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Bond Rupture in the Radiolysis of *n*-Alkanes: An Application of Gel Permeation Chromatography to Studies of Radical Scavenging by Iodine

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A study of the distribution of radicals produced in the radiolysis of liquid normal alkanes from C_5 to C_{12} is presented as an illustrative example of the use of gel permeation chromatography (GPC) in iodine scavenging studies. Separation of the alkyl iodides by GPC offers particularly attractive possibilities because elutions are carried out at room temperature, minimizing decomposition of the product iodides. Chromatograms recorded spectrophotometrically in the characteristic absorption bands of the alkyl iodides at ∼260 nm show that the only radicals produced in appreciable yield from the normal alkanes are those expected from simple bond rupture. Contour plots of three-dimensional chromatographic data obtained with a diode array detector show little interference at 260 nm from other products. The absence of any significant yield of iodine-containing products other than those expected is conclusively demonstrated by complementary radiotracer studies using $^{125}I_2$. Both monitoring approaches show that scission of the carbon skeleton accounts for ∼25% of the radicals formed and occurs most frequently in the region of the central carbon−carbon bonds. Elimination of a terminal methyl group is relatively infrequent. An expression that describes the yields of radicals produced by rupture of the carbon backbone is derived from the observed fragmentation patterns. The present studies are particularly important in that the yields of primary and secondary radicals produced by H elimination from the normal alkanes are readily determinable since their respective iodides are well-resolved chromatographically. For the normal alkanes it is found that H-atoms are lost approximately three times more rapidly from a secondary position than from a primary position and that loss from the different secondary positions is essentially statistical. These studies provide considerably greater detail on the competing processes involved in bond rupture than has heretofore been available and serve as the basis for modeling the overall processes that produce radicals in the radiolysis of normal alkanes.

Introduction

ESR measurements during the irradiation of liquid aliphatic hydrocarbons[1−3] demonstrate conclusively that free radicals are important intermediates in the radiolytic decomposition. While a variety of radicals is expected from the various C−C and C−H bond rupture processes that compete following ionization and excitation, the ESR studies mainly provide structural information on the principal radicals produced and very little information on radicals produced only in low yield. It is the purpose of this study to provide the detailed quantitative information on the resultant distribution of radicals required for modeling the overall radiolytic processes.

Quantitative determination of yields from the ESR results involves assumptions about radical lifetimes. Only in special cases, such as the radiolysis of propane,[2] is one able to estimate the relative importance of the major radicals. Although various investigators[4−6] have attempted to derive radical yields from studies of the hydrocarbons formed, products from nonradical intermediates complicate interpretation of product distributions obtained in the absence of scavengers. Studies of mixtures show that in the absence of an appropriate radical scavenger hydrogen atom transfer reactions also can complicate interpretation of the results.[7] One must rely on scavenging studies to obtain detailed quantitative data on the distribution of radicals initially produced.

Scavengers, including molecular iodine,[8−11] hydrogen iodide,[12−14] *n*-butyl mercaptan,[15] and stable radicals such as diphenylpicrylhydrazyl[16] and Galvinoxyl,[17] have been used since the early 1950s to examine radical production. The earliest studies largely focused on the total radical yields as measured by the loss of scavenger. Some information on radical distributions is also available from early radiochemical experiments using carrier isolation methods, including the studies of Williams and Hamill[18] and Gevantman and Williams[8] on gaseous alkanes and those of McCauley and Schuler[19] on liquid butane. These studies showed that chain rupture and loss of hydrogen are of comparable importance. The sampling experiments of Holroyd,[20,21] using carbon-labeled methyl and ethyl radicals prepared in situ, also provide information on the relative yields of radicals produced from a number of alkanes. These various early studies are summarized in 1958[22] and 1968[23] reviews. In a more recent study Isildar[14] used gas chromatography to examine the tritiated hydrocarbons produced by scavenging the radicals with tritium iodide (TI). As discussed below, his studies provide considerable information on the radicals produced by rupture of the hydrocarbon chain but not on those produced by elimination of H from the primary and secondary positions. Interpretation of these results is also somewhat complicated by ionic processes involving HI.

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Of the scavengers studied, iodine appears to be the simplest. Because the iodine atoms produced in reaction 1

$$R\bullet + I_2 \xrightarrow{k_1} RI + I\bullet \qquad (1)$$

are relatively inert and combine to reform I_2, i.e.,

$$I\bullet + I\bullet \rightarrow I_2 \qquad (1a)$$

the radical yield should be twice that for the consumption of I_2. Reaction 1 is diffusion controlled ($k_1 \sim 10^{10}$ M^{-1} s^{-1})[24] and has been shown to be quantitative even at low iodine concentrations.[25] As a result, a fair number of studies of radical production in the radiolysis of hydrocarbons have been carried out to date using iodine as the scavenger. With the development of gas chromatography it became possible to separate the alkyl iodides in the absence of added carriers. Schuler and Kuntz, for example, used a gas chromatographic approach to obtain yields for production of methyl radicals from a large number of alkanes.[26] During recent years more general studies of the distribution of radicals produced in the radiolysis of hydrocarbons have awaited development of better analytical methods and have been very sporadic. Gel permeation chromatography (GPC) provides an attractive alternative to the separation methods previously used since, as shown here, many of the iodides of interest can be readily separated at room temperature, minimizing their decomposition. The saturated alkyl iodides can be readily detected spectrophotometrically at their characteristic absorption maximum at ∼260 nm[27,28] or radiochemically by using radioactive iodine as the scavenger.

In general, there currently is very little quantitative information on the distribution of radicals from either ESR or scavenging studies and essentially none on radicals produced in low yield. The present study expands on the earlier scavenger studies and provides a comprehensive picture of bond rupture in the radiolysis of the normal alkanes. Focus is particularly on distinction between the radicals produced by loss of H from the primary and secondary positions for which relatively little information is currently available. These radicals will be subsequently referred to as parent radicals and the iodides resulting from their scavenging as parent iodides. Quantitative information on the radicals produced by rupture of the hydrocarbon skeleton, i.e., the fragment radicals, complements that from the earlier study[14] where TI was used as the scavenger. The present study also serves as an illustrative example of the use of GPC in product analysis studies and provides the experimental basis for future studies of bond rupture in the radiolysis of branched and cyclic hydrocarbons. The ultimate objective of these various scavenger studies is the development of a sufficient database to enable correlation of bond rupture patterns with hydrocarbon structure.

