. The middle fraction of the distillate was collected and passed through a 40-cm-long column (internal diameter of 2 cm) containing silver nitrate on alumina prepared by the method of Murray and Keller.[15] Cyclooctane thus produced had a purity of at least 99.99% and contained no detectable impurities of the products formed during radiolysis.

Cyclooctene and pentalane used for quantitative analysis were obtained from Fluka and Wiley Organics, respectively. Cyclooctyl iodide was prepared by Landini and Rolla's[16] method of adding hydrogen iodide to cyclooctene in a phase-transfer reaction using hexadecyltributylphosphonium bromide as a catalyst. The product was then distilled *in vacuum*. Bicyclooctyl was produced through the Grignard reagent starting from cyclooctyl bromine (Pfaltz and Bauer, Inc.). The reagent was treated with anhydrous cupric chloride, and the organic fraction was collected and distilled in vacuum.

Results and Discussion

γ-Irradiations. Experiments with γ-irradiation were carried out using two ^{60}Co sources with dose rates that differed by about 1 order of magnitude. No differences were found for the product yields in the iodine-containing solutions. However, in neat cyclooctane, the yields of cyclooctene and bicyclooctyl were found to be ~10% lower at the lower dose rate than at the higher dose rate. This small difference is probably due to impurities which remained in the sample and/or the diffusion of oxygen into the sample during the long exposure time (~100 min). Even at the lowest iodine concentration (10^{-4} M) used in these studies, its reaction with cyclooctyl radicals was more rapid than that of impurities or oxygen.

TABLE 1: Dose Dependence of the Product Yields from Neat Cyclooctane for γ-Radiolysis at a Dose Rate of 156 rad/s

dose (krad)	*G* values			
	cyclooctene	bicyclo[3.3.0]octane (pentalene)	bicyclo[5.1.0]octane	bicyclooctyl
25	3.20	0.66	n.d.[a]	1.90
50	3.25	0.64	n.d.	1.93
100	3.00	0.62	n.d.	1.90
1000	2.75	0.53	n.d.	1.75
2000[b]	2.9	0.74	0.06	1.84

[a] Not determined. [b] Reference 9.

The measured yields of products produced in cyclooctane with γ-rays at the higher dose rate to total doses of 25, 50, 100, and 1000 krad are shown in Table 1. The yield of bicyclo[5.1.0]octane was not measured in the present work due to the lack of an authentic sample for quantitative identification and due to its very low yield. A small peak appeared on the chromatograms which eluted between pentalane and cyclooctane. According to the published retention data[17] it was probably bicyclo[5.1.0]octane, but mass spectral analysis was not definitive. Selective ion monitoring of the elution of the compounds from the chromatographic column at mass 67 found that its peak area was about 1 order of magnitude smaller than the peak area of pentalane, in agreement with the previously measured yield of 0.06.[9] All of the other product yields measured here at a dose of 1000 krad agree well with the previously reported values at 2000 krad.[9]

The data in Table 1 indicate that at doses below 100 krad there is no significant dependence of the product yields on dose. However, with an increase to 1000 krad, the yields are observed to decrease somewhat. The average product *G* values measured for the γ-irradiation of cyclooctane at low doses are the following: cyclooctene, 3.22; pentalane, 0.65; bicyclooctyl, 1.92. If the yield of bicyclo[5.1.0]octane is taken as 0.06 then the total yield of products involving carbon–carbon bond formation is 5.85. This value agrees extremely well with the complementary yield of $G(H_2) = 5.9$ obtained by measurements at doses in the 1.5–16-Mrad range and extrapolated to zero dose.[2]

The iodine scavenging experiments were carried out with the application of 25- and 50-krad doses. It is seen in Figure 1 that there are no basic differences between the two sets of measurements. At an iodine concentration of 10^{-4} M, scavenger depletion effects were observed with a dose of 50 krad, and from the observed product yields, one can calculate an iodine consumption of 2.0 nM/rad. The yields of cyclooctene, bicyclooctyl, and cyclooctyl iodide at 10^{-4} M iodine are found to be 2.25, 0.60, and 4.60 molecules/100 eV, respectively, at a dose of 25 krad, and it is assumed that these yields are representative of the γ-radiolysis of cyclooctane.

