linear with a slope related to k_s. By using eq VIII, a plot of

$$k_s\left[1+\frac{1}{K_{\text{eqII}}[O_2]}\right] \quad \text{vs} \quad \frac{1}{K_{\text{eqII}}[O_2]}$$

should be linear with a slope of k_3 and an intercept of k_4, the rate coefficients for reactions 3 and 4, respectively.

Figure 7 shows a plot of

$$k_s\left[1+\frac{1}{K_{\text{eqII}}[O_2]}\right] \quad \text{vs} \quad \frac{1}{K_{\text{eqII}}[O_2]}$$

for data obtained in the temperature range 191-240 K. As can be seen, k_3 or the slope of the plot is independent of temperature. Values of $(2.15 \pm 0.13) \times 10^{-10}$ and $(1.7 \pm 3.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} were obtained for k_3 and k_4, respectively. The reported errors are twice the standard deviation of the slope and intercept values obtained from a linear least-squares fit of the data. The large error in the value of k_4 is due to the large extrapolation involved in calculating the intercept. Therefore, we quote an upper limit of $k_4 < 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

The value of k_3 obtained in this study is larger than the currently recommended[25] value of 1.48×10^{-10} cm^3 molecule^{-1} s^{-1} but is in reasonable agreement with the value of 2.7×10^{-10} cm^3 molecule^{-1} s^{-1} measured recently by Baer et al.[22] The studies summarized in ref 25 all involved the use of chemical models to obtain a value of k_3. We also assume a reaction scheme; however, we have directly monitored ClOO and used an independent measurement of the ClOO absorption cross section. Hence, we believe our result to be accurate.

Only Baer et al.[22] have reported a value for k_4. In their study they were able to use high enough $[O_2]$ to measure ClOO loss rates at $1/(K_{\text{eqII}}[O_2])$ values much closer to zero than we could. Therefore, they could convert almost all Cl to ClOO, and hence were able to precisely determine k_4. Our upper limit for k_4 ($<2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) is consistent with their value of 1.6×10^{-11} cm^3 molecule^{-1} s^{-1}.

Conclusions

The shape of the UV absorption spectrum of ClOO measured here is in reasonable agreement with those of Johnston et al.[7] and Cox et al.[9] However, the peak cross section we measured is a factor of 2.2 larger than that reported by Johnston et al. and is in excellent agreement with the recent determination of Baer et al.[22]

The value of the equilibrium constant for reaction 2, measured at 191 K, is slightly higher than would be expected using the value of Nicovich et al.[10] obtained at 185 K yet well within their reported uncertainty. Our value for $\Delta^\circ H_{r0}$ is in excellent agreement with those measured by Nicovich et al. and Baer et al.

The measurement of the rate coefficient for removal of ClOO indicates that the rate coefficient is independent of temperature as previously reported.[22,25] The value measured here is larger by a factor of 1.5 from the currently recommended value[25] and in reasonable agreement with that measured by Baer et al.[22] This larger value can partially account for the discrepancy between the cross section values measured in this study and those of Johnston et al.[7]

Acknowledgment. We thank Professor J. Troe, Dr. H. Hippler, J. M. Nicovich, and Dr. P. H. Wine for communicating their results to us prior to publication and for helpful discussions. We are also grateful to Robert Wilson for development of the diode array data acquisition software. This work was funded in part by the Upper Atmosphere Research Program of the National Aeronautics and Space Administration.

Registry No. Cl, 22537-15-1; ClOO, 17376-09-9; Cl_2, 7782-50-5; O_2, 7782-44-7.

Intratrack Reactions of Cyclohexyl Radicals in the Heavy Ion Radiolysis of Cyclohexane

Jay A. LaVerne,*,[†] Robert H. Schuler,[†] and Gabor Foldiak[‡]

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, and Institute of Isotopes, Hungarian Academy of Sciences, P.O. Box 77, Budapest, H-1525 Hungary *(Received: September 19, 1991)*

The intratrack reactions of cyclohexyl radicals produced in the radiolysis of cyclohexane with helium and carbon ions have been examined using iodine-scavenging methods. It is found that in contrast to electron radiolysis, where most of the cyclohexyl radicals diffuse out of the radiolysis spurs and are readily scavenged at iodine concentrations of $\sim 10^{-4}$ M, iodine interferes with the intratrack reactions of heavy ions only at much higher concentrations. From the concentration dependence, it is estimated that the intratrack reactions between radicals occur mainly on the 10^{-9}–10^{-7} s time scale for 10-MeV helium ions (LET $\sim$ 10 eV/Å) and at 1 order of magnitude shorter times for 10-MeV carbon ions (LET $\sim$ 75 eV/Å). These time scales establish the initial radical concentrations in the core of the track as being of the magnitude of 0.04 M for the helium ions and 0.8 M for the carbon ions.

Introduction

Cyclohexane has been the subject of many previous radiation chemical studies, mainly with γ-rays, which have shown that the principal radical intermediates are cyclohexyl radicals and hydrogen atoms.[1] In the case of γ-ray and fast electron radiolysis, these radicals, for the most part, diffuse out of the radiolysis spurs and react homogeneously in nontrack processes. For heavy ions, the spurs coalesce into columnar tracks so that intratrack reactions can compete more effectively with diffusion and one expects that with increased particle LET (i.e. linear energy transfer (LET) $= -dE/dx$; stopping power) fewer radicals will escape from the track. This importance of intratrack reactions has long been known to be the case for the heavy particle radiolysis of water.[2] Since the second-order rate constants for reactions between alkyl

---

[†] University of Notre Dame.