Experimental Section

GPC Studies Using Spectrophotometric Detection. In general liquid chromatographic studies using spectrophotometric detection benefit appreciably from the use of a diode array detector that permits three-dimensional display of the spectral data.[29] The chromatographic system used in the studies carried out at the Notre Dame Radiation Laboratory (NDRL) consists of a Waters pump, a loop injector, the Phenomenex columns described below, a Waters 996 diode array detector (PDA) and a Pentium processor. Chromatographic data were recorded from 200 to 400 nm every second in 3-D format using Waters Millennium 2010 software. Spectral resolution was 1.2 nm. With a recording time constant of 1 s the noise level was ∼0.00002 absorbance units (AU). Spectra and chromatograms were monitored during elution and subsequently reviewed on a color monitor. The richness of the chromatographic details available in these 3-D recordings, particularly when the data are presented in color, is illustrated very well in Figure 1. In practice one relies more on contour plots extracted from such 3-D data to provide qualitative information on possible interferences with the components of interest. Comparison of elution times and spectra extracted at the chromatographic peaks with authentic samples allow positive identification of the alkyl iodide contributions. Chromatograms extracted at specific wavelengths provide the information necessary for quantitative determination of the individual components.

In the present studies sample sizes were from 50 to 250 μL. At the flow rate used, 0.01 mL/s, these sample volumes correspond to injection times of 5 to 25 s. Under the conditions used the chromatographic peaks have intrinsic widths of ∼25 s so that no appreciable broadening is observed for the 50 μL samples. The detector cell volume of 50 μL does not contribute significantly to the peak width. In cases where maximum resolution was required, 50 μL samples were used.

GPC Studies Using Radiochemical Detection. Radiochemical studies were carried out at the Hungarian Institute of Isotope and Surface Chemistry (IISC). Iodine containing ^{125}I (60-day half-life) was prepared as described by Toth and Miller[30] by electrolytically depositing the carrier-free isotope on platinum. The radioiodine was then exchanged with inactive iodine at an appropriate concentration in the hydrocarbon of interest. The resultant radioiodine had a specific activity of ∼1 curie/mol (37 GBq/mol). The GPC columns, sample volumes, and elution rates were as in the spectrophotometric studies. The column effluent passed through a scintillation counter in a flow cell having a volume of ∼50 μL and was monitored continuously. The instantaneous counting rate was recorded every 0.5 s at a time constant of 1 s. Total counts over periods of 2 s were also recorded. To correlate the radiochemical and spectrophotometric studies data were also recorded at 260 nm with a monochromatic detector in series with the radiochemical detector.

The GPC Columns. To get acceptable resolution, two 300 mm × 7.8 mm Phenomenex Phenogel 5μ 50 A columns were used in series. These columns were obtained from the supplier packed in hexane. Alkanes were chosen as eluents so that measurements could be made down to 200 nm. In the studies reported here Fisher OPTIMA grade hexane, which had an absorbance <0.2 at 220 nm, was used as the eluent. Because the gel packing shrinks appreciably when in contact with hexane one has to be extremely careful to avoid high pressures and abrupt pressure changes that can disturb the packing and affect the chromatographic resolution so that a relatively low flow rate (∼0.6 cm^3/min) was used. As a result the sample front appeared at ∼25 min and the normal iodides required from 30 to 60 min for elution. Eluents were purged with helium to remove dissolved oxygen which absorbs significantly below ∼220 nm.

Hydrocarbons. The alkanes used in these studies were from a variety of sources including Aldrich, Fisher, Fluka, Lancaster, Pfalz and Bauer and Phillips Petroleum. They were first treated by passing them through a silica gel column to minimize olefinic impurities which otherwise interfered with the determinations. Before preparing the samples for irradiation an additional column treatment with silver nitrate on alumina, as recommended by Murray and Keller,[31] was used to remove residual olefins.

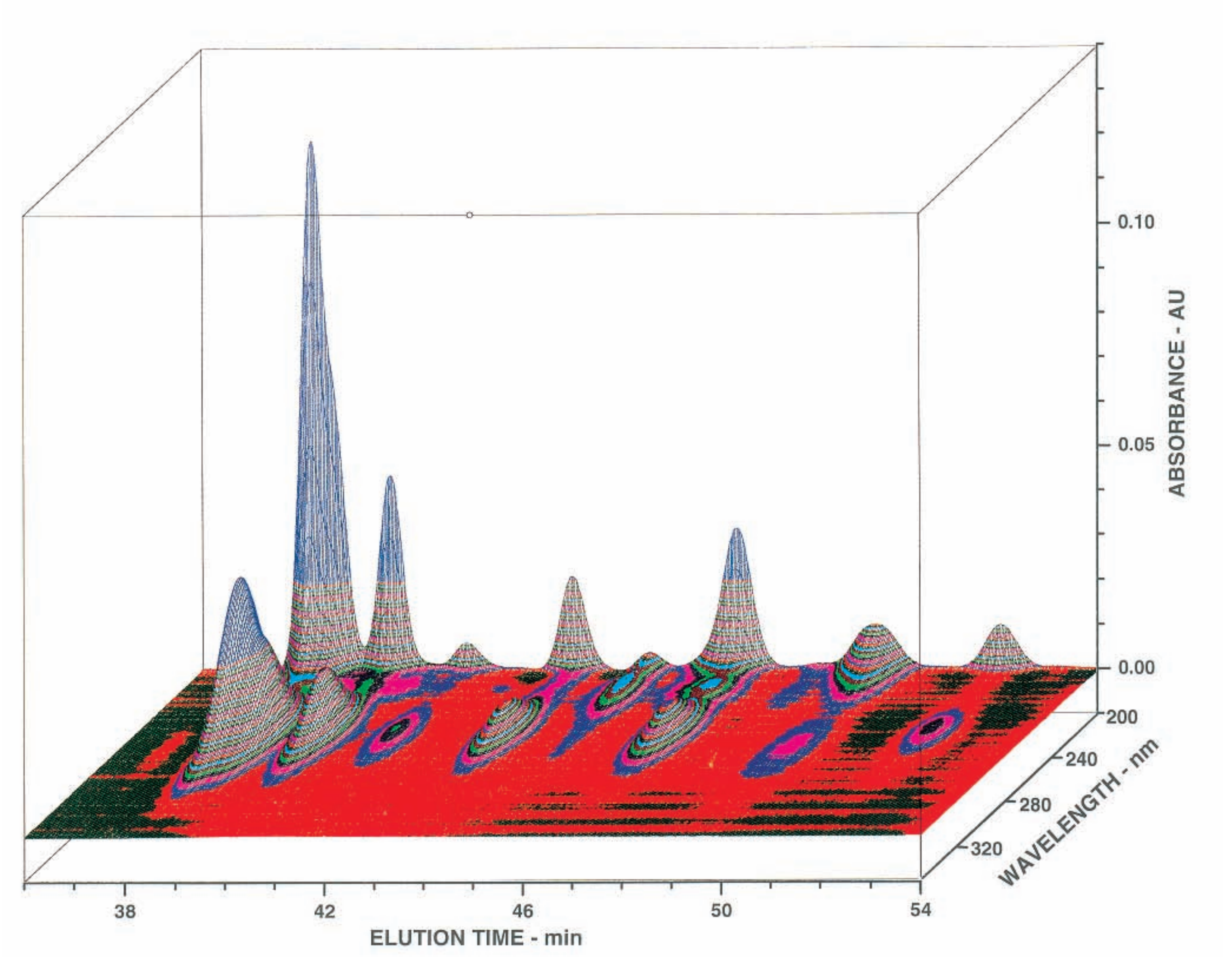

Figure 1. Three-dimensional plot of chromatographic data recorded for a pentane sample containing 1 mM I_2 irradiated to a dose of 200 krads. See the discussion on pentane for identification of the major peaks that include all of the seven alkyl iodides expected from simple bond rupture.