The loss of iodine in γ-irradiolysis was also measured directly by spectrophotometrically monitoring its concentration at 525 nm using an extinction coefficient of $\epsilon_{525} = 939$ M^{-1} cm^{-1}. The disappearance of iodine at low concentrations (<0.8 mM) and low doses (<150 krad) was found to be linear with dose at a rate of 2.28 nM/rad, which corresponds to $2G(-I_2) = 5.26$. The measured yield of cyclooctyl iodine is somewhat lower than this value and is probably due to formation of other iodine-containing compounds such as hydrogen iodine and higher molecular weight alkyl iodides. High molecular weight alkyl iodides were found in the radiolysis of cyclohexane solutions.[18]

As seen in Figure 1, the γ-irradiation of 10^{-4} M iodine solutions at a dose that does not completely consume the iodine gives yields of cyclooctene and bicyclooctyl which are, respectively, 0.97 and 1.32 *G* units less than observed in the neat alkane. From the measured decrease in these products, one obtains the equivalent of the loss of 4.5 cyclooctyl radicals/100 eV, which agrees well with the observed yield of 4.6 for the formation of cyclooctyl iodine. It is therefore reasonable to assume that on the addition of 10^{-4} iodine all of the decrease in the cyclooctene and bicyclooctyl yields is due to the scavenging of cyclooctyl radicals. One then obtains the value of 0.73 ± 10% for the ratio of the disproportionation to combination reaction rates for the cyclooctyl radical.

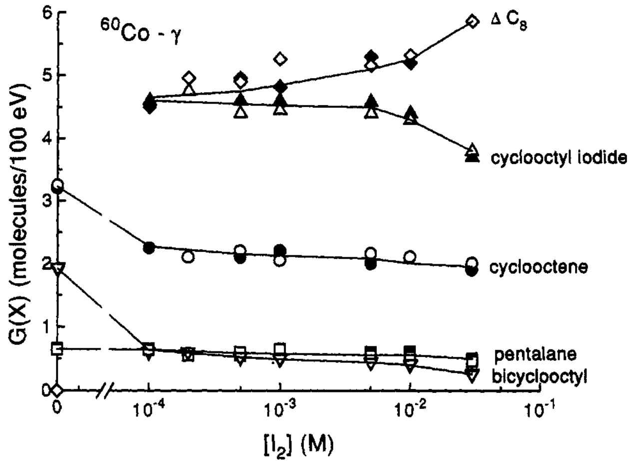

Figure 1. γ-Radiolysis of cyclooctane as a function of iodine concentration: (○,●) cyclooctene, (▽,▼)bicyclooctyl, (□,■) pentalane, (△,▲) cyclooctyl iodide, and (◇,◆) twice the net changes in cyclooctene and bicyclooctyl from those observed in the neat solution. The closed symbols are at 25 krad and the open symbols at 50 krad.

This ratio is lower than the values of 0.94[19] and 1.1[20] found with cyclohexyl radicals. The present experiments and those of ref 19 were performed with very little conversion and therefore should be more accurate than the value of ref 20.