[‡] Hungarian Academy of Sciences.

(1) Foldiak, G., Ed. *Radiation Chemistry of Hydrocarbons*; Elsevier: Amsterdam, 1981.

(2) Allen, A. O. *The Radiation Chemistry of Water and Aqueous Solutions*; Van Nostrand: New York, 1961.

radicals are about 1 order of magnitude lower than those for the primary radicals from water, intratrack radical reactions in the case of hydrocarbons should become important only for particles of relatively higher LET. Early studies of radicals escaping from the tracks of 18 MeV deuterium ions (LET $\sim$ 0.5 eV/Å) and 34-MeV helium ions (LET = 2 eV/Å) in typical hydrocarbons,[3] as measured by the loss of iodine as the radical scavenger, have shown reductions of only 10–30% from the yields observed for fast electrons. In 1966, Blackburn and Charlesby[4] demonstrated that the effect of iodine on the bicyclohexyl yield is smaller for 1 MeV α-particles than for γ-rays and found that the yield of cyclohexyl iodide, while considerably less for α–particles than for γ-rays, increased with iodine concentration. They discussed these observed differences in terms of the increased importance of scavenging relative to diffusion in cylindrical tracks using the track models extant at the time of their work. There have been no studies of scavenger effects in the heavy particle radiolysis of hydrocarbons since these early works. A preliminary report on the present work has, however, appeared in the 7th Tihany Symposium on Radiation Chemistry.[5]

Because of its relatively simple radiation chemistry and the fact that in the case of fast electron radiolysis most radicals escape spur reactions, cyclohexane provides a particularly good system with which to examine the LET dependence of the competition between the intratrack reactions of radicals and their diffusion out of the track. In the present study, we use iodine-scavenging methods to examine this competition and to provide information on the time scale of the intratrack processes for 10-MeV helium and carbon ions which deposit energy at, respectively, $\sim$10 and $\sim$75 eV/Å.[6]

Experimental Section

Helium and carbon ion irradiations were carried out with the 9-MV FN Tandem Van de Graaff of the Notre Dame Nuclear Structure Laboratory. This facility is capable of producing ions with an energy resolution of better than 0.1%. The accelerator facility, the window assembly, and radiolysis procedures used in the present study have been described elsewhere.[7,8] The sample cells had internal magnetically driven stirrers and mica windows, typically 6–8 mg/cm^2 thick, epoxied to them. Dissolved air was removed from the sample by a nitrogen stream saturated with cyclohexane in a prebubbler that was passed through the cell throughout the radiolysis. Particle energy incident to the window assembly was determined by magnetic analysis. Energy loss to the windows was obtained using standard stopping power tables.[9] Uncertainties in energy determination correspond to ±0.3 mg/cm^2 in the particle range, which is equivalent to 1 and 14% for 10-MeV helium and carbon ions, respectively. The total dose was determined from the particle energy and the charge collected from the sample cell and exit window. Beam currents were $\sim 5 \times 10^{-9}$ A and uniform over the radiolysis area of about 0.3 cm^2. Energy input to the samples was typically $(2\text{–}5) \times 10^{19}$ eV in 20–30 cm^3 of sample (total dose of 20–30 krad delivered in $\sim$300 s). Because of the very short range of the particles (<0.04 cm), local dose rates were, however, considerably higher. Following the radiolysis, a portion of the solution was sealed in a separate vial and held for analysis. Samples sealed in such a manner were found to be stable for several weeks.

Comparative irradiations with γ-rays were made using a ^{60}Co source having a dose rate of 20 krad/min. The sample cell was made from a quartz cuvette which contained about 2 cm^3 of solution. The sample was purged with nitrogen and sealed with a rubber septum before the radiolysis. Dosimetry was with the same sample cell using the Fricke dosimeter. The ferric ion yield was determined spectrophotometrically at 304 nm, taking the extinction coefficient as 2174 M^{-1} cm^{-1} at 23.7 °C and a G value of 15.45 molecules/100 eV.[10] The absorbed dose was assumed to be proportional to the electron density of the sample relative to the Fricke dosimeter.

Product analysis was within a few days of the irradiations with an EXTREL gas chromatograph–mass spectrometer operating in an ion selective mode. This apparatus is capable of accurately determining product concentrations as low as 5 μM by monitoring selected masses of the products. Product separation was achieved with a 25-m capillary column (0.32-mm i.d.) with a slightly polar coating 1.2 μm thick (Chrompack Inc. CP-SIL 8 CB). Helium was used as the carrier gas with a flow rate of about 3 cm^3/min. The initial column temperature was maintained at 35 °C for 6 min and then increased to 150 °C at the rate of 30 °C/min. A typical chromatogram took about 15 min. All the products of interest were completely separated. Qualitative analysis was determined from retention times and the complete mass spectra of samples irradiated to doses of several megarads. Once the retention times of the products were determined, the detector was set to monitor the base peak and at least one other mass fragment for each product. The ratio of the areas of the peaks for any compound never varied by more than a few percent. In appropriate cases, mass 127 was also monitored to examine for possible production of organic iodides. Quantitative analyses were performed with standard solutions of the specific products at concentrations comparable to those of the irradiated samples. Estimated errors are about 5%. For the experiments with γ-rays and the heavy particles at the higher energies, error limits on the yields were controlled largely by uncertainties in the product analysis. Energy uncertainties limit the accuracy for the lowest energy heavy ions. The cyclohexane, Aldrich HPLC grade, contained no detectable unsaturated compounds or products of interest. Iodine, cyclohexyl iodide, cyclohexene, and bicyclohexyl were used as received from Aldrich. The solubility of iodine in cyclohexane limited these studies to concentrations of 0.04 M and lower.