Sample Preparation and Irradiation. Dissolved air (oxygen) was removed from the samples either by purging with helium or by evacuation using a freeze−thaw technique. The irradiation cells had attached quartz cuvettes so that iodine concentrations could be monitored spectrophotometrically during the irradiations. Irradiations with ^{60}Co γ-rays were at ~25 C. Total doses were mostly from 100 to 400 krads (1 krad = 6.24 × 10^{16} eV g^{-1} in water). The dose rate at NDRL was ~400 krads/h (6.8 × 10^{15} eV g^{-1} s^{-1}) and at IISC ~100 krads/h (1.7 × 10^{15} eV g^{-1} s^{-1}). At an iodine concentration of 1 mM ~50% of the iodine is consumed at a dose of ~250 krads. Dosimetry was based on the Fricke dosimeter with $G(Fe^{3+})$ as 15.5[32] taking into account the electron density of the alkane relative to the Fricke system. *Radiation chemical yields are given in the text and tables as values of G in units of molecules per 100 eV of absorbed energy.*

Reference Samples. Reference samples of the alkyl iodides were obtained from Aldrich, Lancaster, Pfalz and Bauer and ICN. Except for the secondary iodopentanes, chromatographic analysis showed these samples to be sufficiently pure (>98%) as to provide adequate references. GPC analysis of the available samples of 2-iodo- and 3-iodopentane showed that they contained, respectively, 10 and 28% of the other isomer for which an appropriate correction was made.

Spectrophotometry. A Hewlett-Packard 8452A diode array spectrophotometer was used to examine the reference alkyl iodide and to determine their extinction coefficients. Spectra of solutions of known concentrations of the alkyl iodides recorded with the Hewlett-Packard spectrophotometer were similar to those of the chromatographically resolved components recorded with the Waters system.

Chromatographic Sensitivities. Saturated alkyl iodides all have absorption maxima in the 257−270 nm region with extinction coefficients of 350−550 M^{-1} cm^{-1} (see Table 1S). For primary iodides λ_{max} is at ~257 nm, and for secondary iodides at ~261 nm (for tertiary iodides λ_{max} is at ~ 267 nm).[27,28] Because of this difference 260 nm was chosen as an appropriate monitoring wavelength. The absolute sensitivities determined from areas of resolved peaks for reference samples of known concentrations are given in column 2 of Table 1S in units of AU s M^{-1}.

Sensitivities can also be determined indirectly from the extinction coefficients if the chromatographic parameters are known. In the spectrophotometric studies the area under a chromatographic peak (Area) depends on the sample concentration ([C]), the extinction coefficient (ϵ) at the wavelength of recording, the elution rate (F), the optical path length (L), and the injection volume (V). The sensitivities are given by eq 2:

$$\text{Sensitivity} = \frac{\text{Area}}{[\text{C}]} = \frac{\epsilon LV}{F} \qquad (2)$$

With an injection volume of 0.25 cm^3, a cell length of ~1 cm and a flow rate of ~0.010 $cm^3\ s^{-1}$ the sensitivity should be 25ϵ in units of AU s M^{-1}. Equation 2 was used to normalize data for differences in sample volumes and elution rates. The sensitivities determined from the measured extinction coefficients (column 4 of Table 1S) agree very well with those measured directly.

The sensitivities of the normal iodides rise smoothly with increased chain length and are similar above C_5 at ~11500 AU s M^{-1}. At 260 nm the sensitivities of the available secondary iodides are ~12% greater than those of the corresponding normal iodides. In the analyses it was assumed that this difference persists for the secondary iodides where reference samples were not readily available.

Radiochemical Sensitivities. The radiochemical sensitivities obey a relation similar to eq 2 with ϵ replaced by the specific activity of the radioiodine. Because of the procedure used in preparing the radioiodine the specific activities varied considerably from sample to sample. As a result these radiochemical experiments provide information only on the relative concentrations of the individual products.

Data Analysis. The three-dimensional Millennium recordings were first displayed on the chromatographic monitor as contour plots to examine for any significant interference from components other than the alkyl iodides. Spectra at the peaks of interest were extracted from the recordings and compared with reference spectra. Chromatograms were extracted at 260 nm. Areas of resolved peaks were determined by integration using the Millennium software. These chromatograms were also converted to ASCII data sets that served as input to the "ORIGIN" data analysis program.[33] It was found that the peak profiles of isolated peaks could be fitted quite well by a single Gaussian that gave an area that agreed with areas determined by the Millennium integrations. For peaks that were not well resolved, the areas of the individual components were determined using multiple Gaussians on the assumption that adjacent peaks have the same widths.

In the radiochemical studies the ratemeter data were recorded as ASCII data sets. After subtraction of an appropriate background they were smoothed using the 25 point adjacent averaging routines available in "ORIGIN". The peak areas were determined by Gaussian analysis.

Results

Iodine Consumption. Spectra recorded during the incremental irradiation of heptane containing 1 mM I_2 are given in Figure 2. It is seen that as the iodine is consumed the absorption of its bands at 230 and 520 nm decreases monotonically with increased dose, while the absorption at 260 nm increases as the result of the complementary formation of alkyl iodides. We particularly note the isosbestic point at 248 nm. Similar isosbestic points were also observed in the irradiation of solutions of iodine in the other hydrocarbons. These isosbestic points gradually shift from 245 nm for pentane to 252 nm for decane as the result, as is noted below, of the increased relative importance of the production of secondary iodides. The existence of these isosbestic points indicates that complicating secondary reactions of the alkyl radicals are essentially absent. The iodine absorption at 520 nm, where the absorption of the alkyl iodides is negligible and where its extinction coefficient is ~900 M^{-1} cm^{-1}, was used to monitor the iodine consumption yields.