No value of the rate constant for the reaction of iodine with cylooctyl radical has been published. Examination of the measured rate constants with cyclopentyl and cyclohexyl radicals[21] suggests that a scaling by the viscosity or the self-diffusion coefficients of the parent molecules would give a quite accurate value for cyclooctyl radicals. From the self-diffusion coefficients[22] one can estimate a rate constant of about 6×10^9 M^{-1} s^{-1} for the iodine scavenging of cyclooctyl radicals. Therefore, the average lifetime for a cyclooctyl radical with respect to 10^{-4} M iodine is about 1.5 μs at this concentration so one is essentially scavenging radicals which have escaped the spur and would have reacted in the bulk solution. The much smaller percentage of decrease in the yield of cyclooctene (30%) compared to that of bicylcooctyl (69%) upon the addition of 10^{-4} M iodine indicates that in addition to the radical pathway for its formation there is also a nonradical mechanism for producing this compound as has been suggested previously.[8,9] If the bicyclooctyl yield in neat solution is assumed to be entirely due to cyclooctyl radicals, then with the use of the above ratio for the disproportionation to combination rate constants, one can calculate a total yield of 6.6 cyclooctyl radicals/100 eV. The measured yield of 4.6 for cyclooctyl iodide at 10^{-4} M iodine shows that approximately 70% of all the cyclooctyl radicals would normally react in the bulk solution in the γ-radiolysis of cyclooctane. This percentage is somewhat lower than, but comparable to, the 83% value found in cyclohexane radiolysis.[19] Such a large percentage of radical reaction in the bulk is consistent with the generally accepted view that in γ-radiolysis the individual spurs contain only a few radicals and are separated by large distances. Radicals can easily escape the spur and react homogeneously with each other or with other additives in the bulk.[19]

Increasing the iodine concentration from 10^{-4} to 0.03 M leads to a steady decrease of about the same magnitude for both the cyclooctene and the bicyclooctyl yields. Unlike the γ-radiolysis of cyclohexane,[19] it appears that in cyclooctane the radical combination product will be completely scavenged at high iodine concentrations. On the other hand, the disproportionation product in cyclohexane was much more sensitive to iodine concentration than is found for cyclooctene. These observations reinforce the assumption that at least up to 0.03 M iodine only the radical precursors to cyclooctene and bicyclooctyl are being scavenged. Each of these products represents two cyclooctyl radicals, and twice the net change in the yields from that found in neat solutions agrees well with the observed cyclooctyl iodide yield at low iodine concentrations. In cyclohexane systems, iodine was shown to intercept positive ions and thereby inhibit the electron–cation recombination which is the main source of radical formation.[18] Such an effect appears to be negligible in cyclooctane solutions at these iodine concentrations.

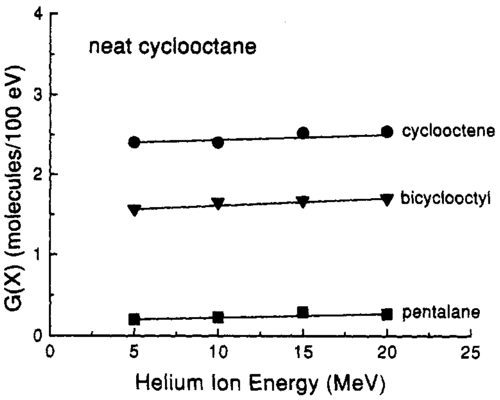

Figure 2. Radiolysis of neat cyclooctane as a function of initial helium ion energy: (●) cyclooctene, (▼) bicyclooctyl, and (■) pentalane.

At iodine concentrations between 0.01 and 0.03 M, there is a sharp drop in cyclooctyl iodide yields while the cyclooctene and bicyclooctyl yields also decrease. This result is probably due to the scavenging of thermal hydrogen atoms which would otherwise abstract H atoms from cyclooctane molecules to produce cyclooctyl radicals. At 0.03 M iodine the difference between the measured cyclooctyl iodide yield and the net change in cyclooctene and bicyclooctyl yields is 2.05. It was previously determined[18] that the ratio of the rate constant for H atom scavenging by iodine to that for its abstraction in cyclohexane is 4.7×10^3. This ratio is expected to be controlled by the thermodynamics of the carbon–hydrogen bond dissociation energy, but no measurements with H atoms in cyclooctane have been reported. Competitive reactions with chlorine atom complexes which should also be regulated by the same thermodynamics show a variation of 3.8 from cyclohexane to cyclooctane.[23] The ratio of iodine scavenging to H atom abstraction in cyclooctane is therefore expected to be about 1.2×10^3. At 0.03 M iodine, about 82% of the H atoms should be scavenged, which gives a total yield of about 2.5 H atoms/100 eV in cyclooctane. This value is considerably larger than the yield of 1.5 found in cyclohexane[24] and reflects the difference in the very fast ionic and excited state chemistry of these two compounds. It should also be observed that even though the H atom yields are very different the yield of the initially produced cyclooctyl radical is 4.1, which agrees very well with the estimated yield of 4.4 for cyclohexyl radical in cyclohexane.[19]