Results and Discussion

γ-ray Studies. Initial experiments were carried out with γ-rays in order to verify experimental techniques and to obtain results at doses comparable to those used in the heavy ion experiments. Many previous studies on neat cyclohexane used doses in the megarad range and exhibited poor material balance. In those studies with good material balance, it was found that cyclohexene and bicyclohexyl constituted $\sim$90% of the carbon-containing products.[11,12] The present experiments were performed at doses of $\sim$25 krad, which is at least 1 order of magnitude lower than in most previous studies. The yields (G values in molecules/100 eV) of cyclohexene (C_6H_{10}) and bicyclohexyl ($(C_6H_{11})_2$ found in the present work are given by the dashed lines in Figure 1. These yields, 3.12 and 1.76, respectively, agree very well with those in the literature obtained at somewhat higher doses. This comparison suggests that complications resulting from product buildup become important only at doses well above 0.5 Mrad. In addition to the desire to determine "initial" yields, low dose irradiations are crucial to the present studies because of the limited availability of beam time, which is exacerbated by the low currents at which the heavy ion experiments must be carried out. Studies at low scavenger concentrations, of course, also require correspondingly low doses

---

[3] Schuler, R. H. *J. Phys. Chem.* **1959**, *63*, 925.

[4] Blackburn, R.; Charlesby, A. *Proc. R. Soc. London, A* **1966**, *293*, 51.

[5] LaVerne, J. A.; Schuler, R. H.; Foldiak, G. In *Proceedings of the Seventh Tihany Symposium on Radiation Chemistry*; Dobo, J., Nyikos, L., Schiller, R., Eds.; Hungarian Chemical Society: Budapest, 1991.

[6] The LETs used in this paper are track averaged as defined by $1/E_0\int_0^{E_0}(-dE/dx)\,dE$ where E_0 is the energy of the particle incident to the solution. The stopping powers for cyclohexane were obtained using a Bragg additivity rule, and the stopping powers of carbon and hydrogen as given in ref 9. It should be noted that, in general, differential yields and instantaneous LETs are superior to track averaged values for describing track processes. However, when product yields are relatively independent of incident particle energy, as in the present studies, then the use of track averaged LETs is acceptable.

[7] LaVerne, J. A.; Schuler, R. H. *J. Phys. Chem.* **1984**, *88*, 1200.

[8] LaVerne, J. A.; Schuler, R. H. *J. Phys. Chem.* **1987**, *91*, 6560.

[9] Northcliffe, L. C.; Schilling, R. F. *Nucl. Data, Sect. A* **1970**, *7*, 233.

[10] Schuler, R. H.; Allen, A. O. *J. Chem. Phys.* **1956**, *24*, 56.

[11] Freeman, G. R. *J. Chem. Phys.* **1960**, *33*, 71.

[12] Dyne, P. J.; Stone, J. A. *Can. J. Chem.* **1961**, *39*, 2381.

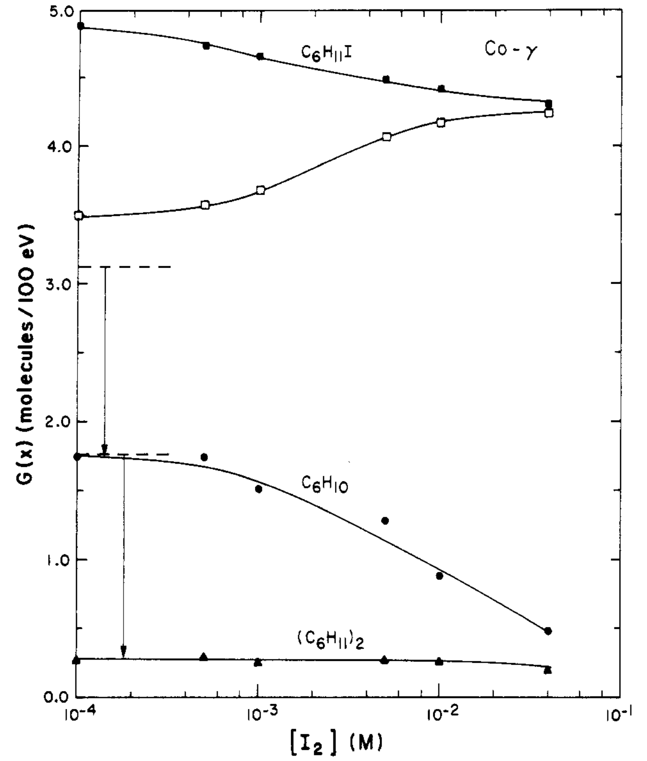

Figure 1. The γ-radiolysis of cyclohexane as a function of iodine concentration: (▲) bicyclohexyl; (●) cyclohexene; (■) cyclohexyl iodide; (□) cyclohexyl iodide corrected for H atom scavenging; see text. The cyclohexene and bicyclohexyl yields with no added iodine are shown as dashed lines.

to avoid gross scavenger depletion. Fortunately iodine consumption is essentially linear in dose[13] so that at doses of 25 krad one can examine solutions with iodine concentrations as low as 10^{-4} M.