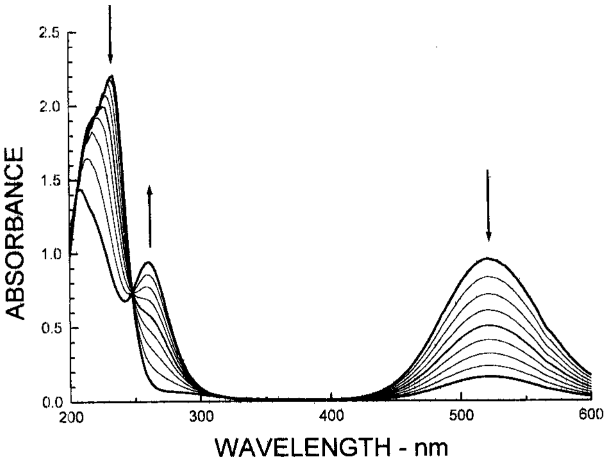

Figure 2. Spectra recorded during the irradiation of heptane containing 1 mM I_2 with incremental doses of 50 krads. The decreases in absorption at 230 and 520 nm represent the consumption of I_2 and the increases at 260 nm the production of alkyl iodides. The isosbestic point at 248 nm indicates the absence of complications in the scavenging.

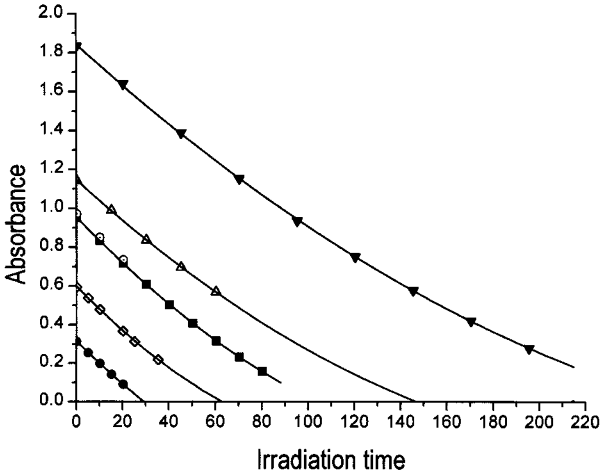

Figure 3. Consumption of iodine for heptane solutions initially containing ● − 0.35, ◇ − 0.67, ■ − 1.07, ⊙ − 1.09, △ − 1.28 and ▼ − 2.06 mM I_2. Absorbances were measured at 520 nm. The curves represent the quadratic dependencies corresponding to eq 6 (see text). The initial slopes correspond to an initial iodine consumption yield of 5.6.

Dose Dependence. Early studies of the radiolysis of heptane[10,11] and cyclohexane[25] indicated that below millimolar the *initial* yield for consumption of iodine is independent of concentration. However, a modest decrease in the yield was observed after a substantial fraction of the iodine was consumed. In the case of cyclohexane radiochemical methods were used to demonstrate that the initial radiation chemical yield for production of iodine-containing products is constant for iodine concentrations from millimolar down to 10^{-5} M.[25] It is clear that at the low dose rates used in these experiments second-order reactions between radicals do not compete significantly with scavenging at iodine concentrations of the order of millimolar.

Typical dependencies of absorbance on dose are illustrated in Figure 3 for heptane samples subjected to increasing radiation doses. A distinct curvature is noted in the plots, particularly at the higher iodine concentrations. The observed decrease in yield as the iodine is consumed can be attributed to a large extent to increased competition in the scavenging processes by the hydrogen iodide formed in the reaction of hydrogen atoms with the iodine.

$$\mathrm{H}\bullet + \mathrm{I}_2 \xrightarrow{k_3} \mathrm{HI} + \mathrm{I}\bullet \tag{3}$$

At low iodine concentrations, i.e., below millimolar, hydrogen atoms preferentially abstract H from the hydrocarbon.

$$\mathrm{H}\bullet + \mathrm{RH} \xrightarrow{k_4} \mathrm{H}_2 + \mathrm{R}\bullet \tag{4}$$

Little HI is formed and one observes that consumption of iodine is nearly linear. Taking k_4 as 10^7 M^{-1} s^{-1} one estimates that ~5% of the hydrogen atoms are scavenged by iodine at millimolar concentrations. Reaction 4 is in effect a radical transfer reaction and should, in itself, have no effect on the yield for iodine consumption. However, Perner and Schuler[13] have shown that the rate constant for radical scavenging by HI

$$\mathrm{R}\bullet + \mathrm{HI} \xrightarrow{k_5} \mathrm{RH} + \mathrm{I}\bullet \tag{5}$$

is comparable to that for Reaction 1. Since an iodine atom is produced rather than being consumed, the overall effect of Reaction 5 on the differential yield for iodine consumption is doubled. Thus, one expects the yield to decrease gradually with dose as HI builds up, particularly at iodine concentrations much above millimolar where Reaction 3 competes to an increasingly greater extent with Reaction 4. While the curvature noted in the figure is expected, the fact that it is not more pronounced shows that where the ratio $[\mathrm{HI}]/[\mathrm{I}_2]$ is low Reaction 5 is of relatively minor importance. Also, because the observed yields for alkyl iodide formation account for most of the iodine consumed (i.e., >95%; see material balance below) electron scavenging by iodine can only be of minor importance at iodine concentrations below millimolar.

In the present study, one is primarily interested in the total yield for radical production. In the absence of second-order reactions between radicals the total radical yield, including that of H-atoms, should be twice the initial yield for consumption of I_2. Determination of the initial yields is complicated because the variables in the appropriate differential equations describing the competition cannot be separated where Reaction 5 contributes significantly. As a result, no general analytical expression for the dependence of the yield on dose is available.[13] However, as is shown in Figure 3, the observed dependence of the iodine absorbance (Abs) on dose (D) can be fitted extremely well empirically by a quadratic of the form

$$\mathrm{Abs}_0 - \mathrm{Abs} = A\cdot D - \mathrm{B}\cdot \mathrm{D}^2 = A\cdot D\cdot(1 - (B/A)\cdot D) \tag{6}$$

In Figure 3 the average of the initial slopes corresponds to a radiation chemical yield for consumption of iodine in heptane of 5.56 ± 0.10.

While the initial yields may be slightly overestimated by this treatment they are clearly underestimated by considering the iodine consumption to be linear in dose. For example, where 50 and 85% of the iodine is consumed the average slopes of the data at 1.07 mM I_2 in Figure 3 are, respectively, only 90 and 80% of the initial slope given by the quadratic treatment. Determination of the yields of specific radicals effectively involves correcting the measured alkyl iodide yields to take into account the decreases that occur as the radiolysis progresses. However, because the factor correcting for the dose dependence $(1 - (B/A)\cdot D)$ is only somewhat less than unity (i.e. >0.8), possible errors in this correction are small for experiments where less than 90% of the iodine has been consumed.