The *G* value of pentalane, 0.65, is independent of the iodine concentration in agreement with its nonradical mechanism of formation.[8,9] Concentrations of up to 0.03 M iodine do not appear to quench or otherwise alter the yield of the excited S_1 singlet state of cyclooctane produced in γ-radiolysis. In the photolytic measurements of liquid cyclooctane at 7.1 and 7.6 eV, the quantum yield of pentalane was found to be $\Phi = 0.33$.[8,9] Therefore, the *G* value of the corresponding lowest singlet excited state in γ-radiolysis is estimated to be 2.0.

Helium Ion Radiolysis. Helium ion irradiations were carried out with ion energies of 5, 10, 15, and 20 MeV incident to the sample. The range of a 20-MeV helium ion is only about 40 μm in cyclooctane, so the particles were completely stopped in the liquid and the measured product yields are averaged over the entire track. As indicated in Figure 2, a very slight increase in the yields with increasing particle energy was found. It may be expected that the yields of cyclooctene and bicyclooctyl might increase with decreasing particle energy because of the increase in radical disproportionation and combination reactions in the

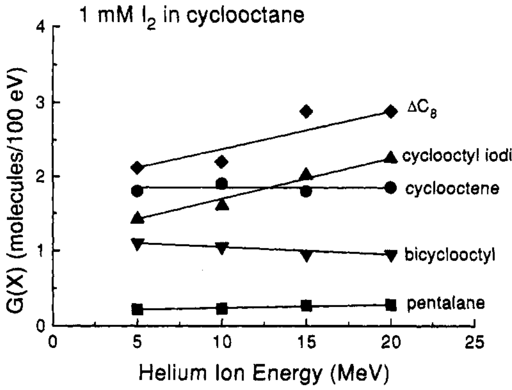

Figure 3. Radiolysis of 10^{-3} M iodine in cyclooctane as a function of initial helium ion energy: (●) cyclooctene, (▼) bicyclooctyl, (■) pentalane, (▲) cyclooctyl iodide, and (◆) twice the net changes in cyclooctene and bicyclooctyl from those observed in the neat solution.

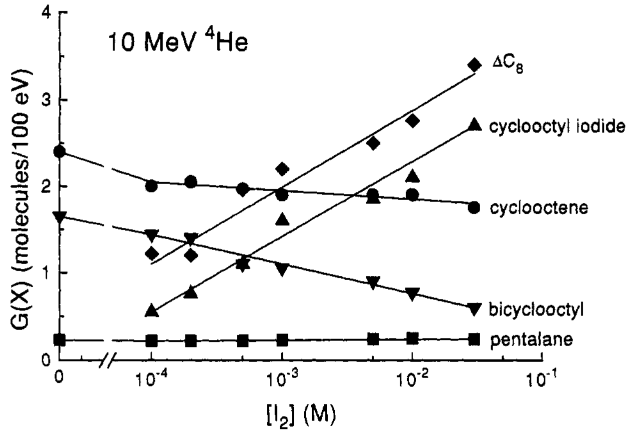

Figure 4. 10-MeV helium ion radiolysis of cyclooctane as a function of iodine concentration: (●) cyclooctene, (▼) bicyclooctyl, (■) pentalane, (▲) cyclooctyl iodide, and (◆) twice the net changes in cyclooctene and bicyclooctyl from those observed in the neat solution.

higher LET tracks. However, a similar trend in the product of the cyclohexyl radical was found in the helium ion radiolysis of cyclohexane.[19] For 10-MeV helium ions, the track average LET in cyclooctane is about 106 eV/nm and the measured product yields are as follows: cyclooctene, 2.40; bicyclooctyl, 1.65; pentalane, 0.23. These yields are about 74, 86, and 35%, respectively, of those observed in γ-radiolysis. It is surprising that pentalane, formed by a nonradical mechanism, exhibits the highest decrease from γ-radiolysis to 10-MeV helium ion radiolysis. Cyclooctene formed by both radical and unimolecular pathways shows the second largest reduction, while bicyclooctyl produced only by radical processes shows the least decrease in yield with increasing LET.