As indicated in Figure 1, addition of 10^{-4} M I_2 depresses the bicyclohexyl yield from 1.76 to 0.30 and cyclohexene yield from 3.12 to 1.75. The period for reaction of cyclohexyl radicals with iodine at this concentration is 0.8 μs ($k = 1.2 \times 10^{10}$ m^{-1} s^{-1})[14] whereas the median radical lifetime at the dose rates used is ~16 ms. At this concentration, the iodine should effectively scavenge all the cyclohexyl radicals which escape into the bulk but not appreciably affect the spur processes. Hydrogen atoms, however, abstract from the cyclohexane with a period of ~15 ns and are effectively scavenged only at a much higher I_2 concentration. They, therefore, produce additional cyclohexyl radicals in the bulk so that the observed cyclohexyl iodide represents both cyclohexyl radicals produced directly and those produced by H atom abstraction.

The decreases in the yields of hydrocarbon products observed at 10^{-4} M iodine essentially reflect interference with the combination and disproportionation of cyclohexyl radicals distributed homogeneously in the solution. The disproportionation/combination ratio estimated from these decreases, 0.94, is slightly lower than the previous estimate of 1.1.[15] The fact that the 10^{-4} M iodine interferes with only ~40% of the cyclohexene production confirms that a major fraction of this product results from nonradical processes. The total yield of radicals represented by these differences, 5.66, is somewhat higher than the yield of cyclohexyl iodide determined in the present study (4.89) and that reported in earlier measurements, 5.0[13] and 5.35.[16] It was shown in the latter study that ~3% of the iodine consumed appeared in products having a molecular weight lower than cyclohexyl iodide and ~10% of it in products having a higher molecular weight so that side reactions represent 10–15% of the radical chemistry.

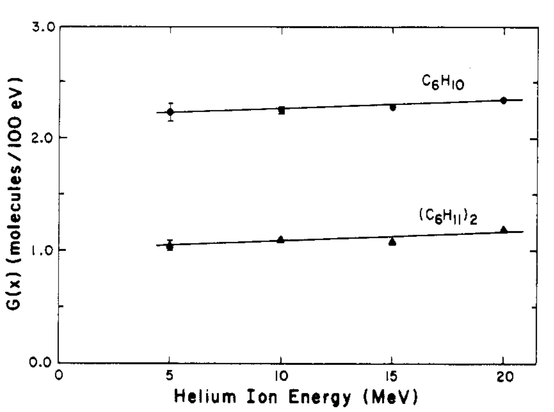

Figure 2. The radiolysis of neat cyclohexane as a function of helium ion energy: (▲) bicyclohexyl; (●) cyclohexene, this work. The error bars reflect the uncertainty in particle energy.

As is shown in Figure 1, the yield of cyclohexyl iodide produced by γ-rays decreases at iodine concentrations above 10^{-3} M. As discussed in great detail in the earlier study of Bansal and Schuler,[16] this decrease results to a large extent from the scavenging of H atoms by the iodine. The yields corrected for this scavenging, assuming a H atom yield of 1.46[17] and a ratio of the scavenging and abstraction rate constants of 4.7×10^3,[16] are given in Figure 1. The observed dependence of cyclohexyl radicals on I_2 concentration suggests that ~20% are scavenged from the spurs at an iodine concentration of ~0.04 M; that is, ~80% of the cyclohexyl radicals diffuse into the bulk. Such an interpretation is, however, complicated by possible interference by iodine with the ionic processes[17] which could affect the initial cyclohexyl radical yield.

It is seen in Figure 1 that the low yield of bicyclohexyl observed in the presence of iodine (~0.3) is virtually independent of iodine concentration. If one assumes that cyclohexyl radicals contribute equally to the production of cyclohexene and bicyclohexyl, then these products account for a yield of 1.2 of cyclohexyl radicals which react within the spur. This value is slightly greater than the spur scavenged yield of 0.8 seen in Figure 1. It appears that some of the bicyclohexyl must be produced in nonradical processes. This result coincides with the relative independence of bicyclohexyl yields with I_2 concentration. At iodine concentrations above 10^{-3} M, the cyclohexene yield dramatically decreases and approaches the bicyclohexyl yield at concentrations >0.04 M. This decrease is reflected in an increased yield of high molecular weight iodides, as reported earlier,[16] and must result from interference of the iodine with nonradical processes responsible for the large cyclohexene yield. This interference greatly complicates possible interpretation of the dependence of the cyclohexene yield on the iodine concentration in the heavy ion experiments.

Helium Ion Studies. There have been relatively few studies of the radiolysis of cyclohexane with heavy ions, and many of these have been carried out with helium ions.[2,3,18–23] Figure 2 shows results obtained during the present study for the production of cyclohexene and bicyclohexyl in the absence of iodine for helium ions having incident energies of 5–20 MeV. The error bars on the data correspond to the uncertainties in energy determination, which decrease from 4 to 0.4% with increasing particle energy. It is seen that even though, as indicated below, the yield of scavengable cyclohexyl radicals increases slightly with particle energy there is no measurable dependence of the hydrocarbon products on energy. The average yields, 1.10 ± 0.06 for bicyclohexyl and 2.28 ± 0.05 for cyclohexene, are, however, only 60–70% of those

---

[13] Fessenden, R. W.; Schuler, R. H. *J. Am. Chem. Soc.* **1957**, *79*, 273.

[14] Foldiak, G.; Schuler, R. H. *J. Phys. Chem.* **1978**, *82*, 2756.

[15] Cramer, W. A. In *Aspects of Hydrocarbon Radiolysis*; Gaumann, T., Hoigne, J., Eds.; Academic Press: New York, 1968; p 153.

[16] Bansal, K. M.; Schuler, R. H. *J. Phys. Chem.* **1970**, *74*, 3924.

[17] Asmus, K.-D.; Warman, J. M.; Schuler, R. H. *J. Phys. Chem.* **1970**, *74*, 246.