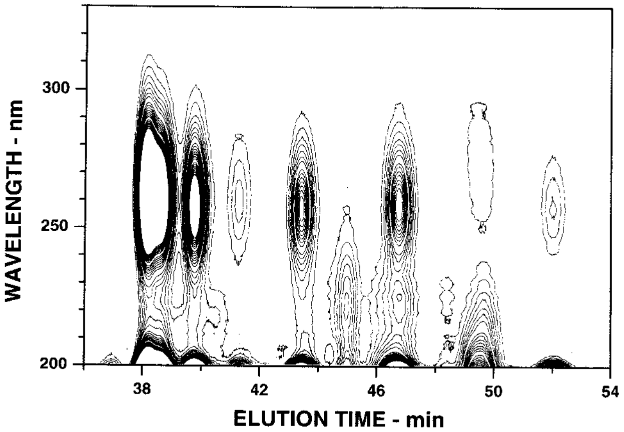

Figure 4. Contour plot extracted from the data of Figure 1. Contours are displayed at intervals of 0.0004 AU from 0.00 to 0.01 AU. The six peaks at 260 nm are assignable, from left to right, to 2- and 3-iodopentane (unresolved), 1-iodopentane, 1-iodobutane, 1-iodopropane, ethyl iodide, and methyl iodide. Most of the contributions noted at short wavelengths represent non-iodine-containing products.

Pentane. *Spectrophotometric Studies*. The presence of the seven alkyl iodides expected from the radicals resulting from loss of a hydrogen atom or rupture of the hydrocarbon chain are readily noted by their absorption maxima at ~260 nm in Figure 1. A contour plot of the data is presented in Figure 4 and a chromatogram extracted at 260 nm in Figure 5. As is typical of GPC chromatography, the iodides are eluted in inverse order of their molecular weight. The first major peak, observed at an elution time of 38.5 min, represents the partially resolved contributions of 2-iodo- and 3-iodopentane (see below). This peak is followed consecutively by peaks that are attributable to 1-iodopentane, 1-iodobutane, 1-iodopropane, ethyl iodide, and methyl iodide at elution times, respectively, of 39.7, 41.3, 43.4, 46.2, and 52.0 min.

It is seen in Figure 4 that in the region of 260 nm the contours of the primary iodides are symmetric. As is obvious in the contour plot, the peak at ~38.5 min is highly asymmetric. This asymmetry is attributed to the partial resolution of 2-iodo- and 3-iodopentane. Chromatography of reference samples shows that 3-iodopentane elutes ~25 s after 2-iodopentane but ~60 s before 1-iodopentane. Both are well resolved from 1-iodopentane.

Spectra recorded at the chromatographic peaks of the normal iodides are given in Figure 6A. Except for ethyl iodide these spectra are identical to those from reference samples, ensuring proper identification of these peaks. The spectrum at the chromatographic peak of ethyl iodide does show a modest absorption at ~220 nm in excess of that ascribable to ethyl iodide. As discussed below, this additional absorption appears to be due to an unresolved contribution from vinyl iodide. It is seen in Figure 6B that the secondary iodopentanes absorb at a slightly greater wavelength ($\lambda_{\max}$ 260−262 nm) than does the primary iodide (257 nm).

In the chromatogram 3-iodopentane is observed as a shoulder on the more intense peak of 2-iodopentane. Determination of the individual contributions using the Gaussian analysis approach described above is illustrated in Figure 7A. The peak of 1-iodopentane is described very well by a single Gaussian with a width of 24 s. The chromatogram in the region of the iodopentanes is resolved into three components with areas that correspond to relative yields of 1:2.2:1.1 for the production of 1-iodo-, 2-iodo-, and 3-iodopentane (taking into account the

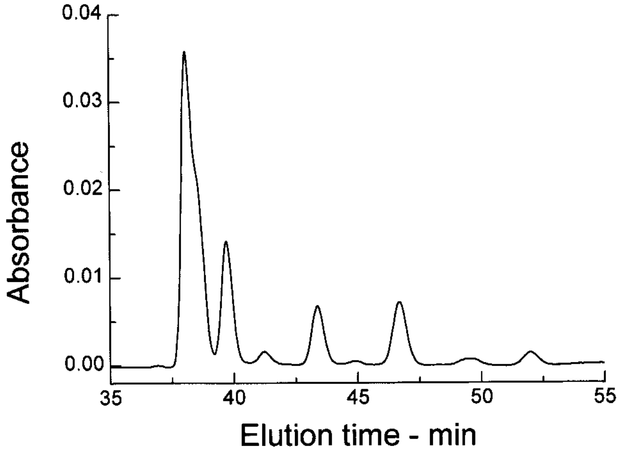

Figure 5. Chromatogram extracted from the data of Figure 1 at 260 nm. Assignment of the major peaks is as in Figure 4.

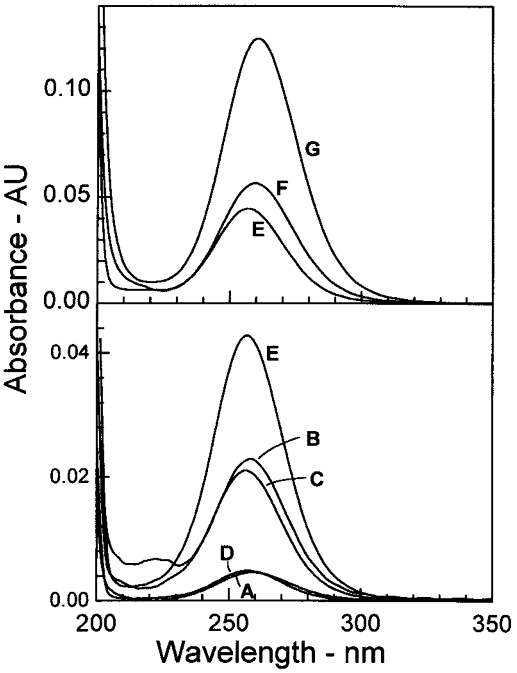

Figure 6. Spectra extracted from Figure 1 at the chromatographic maxima of (A) methyl iodide, (B) ethyl iodide, (C) 1-iodopropane, (D) 1-iodobutane, (E) 1-iodopentane, (F) 3-iodopentane, and (G) 2-iodopentane. In the region of 260 nm these spectra are identical to reference spectra. The spectrum recorded at the ethyl iodide maximum manifests a contribution at 220 nm that is ascribed to vinyl iodide (see Figure 8).