Solutions of 10^{-3} M iodine in cyclooctane show a slight decrease in the yields of cyclooctene and bicyclooctyl with increasing helium ion energy as shown in Figure 3. The yield of cyclooctyl iodide increases from 1.42 to 2.25 with increasing helium ion energy from 5 to 20 MeV. This increase closely matches twice the decrease in cyclooctene and bicyclooctyl yields from those found in the neat cyclooctane. At 10^{-3} M iodine one samples cyclooctyl radicals at about 150 ns so that the decreasing yield of cyclooctyl iodide with increasing helium ion LET (decreasing energy) indicates that fewer radicals are escaping intratrack reactions.

The effect of iodine concentration on the radiolytic yields in cyclooctane irradiated with 10-MeV helium ions is shown in Figure 4. At 10^{-4} M iodine the cyclooctene and bicyclooctyl yields are smaller by about 0.4 and 0.2 G value units, respectively, than in the neat alkane. These values amount to decreases of 17 and 13%, whereas values of 30 and 69%, respectively, were found in the corresponding γ-radiolyses. In the γ-radiolytic studies it was noted that at 10^{-4} M iodine concentration all the cyclooctyl radicals that escape the spur are readily scavenged. There may be no equivalent to radical escape from heavy ion tracks as is found in the spurs produced by γ-radiolysis because the probability for radical–radical reactions in the track remains high at all times.[19,25] Assuming again that all of the bicyclooctyl is produced by radical reactions, then using the ratio of disproportionation to combination rate constants as determined from the γ-radiolysis studies a G value of 5.7 total radicals is estimated for 10-MeV helium ions, which compares well with the value of 6.6 found in γ-radiolysis. The decrease with helium ions is probably due to very fast recombination of H atoms and cyclooctyl radicals in the track. Only about 8% of all the radicals survive to 1.5 μs in the tracks of 10-MeV helium ions, whereas a value of 70% was found in γ-radiolysis. Clearly, a much larger fraction of the radicals undergo reactions in the tracks of helium ions than in γ-radiolysis and those reactions occur at times less than a few hundred nanoseconds.

As the iodine concentration is increased from 10^{-4} to 0.03 M the cyclooctene yield with 10-MeV helium ions decreases slightly from $G = 2.0$ to 1.75 while the bicyclooctyl yield decreases from 1.44 to 0.60. Over the same iodine concentration the yield of cyclooctyl iodine increases steadily from 0.55 to 2.70. At all iodine concentrations the cyclooctyl iodide yield is about one-half of a unit lower than twice the decrease in cyclooctene and bicyclooctyl yields from their values in neat cyclooctane. No obvious explanation for this discrepancy exits. There is no apparent iodine scavening of hydrogen atoms as observed in the γ-radiolysis, so hydrogen atom reactions must be occurring very fast in helium ion tracks. The variation in product yields reflects the competition between scavenging and intratrack processes in the particle track. With increasing concentration, iodine can compete more effectively with the disproportionation and combination reactions of cyclooctyl radicals.

The data in Figure 4 suggest that the yield of cyclooctyl iodide is equal to one-half of the maximum of 4.1 of cyclooctyl radicals produced initially at an iodine concentration of about 6×10^{-3} M. The cyclooctyl radical lifetime at this concentration is about 30 ns. The second-order combination rate constant for cyclohexyl radicals is $2k = 2.4 \times 10^9$ M^{-1} s^{-1}, and scaling this value by the ratio of the self-diffusion constants gives a value of $2k = 1.2 \times 10^9$ M^{-1} s^{-1} for cyclooctyl radicals. One can then calculate a track-averaged cyclooctyl radical concentration of 0.03 M with helium ions. This concentration is very close to the previous value of 0.04 M estimated for cyclohexyl radicals in cyclohexane.[19] The results are very gratifying, especially since the initial energy deposition density is expected to be the same in both compounds.