[18] Dewhurst, H. A.; Schuler, R. H. *J. Am. Chem. Soc.* **1959**, *81*, 3210.

[19] Falconer, J. W.; Burton, M. *J. Phys. Chem.* **1963**, *67*, 1743.

[20] Burns, W. G.; Parry, J. R. *Nature* **1964**, *201*, 814.

[21] Burns, W. G.; Marsh, W. R.; Reed, C. R. V. *Nature* **1968**, *218*, 867.

[22] Burns, W. G.; Reed, C. R. V. *Trans. Faraday Soc.* **1970**, *66*, 2159.

[23] Boyd, A. W.; Connor, H. W. J. *Can. J. Chem.* **1964**, *42*, 1418.

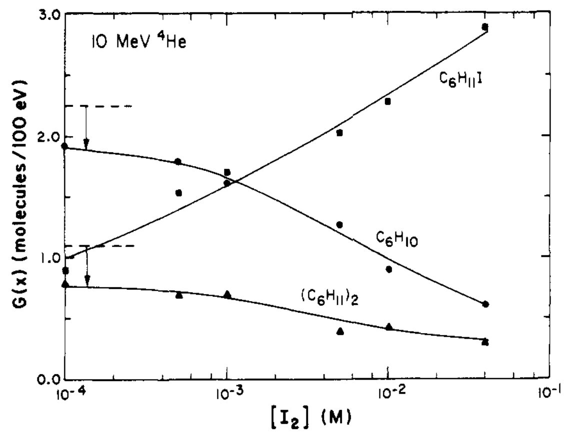

Figure 3. The radiolysis of cyclohexane with 10-MeV helium ions as a function of iodine concentration: (▲) bicyclohexyl; (●) cyclohexene; (■) cyclohexyl iodide. The cyclohexene and bicyclohexyl yields with no added iodine are shown as dashed lines.

observed in γ-radiolysis. Burns and co-workers[20,21] indicated a greater energy dependence from their studies. Their results at high energies are in good agreement with the present results, however, but they found slightly lower yields at low helium ion energies. The yield for bicyclohexyl is in very good agreement with that reported for 1-MeV α-particles by Blackburn and Charlesby.[4]

The studies using iodine as a radical scavenger are more complicated since one has to be concerned about scavenger depletion, both within the track core and in the bulk of solution. Detailed modeling of scavenger depletion within the track, reported elsewhere,[24] shows that the local concentration of iodine in the core of helium ion tracks reaches a minimum at ~1 ns and then increases to that of the bulk solution as iodine diffuses back into the track. For solutions 10^{-4} M in iodine, where the period for scavenging is ~1 μs, the effect of depletion within the core is very small. At 10 eV/Å, we estimate the net effect will result in a decrease in the observed yield of scavenged radicals by less than 10%. For solutions 0.04 M in iodine, scavenging occurs on a time scale comparable to that of the intratrack processes and the effect is somewhat more severe, possibly as much as ~20%. These modeling studies must at this point be regarded as preliminary, but they strongly indicate that for helium ions scavenger depletion within the track does not have any major effect on the observed yields.

Gross depletion in the irradiation zone is more of a problem, but we estimate that with the efficient stirring employed in these experiments the residence time of the sample in the irradiation zone is <1 ms and that consumption of the scavenger in the irradiation zone is $<10^{-5}$ M. Previously[3] it was shown that in radiolysis with 34-MeV helium ions at 10^{-3} M I_2 the yields for consumption of iodine was independent of current below 5 nA. During the present study, no significant dependence of the yields of cyclohexyl iodide or the hydrocarbon products was noted for currents up to 10 nA. For solutions 5×10^{-3} M in I_2, the yields were also dose independent up to 250 krads. The results reported below were obtained at beam currents of 5 nA under stirring conditions where there is no apparent effect of scavenger depletion in the irradiation zone.

Figure 3 shows the dependence of the yields of bicyclohexyl, cyclohexene, and cyclohexyl iodide on iodine concentration for irradiations with 10-MeV helium ions which have a track average LET of 10 eV/Å. It is seen that 10^{-4} M I_2 depresses the yield of each of the hydrocarbon products by only ~0.3 in contrast to the decrease of ~1.4 noted above with γ-rays. As shown in the γ-ray studies, any radicals which diffuse into the bulk solutions are readily scavenged at this iodine concentration. If one assumes that most of the bicyclohexyl and an equivalent amount of cyclohexene are due to radical precursors, then ~75% of the cyclohexyl radicals react within the track. The complementary yield of cyclohexyl iodide is correspondingly low (0.90), i.e. only about 20% of that observed for γ-rays. Since any hydrogen atoms that diffuse into the bulk would abstract from the solvent at this iodine concentration and contribute to the observed cyclohexyl iodide yield, it is clear that very few escape intratrack processes.

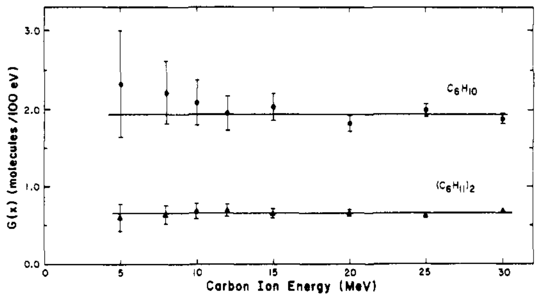

Figure 4. The radiolysis of neat cyclohexane as a function of carbon ion energy: (▲) bicyclohexyl; (●) cyclohexene. The error bars reflect the uncertainty in particle energy.