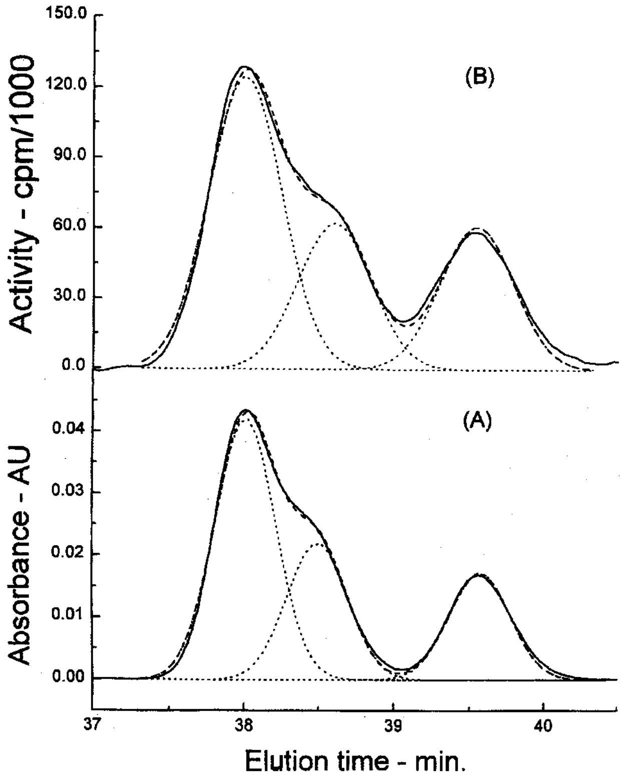

Figure 7. Resolution of the secondary iodopentane peak into its 2- and 3-iodopentane components by Gaussian analysis; (A) spectrophotometric chromatogram and (B) radiochromatogram.

higher sensitivity of the secondary iodides). Since pentane has twice as many H-atoms at the 2-position than at the 3-position, the observed ratio of the yields of the secondary iodides (~2:1) is similar to the relative number of H-atoms at the two secondary positions. This result shows that H-atoms are lost essentially statistically from the different secondary positions of pentane. Pentane has the same number of secondary and primary H-atoms so that the observed ratio of 3.3 for production of secondary and primary iodides provides a measure of the ratio for loss of these two types of H-atoms.

Radiochemical Studies. A radiochromatogram of a pentane sample containing ~1 mM iodine-125, irradiated to a dose of 200 krads, is given in Figure 1S. It is seen in this figure that the distribution of alkyl iodides is similar to that observed spectrophotometrically. The radiochemical results are particularly important in demonstrating that there are no appreciable amounts of iodine-containing products other than those expected from simple bond rupture.

Gaussian analysis of the radiochromatograms of the iodopentanes (Figure 7B) gives their relative yields as 1:2.2:1.1. Since the radiochemical sensitivities of these three components are identical, these measurements provide a direct measure of the relative loss of hydrogen from the 1-, 2-, and 3- positions. These relative yields are essentially identical to those obtained from the spectrophotometric studies.

Vinyl Iodide. While the absorption spectrum of ethyl iodide has a minimum in the 220 nm region similar to that of the spectrum of propyl iodide, the spectrum recorded at the ethyl iodide chromatographic peak in Figure 6A exhibits a weak but significant additional contribution in the 210−225 nm region. In Figure 1 this contribution appears in the saddle of the ethyl iodide profile. A contour plot for the region of the ethyl iodide maximum is given on an expanded scale in Figure 2S. It is apparent in this figure that there is a product that elutes ~10 s after ethyl iodide. In Figure 8A the spectrum recorded at the chromatographic peak of this product is compared with that recorded 10 s before the ethyl iodide peak. In Figure 8B it is seen that the difference between these spectra, though very weak, has a maximum at 221 nm and other features that are similar to those found for an authentic sample of vinyl iodide. The difference in elution time of this peak from that of ethyl iodide is also similar to that observed for a reference sample containing both iodides. There is, therefore, reasonable assurance that the product that elutes at 48.76 min in Figure 2S is vinyl iodide.

Vinyl iodide has a relatively high extinction coefficient of ~3500 M^{-1} cm^{-1} at 221 nm where that of ethyl iodide is at a minimum so it is observable even though it is produced only in low yield. From the net contribution of 0.0035 AU to the absorbance at 221 nm we estimate that vinyl iodide is present at a concentration of only ~1 micromolar. Taking into account

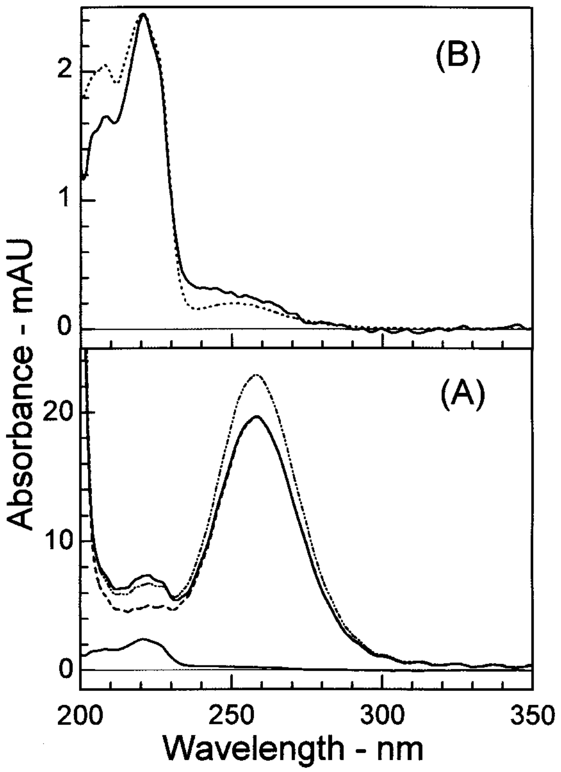

Figure 8. (A) The most intense spectrum is that observed at the ethyl iodide chromatographic maximum (at 48.59 min in Figure 2S). The upper solid and dashed spectra are those observed at 48.76 and 48.42 min. The difference between these is given by the lower solid spectrum. (B) The difference spectrum in (A) is given on an expanded scale as the solid spectum. The spectrum observed for a 500 μM sample of vinyl iodide, reduced by a factor of 740, is given by the dotted spectrum.

the relatively lower extinction coefficient of ethyl iodide, comparison of the spectra in Figure 8A indicates that vinyl iodide is produced in a yield ~2% that of ethyl iodide, i.e., that its radiation chemical yield is ~0.01. Because it absorbs weakly at 260 nm and is produced only in low yield it does not interfere significantly with the determination of the yield of ethyl iodide in the spectrophotometric experiments. In the radiochemical experiments, because it is not resolved from ethyl iodide, it is presumed to contribute ~2% to the activity in the ethyl iodide fraction.