In both γ-radiolysis and in helium ion radiolysis the yield of pentalane is essentially independent of iodine concentration. However, its yield appears to decrease with increasing LET of the radiation. Assuming that pentalane is only produced by the unimolecular decomposition of S_1 singlet excited molecules,[8,9] then the results obtained in this study indicate that the yield of singlet states in 10-MeV helium ion radiolysis is only one-third of that in γ-radiolysis. There can be at least two possible causes for this apparent decrease in the yields of singlet excited states with increasing LET: either they are formed with low efficiency or the singlet excited states are quenched by product molecules rapidly produced at high concentrations in the tracks of high LET particles. The first cause may be due to the high local concentration of electron–cation pairs in the track favoring cross combination with neighboring charged pairs at the expense of geminate recombination. Geminate recombination will lead exclusively to singlet excited states whereas cross combination of multiple electron–cation pairs will produce a 1 to 3 ratio of singlet to triplet excited states.[25,26] Therefore, if cross combination reactions dominate in the tracks of high LET particles, they can strongly reduce the probability of singlet state formation as compared to γ-radiolysis. Another possibility for the reduction of excited singlet state yields was pointed out by Brocklehurst,[27] who suggested that the excited molecules formed in each other's proximity can pool their energy to produce an electron–cation pair.

The second cause for the decrease in excited singlet states can be due to the high concentration of radicals as well as singlet excited states in the tracks of high LET particles. The triplet excited states of alkanes are short lived and most probably decompose during one vibrational period, so they do not likely play a role. In a recent study, Holroyd and co-workers[28] suggested a diffusion-controlled rate constant of 10^{10} M^{-1} s^{-1} for the reaction of radicals with singlet excited molecules in the tracks of low-energy X-rays in *n*-dodecane. Assuming that the rate constant is about the same order in the cyclooctane system and using the estimated lifetime of 0.3 ns for this nonfluorescing alkane,[22] then only 10% of the singlet excited states are expected to be scavenged by radicals. This value is much too low to account for the observed decrease in the pentalane yield. Previous calculations by Miller[29] suggested that scavenging of excited benzene states by the radicals produced in cyclohexane was extensive in helium ion radiolysis. However, in that system, the lifetime of the benzene excited state is about 30 ns. The lifetime of the cyclooctane excited state is just too short, and only at very high LETs will the radical concentrations be sufficiently high to significantly scavenge the excited states. Further experiments and model calculations are planned to support the qualitative picture presented here.

Conclusions

The use of iodine-scavenging techniques has shown that only 8% of the cyclooctyl radicals remain unreacted until microsecond times in the tracks of 10-MeV helium ions as compared to 70% with γ-radiolysis. Clearly, LET can have a profound effect on the radiation chemistry of the radicals produced in hydrocarbons. Experiments with protons of varying energies should give radical yields on the microsecond time scale intermediate between the values obtained here with helium ion and γ-radiolysis, while it is possible that the yields decrease to zero with very high LET particles. However, it is also obvious from the present experiments that LET effects in hydrocarbons cannot solely be attributed to competition between radical reaction and diffusion into the bulk as is generally accepted.[10] There is a large decrease in the yield of singlet excited states, a precursor to both radicals and stable products, with increasing LET. At this time it appears that this decrease is due to the increased probability of cross combination of electron–cation pairs in the track core. Further experiments on the production of excited singlet states in hydrocarbons are clearly in order. Even though the viscosity of cyclooctane is greater than that of cyclohexane, it is found that the average concentrations of radicals are about the same in both hydrocarbons irradiated with 10-MeV helium ions. It is therefore expected that many of the track processes occurring in cyclooctane also occur in other hydrocarbons.

The fraction of H atoms in the total radical production is considerably greater in cyclooctane (38%) than in cyclohexane (25%). The difference in H atom yields is about 1 unit, which is the equivalent of two cyclooctyl radicals/100 eV. Although the detailed mechanism is not known, it appears that the decomposition pathways of ionic precursors are very different for the two hydrocarbons. Further experiments on the production of molecular hydrogen and higher molecular weight products are planned and should help elucidate the reaction mechanism.

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