As the iodine concentration is increased to 0.04 M, the yield of bicyclohexyl decreases by ~0.5 to a value of 0.30, only 0.1 higher than that observed for γ-rays at the same I_2 concentration. The yield of cyclohexyl iodide increases by 1.99 or about 4 times the decrease in bicyclohexyl, as would be expected if the combination/disproportionation ratio is close to unity. These changes appear to reflect directly the competition between scavenging and intratrack processes in the core of the track.

As expected from the γ-ray studies, the effect of iodine on cyclohexene production is more complicated. In comparison of Figures 1 and 3, it is noted that the cyclohexene yields are similar at all iodine concentrations for the γ-ray and helium ion irradiations. If the effect on cyclohexene production was simply the result of intratrack processes, one would expect a dependence on iodine concentration parallel to that observed for bicyclohexyl or only about one-third of that observed. One must conclude that the effect of iodine on the nonradical processes responsible for cyclohexene production by the helium ions is largely the same as that for γ-rays. However the magnitude of this contribution, as measured by the difference between the cyclohexene and bicyclohexyl yields at 10^{-4} M I_2, is slightly lower (1.14 vs 1.45). Unfortunately the effect of I_2 on the nonradical processes is superimposed on the effect of intratrack scavenging so it is not possible to separate these effects. Therefore, it is not possible at this point to draw any significant conclusions about the intratrack reactions from the cyclohexene data.

Carbon Ion Studies. We see in Figure 4 that in the absence of iodine there is very little dependence of the yields of the hydrocarbon production on incident particle energy for carbon ion irradiations. The yields are, however, somewhat lower than those for the helium ions. The only study with comparable particles is that of Burns, Marsh, and Reed,[21] who used 115-MeV ^{14}N and found yields similar to those of the present work. Because of their relatively short range, the uncertainty in energy determination for low-energy carbon ions is much larger than that with helium ions. The error bars on the data of Figure 4 correspond to the uncertainties in energy determination, which decrease from 30 to 3% with increasing particle energy.

Figure 5 shows the dependence of the yields on iodine concentration for 10-MeV carbon ions which have a track average LET of 75 eV/Å. The simulations indicate that, while depletion of scavenger within the core at an LET of 75 eV/Å is virtually complete at ~1 ns, the net effect is reduced by rapid diffusion and results in decreases in the yields of scavenged radicals of only ~20% at 10^{-4} M I_2 and ~40% at 0.04 M I_2.[24] The observed yield (0.3) for cyclohexyl iodide formation at 10^{-4} M I_2 indicates that very few radicals (<10%) escape intratrack processes. It is noted in Figure 5 that for I_2 concentrations up to 10^{-3} M there is little effect on the yields of bicyclohexyl or cyclohexene as compared to that of neat cyclohexane. At higher I_2 concentrations, these yields do start to decrease and the cyclohexyl iodide yield increases

---

(24) LaVerne, J. A. Manuscript in preparation.

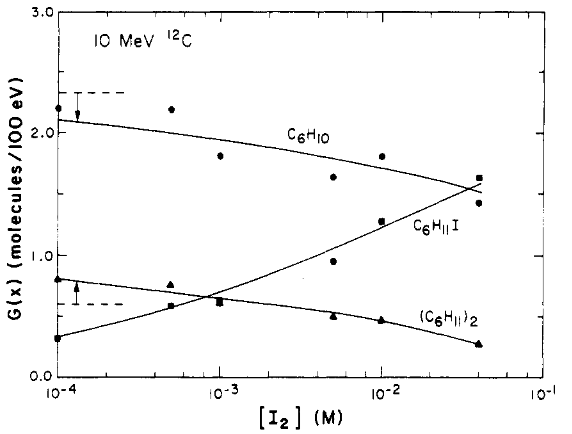

Figure 5. The radiolysis of cyclohexane with 10-MeV carbon ions as a function of iodine concentration: (▲) bicyclohexyl; (●) cyclohexene; (■) cyclohexyl iodide. The cyclohexene and bicyclohexyl yields with no added iodine are shown as dashed lines.

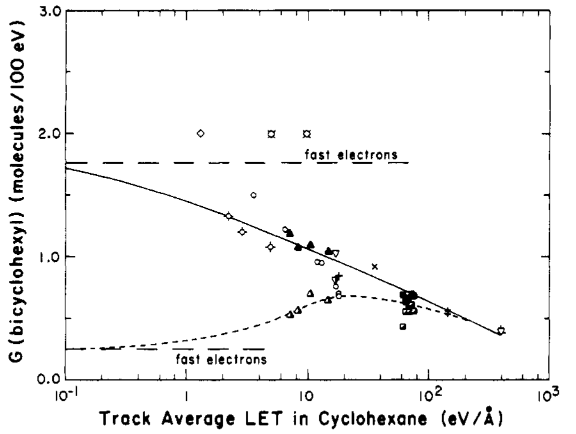

Figure 6. LET dependence of bicyclohexyl yields in neat solutions of cyclohexane: (▲) ^{4}He; (■) ^{12}C, this work; (+) ^{4}He, ref 20; (○) ^{4}He; ref 22; (-◇-) ^{1}H; (×) ^{14}N; (‡) ^{20}Ne, ref 21; (◇) ^{2}H; (¤) ^{4}He, ref 18; (▼) ^{210}Po-α, ref 4; (✡) fission fragment, ref 23. Yields of bicyclohexyl in solutions of 10^{-3} M iodine are: (△) ^{4}He; (▣) ^{12}C, this work; (▽) ^{210}Po-α ref 4. The long dashed lines show the fast electron limits (1.76 and 0.25, this work).

to 1.63. The fact that the bicyclohexyl yield is 0.28 at 0.04 M I_2, only 0.1 higher than that for γ-rays, shows that the iodine is effective in scavenging the radicals and indicates that depletion within the core may be somewhat less severe than indicated by the simulations.