Other Products. In a number of chromatograms a very minor component was found to elute immediately in front of the secondary iodides. It has a maximum at 267 nm that is typical of tertiary iodides. From its absorption spectrum and elution time this component is identified as 2-iodo-2-methylbutane, which is the major iodide produced in the radiolysis of isopentane. Its importance varies from sample to sample so we presume that it results from a trace of isopentane (<1%) in the pentane. Corresponding peaks observed in the radiochemical experiments indicate that this component amounts to ~0.2% of the alkyl iodides. This result shows that it is important that the alkanes being studied be free of branched hydrocarbons.

In Figures 1 and 4, two additional products with elution times similar to those of 1-iodopropene and allyl iodide are manifest at 44.8 and 49.3 min. Their spectra, however, differ from those of authentic samples. In neither case is any significant activity observed in the radiochemical experiments (see Figure 1S). From the radiochromatogram we estimate that these unsaturated iodides cannot account for more than one percent of the iodides produced.

TABLE 1: Radiolytic Yields of Alkyl Iodides from Pentane[a]

	spectrophotometric[b]	radiochemical[c]
2-iodopentane	1.99 ± 0.14[d]	2.07 ± 0.03
3-iodopentane	1.00 ± 0.06[d]	0.89 ± 0.01
2-iodo- + 3-iodopentane	2.99 ± 0.09	2.96 ± 0.04
1-iodopentane	0.89 ± 0.02	0.92 ± 0.01
1-iodobutane	0.11 ± 0.02	0.11 ± 0.02
1-iodopropane	0.51 ± 0.02	0.49 ± 0.02
ethyl iodide	0.58 ± 0.06	0.55 ± 0.03
methyl iodide	0.17 ± 0.03	0.22 ± 0.02
vinyl iodide	(0.01)[e]	
other minor products	(0.01)[e]	(0.01)[e]
total parent	3.88	3.88
2-iodo-/3-iodo	1.99	2.31
secondary/primary	3.36	3.21
fragment fraction	0.265	0.268

[a] Initial yields in units of molecules per 100 ev of absorbed energy at ~1 mM I_2; yields are normalized to a total of 5.3. [b] Average of eight experiments. [c] Average of three experiments. [d] Three experiments only. [e] Estimated upper limit.

Material Balance and Absolute Yields. Because the sensitivities are known in the spectrophotometric experiments the absolute yields of the major products can be readily established. In a typical experiment at an initial iodine concentration of 1.07 mM the total yield of iodine-containing products represents ~95% of the iodine consumed at 50% conversion. The remaining ~5% is largely attributable to HI that is not observed in the chromatography but is expected to be of this magnitude. Iodide ion could also be produced to the extent of several percent as the result of electron scavenging by iodine or by the product alkyl iodides. The good material balance shows that neither of these processes nor the production of compounds other than the saturated alkyl iodides is of major importance.

In Table 1 we summarize the absolute yields of the alkyl iodides normalized to total yields of 5.3 as indicated by 95% of the initial yield for consumption of equivalents of iodine. The standard deviations given in columns 2 and 3 are small, showing that the various measurements are quite reproducible. Except for methyl iodide, the spectrophotometric and radiochemical results are in good agreement. The yield of methyl iodide determined spectrophotometrically is in reasonable agreement with yield of 0.14 reported earlier by Schuler and Kuntz[26] but considerably lower than that given by Geissler and Willard.[34] All other measurements, including those of Bishop and Firestone[35] and Dewhurst,[36] agree that methyl radicals represent only ~3% of the alkyl radicals produced in the radiolysis of pentane. It should be particularly noted in Table 1 that the iodides resulting from the radicals produced by C−C scission represent ~25% of the total.

Hexane and Heptane. Contour plots of the spectrophotometric data obtained in the radiolysis of hexane are similar to the plot for heptane given in Figure 9. Both hydrocarbons exhibit all of the expected primary iodides. This figure shows that the secondary iodides are well resolved from the primary iodide but are not themselves resolved. Chromatograms for hexane and heptane, extracted at 260 nm, are given in Figure 3S. Chromatograms of reference samples of 2-iodo- and 3-iodohexane show that each elutes ~2 min before 1-iodohexane and that they cannot be expected to be resolved under the chromatographic conditions used. However, because the sensitivities of the secondary iodides are similar it is possible to determine the total yields for their production.

A summary of the initial yields for hexane and heptane is given in Table 2 based on a total yield for the iodides of 5.3. Except for the somewhat higher yields of methyl iodide noted

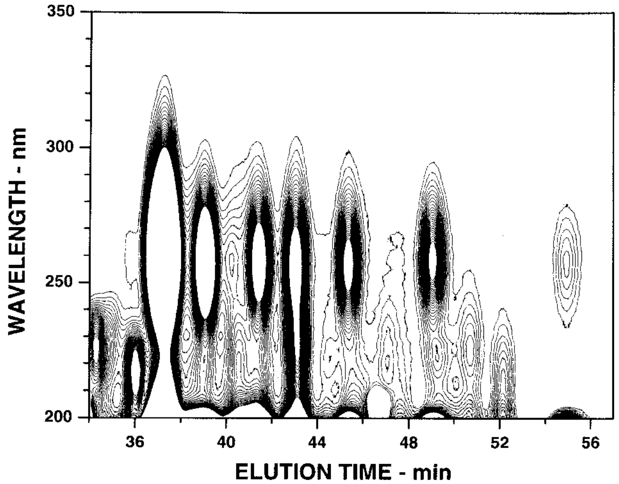

Figure 9. Contour plot for heptane, 1 mM in I_2, irradiated to a dose of 200 krads. Contours are plotted from 0 to 0.01 at an interval of 0.0004.

TABLE 2: Radiolytic Yields of Alkyl Iodides from Hexane and Heptane[a]

	hexane		heptane	
	spectro-chemical	photo-metric	spectro-chemical	radio-photometric
sec-iodoheptanes			3.26	3.19
1-iodoheptane			0.64	0.63
sec-iodohexanes	3.18	3.14		
1-iodohexane	0.74	0.75	0.07	0.06
1-iodopentane	0.08	0.08	0.33	0.31
1-iodobutane	0.41	0.41	0.33	0.32
1-iodopropane	0.36	0.37	0.29	0.37
ethyl iodide	0.40	0.40	0.29	0.34
methyl iodide	0.13	0.15	0.09	0.08
total parent	3.92	3.87	3.90	3.82
secondary/primary iodides	4.30	4.19	5.09	5.06
fragment fraction	0.26	0.27	0.26	0.28

[a] Initial yields at ~1 mM iodine; normalized to a total of 5.3.

in the radiochromatographic experiments, the results from the two analytical approaches agree very well. These results show that in the case of hexane, H-atoms are eliminated 4.3 times more rapidly from a secondary than from a primary position. This ratio increases to 5.1 in the case of heptane.