General Discussion. Figures 6 and 7 summarize the available data on the production of bicyclohexyl and cyclohexene in the various heavy particle studies. Except for the low-energy helium ion studies by Burns and Reed,[22] which appears to be somewhat low, and the early results reported by Dewhurst and Schuler,[18] where the bicylohexyl (but not the cyclohexene) yields are obviously high, the various results, in view of the experimental difficulties, are remarkably consistent. In the absence of iodine, the yields of cyclohexene and bicyclohexyl clearly drop monotonically with increased LET and approach very low values at LETs above 10^3 eV/Å. These effects cannot be explained purely by intratrack reactions between cyclohexyl radicals because the product yields should be identical to those produced by homogeneous reactions of the radicals. However, it was indicated above that very few of the hydrogen atoms diffuse out of the track of the heavy ions. Presumably these atoms are removed by intratrack reactions with cyclohexyl radicals, and as a result the yields of the hydrocarbon products are expected to decrease with LET to some extent. Such an explanation would, however, not account for the fact that the yields approach very low values at high LET. It is clear that the intratrack processes involving the precursors to cyclohexyl radical formation become increasingly complex with increased LET, particularly above 100 eV/Å. We do not wish to imply that all hydrocarbon products and therefore the net decomposition of cyclohexane decreases with increasing particle LET. Studies with very high LET particles indicate that the yield of H_2 increases with LETs above ~10 eV/Å.[22,23] These results suggest that hydrocarbon products are being formed at very high LETs, but they are presumed to be of high molecular weights.

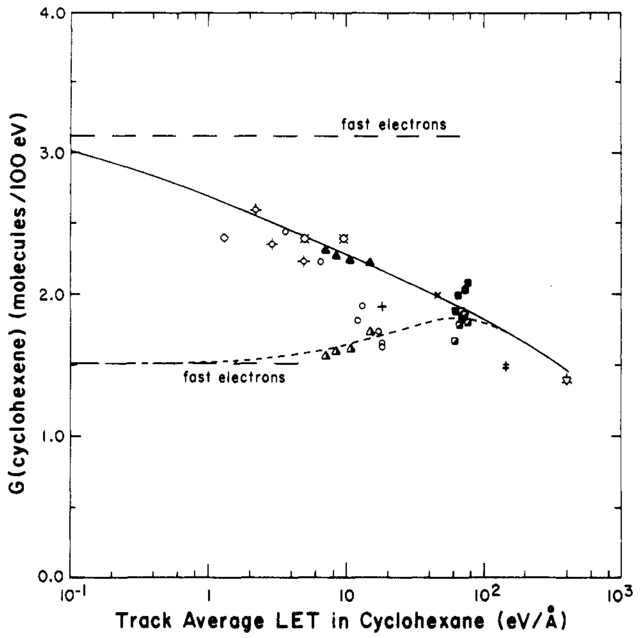

Figure 7. LET dependence of cyclohexene yields in neat and 10^{-3} M iodine solutions of cyclohexane. The symbols and line types are the same as those in Figure 6. The long dashed lines show the fast electron limits (3.12 and 1.51, this work).

Some further insight is obtained by examining the LET dependence of the yield of hydrocarbon products in the presence of 10^{-3} M iodine, which is sufficient to remove the cyclohexyl radicals which escape the track. It is seen in Figure 6 that the yield of bicyclohexyl at first increases with LET, as would be expected from the increased importance of the radical combination processes. However, at LETs above ~50 eV/Å, the bicyclohexyl yield is similar to that observed in the absence of I_2. It is presumed that the bicyclohexyl yield with iodine cannot be greater than that found in neat solutions so its yield must decrease to a value near to zero at LETs above 10^3 eV/Å. We conclude that high-order processes involving the precursors to radical formation become increasingly dominant with increased LET. This effect is also manifest in the data on cyclohexene production. However, in this case the yield does not increase in going from fast electrons to 10-MeV helium ions so some compensatory effects must be present at LETs below 20 eV/Å. At high LETs the cyclohexene yields with 10^{-3} M I_2 approach those of neat cyclohexane and are about 1 unit higher than those for bicyclohexyl production.

We are now in a position to estimate the time scale and concentration of radicals involved in the intratrack processes. Taking the second-order rate constant for scavenging as 1.2×10^{10} M^{-1} s^{-1} [14] gives lifetimes of cyclohexyl radicals with respect to I_2 as shown in Figure 8. Extrapolation of the data for γ-rays to time zero gives an initial cyclohexyl radical yield of 4.4. Most track processes are over by about 1 μs, and 80% of the radicals escape into the bulk medium. At a given time in the evolution of the track, the yield of scavengable cyclohexyl radicals decreases with increasing LET of the particle. Approximately half of the radicals have undergone track processes by 10 and 0.5 ns with 10-MeV helium and carbon ions, respectively. These lifetimes correspond to I_2 concentrations of about 8 and 170 mM, respectively. Using the second-order rate constant for cyclohexyl radicals ($2k = 2.4 \times 10^9$ M^{-1} s^{-1}),[25] it is estimated that their average concentrations are 0.04 and 0.8 M in the tracks of helium and carbon ions,

---

(25) Reitberger, T.; Niblaeus, K. *Chem. Scr.* **1979**, *13*, 52.

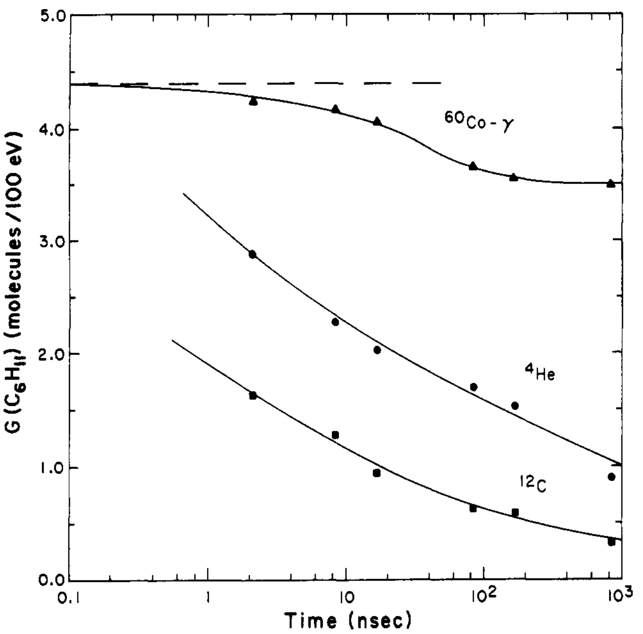

Figure 8. Time dependence of cyclohexyl radicals with respect to the I_2 scavenger for γ-rays and 10-MeV ^{4}He and ^{12}C ions. The dashed line is the initial yield of radicals for γ-rays (4.4).

respectively. This analysis assumes that the initial cyclohexyl radical yield is independent of LET which, considering the previous discussion, is doubtful. The concentrations given are therefore maximum values, but they should be of the correct order of magnitude. Assuming that the radicals are distributed homogeneously over the volume of the track leads to a track diameter of 80 Å for 10-MeV helium ions and 45 Å for 10-MeV carbon ions. In accordance with several studies on the radiolysis of water,[7,8] it is expected that at the same energy the carbon ions would have a smaller track radius than helium ions. The smaller radius is manifested by a 20-fold increase in radical concentration even though the LET increases only by a factor of 7.5. The resulting high densities of ionic and excited species in heavy particle tracks may increase the importance of processes which lead to a decrease in radical yields. Such processes would explain the apparent decrease in cyclohexene and bicyclohexyl yields at LETs greater than ~50 eV/Å as shown in Figures 6 and 7. These estimates of cyclohexyl radical concentration and track diameters are admittedly crude, but they should be representative of the true values. No other experiments have been able to supply these basic parameters of heavy particle tracks in hydrocarbons.

The exact identities of the precursors to the cyclohexyl radical have been ignored here since we are mainly concerned with the effects of track structure on the kinetics. It is implied that cyclohexyl radical formation is reasonably fast compared to its subsequent diffusion and reaction. However, it is known that the excited singlet state of cyclohexane is formed with a yield of 1.45 and it will decay with a lifetime of ~1 ns[26] to give about 20% cyclohexyl radicals.[27] For the most part the yield of 0.3 cyclohexyl radicals formed in this manner is small compared to the total and will have no effect on the track processes discussed here. In the case of carbon ions, the decay of the excited state may coincide with a large fraction of the track processes. However, it is also likely that the large concentration of reactive species in carbon ion tracks will lead to significant quenching of the excited state, as well as ionic species, and the yield of cyclohexyl radicals from this source is minor. All of these processes should be included in a detailed study of the radiolysis of cyclohexane, but the lack of experimental data precludes more discussion here. Further experiments with selected scavengers are warranted. Modeling studies should also supply more details of particle track structures.

Acknowledgment. We thank Prof. C. P. Browne for making the facilities of the Notre Dame Nuclear Structure Laboratory available to us. This facility is supported by the U.S. National Science Foundation. The research described herein was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. This is contribution NDRL-3410 of the Notre Dame Radiation Laboratory.

---

(26) Choi, H. T.; Askew, D.; Lipsky, S. *Radiat. Phys. Chem.* **1982**, *19*, 373.

(27) Schwarz, F. P.; Smith, D.; Lias, S. G.; Ausloos, P. *J. Chem. Phys.* **1981**, *75*, 3800.

Systemization for the King–Altman–Hill Diagram Method in Chemical Kinetics

John Happel*

*Department of Chemical Engineering and Applied Chemistry, Columbia University,
New York, New York 10027*

and Peter H. Sellers

The Rockefeller University, New York, New York 10021 *(Received: October 7, 1991)*

An algorithm is introduced that generates in an appropriate symbolic notation every list of diagrams required by the King–Altman–Hill method for calculating steady-state fluxes in pseudo-first-order mass action chemical systems. A method for complete enumeration of these diagrams would be desirable in complicated cases but to our knowledge is presently not available. We illustrate the application of our procedure in the context of the dihydrofolate reductase system, a complex enzyme reaction, which has previously been treated in some detail. A computer program implementing the algorithm is available for such applications.

Introduction

Hill's[1] formulation of the King–Altman[2] diagram method provides a schematic way of deriving steady-state rates for enzyme-catalyzed reactions, which is only useful when the system is small enough to allow diagrams to be found by inspection. By separating the steady-state mechanism into minimal submechanisms, which Hill calls "cycles", he has shown that these submechanisms can be expressed by appropriate diagrams. By combination of information from such diagrams, the rates for each step in the mechanism may be obtained.

---

(1) Hill, T. L. *Free Energy Transduction and Biochemical Cycle Kinetics*; Springer-Verlag: New York, 1989.

(2) King, E. L.; Altman, C. *J. Phys. Chem.* **1956**, *60*, 1375.