In Figure 9 we see a contribution at ~220 nm immediately after ethyl iodide that is similar to that attributed to vinyl iodide in the case of pentane. This contribution was characterized as described above in discussing Figure 3S. It is clear from the maximum of 0.0016 AU in the difference spectrum at 221 nm that vinyl iodide is produced in the radiolysis of heptane but only in low yield ($G \sim 0.005$). A similar contribution is observed in the contour plot in the case of hexane (and octane) so that, in general, vinyl iodide seems to be produced in the radiolysis of most alkanes, but only in very low yields.

Figure 9 also shows a number of other minor contributions of low intensity that are more or less typical of most of the spectrophotometric recordings. Except for possible interference with the butyl iodide peak at 44.6 min none of these appears to complicate measurements of the iodides produced from heptane. The chromatogram in Figure 35 does not exhibit any unexpected intensity for the butyl iodide peak so that the contribution that interferes at short wavelength does not appear to contribute significantly at 260 nm. For both hexane and heptane complementary radiochromatograms give alkyl iodide yields similar to those determined spectrophotometrically (see Table 2), indicating that the additional contributions manifest in the contour plots do not represent any significant presence of iodides but rather must be assigned to other radiolytic products, very likely unsaturates.

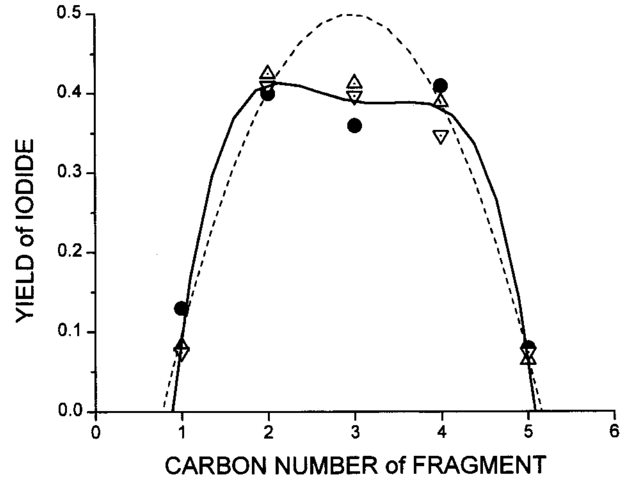

Figure 10. Yields of fragments produced from hexane as measured by TI scavenging (△, ref 14), by I_2 scavenging (●, present study), and by sampling with ^{14}C ethyl radicals (∇, ref 21b). The solid curve is a quartic fit to the observed yields and the dashed curve a parabola through the outermost four points. This comparison indicates that the relative yields for rupture of C_2-C_3 and C_3-C_4 bonds differ by ~25% from the patterns noted below for the higher hydrocarbons.

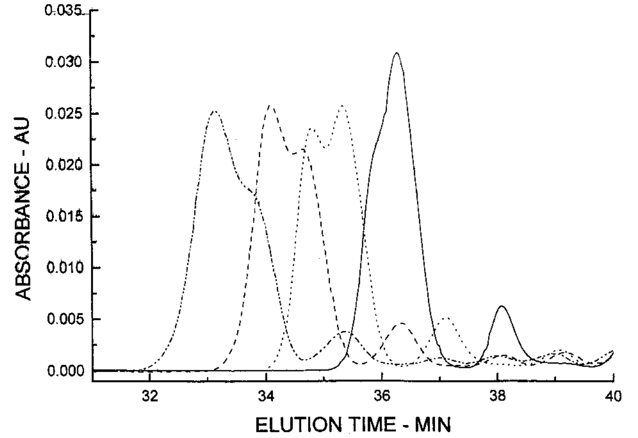

Figure 11. Chromatograms recorded spectrophotometrically in the region of the parent iodides for undecane, decane, nonane, and octane containing 1 mM I_2 irradiated to doses of 200 krads. The major peaks, assignable to the secondary iodides, are eluted with increasing times as the molecular weight of the iodide decreases.

Hexane has been the subject of a number of other scavenging studies.[21b,36−43] Of the various determinations in the literature, Dewhurst,[36] Widmer and Gaumann,[40] and Zaitsev et al.[38] have reported yields 20−30% lower than the values given in Table 2. Their measurements were, however, at iodine concentrations of 10−30 mM and do not represent initial yields.

The yields of methyl iodide reported here for hexane and heptane are ~ 40% higher than those reported by Schuler and Kuntz.[26] This difference is larger than can be explained by the dependence of the yields on dose and needs to be investigated further.

The fragmentation pattern for hexane given by the present experiments is compared in Figure 10 with that reported for hexane by Isildar and Schuler where TI was used as the scavenger[43] (see below) and from the sampling experiments of Holroyd and Klein.[21] The yield of propyl radicals relative to the yields of ethyl and butyl radicals is ~25% lower than

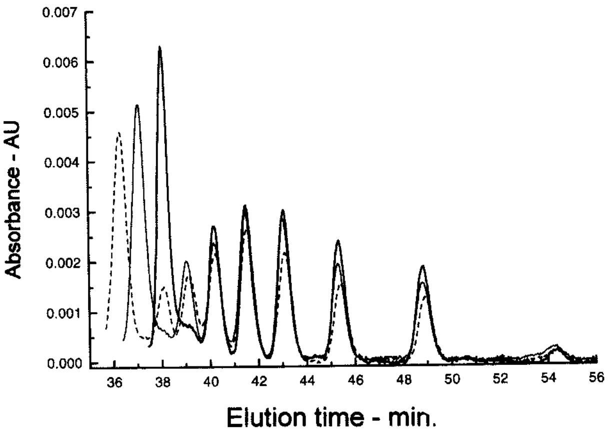

Figure 12. Chromatograms, on an expanded scale, representing the iodides produced from the fragment radicals. The most intense peaks on the left represent 1-iodododecane, 1-iodononane, and 1-iodooctane, as illustrated in Figure 11. The up arrows are at the elution times of the iodides produced by the loss of a methyl group.

TABLE 3: Yields of the Iodides Produced from the Parent Radicals[a]

	octane	nonane	decane	undecane	dodecane
secondary radicals					
spectrophotometric	3.46	3.55	3.53	3.64	3.66
radiochemical	3.48	3.44	3.56	3.69	3.69
primary radicals					
spectrophotometric	0.521	0.454	0.416	0.364	0.338
radiochemical	0.537	0.473	0.426	0.360	0.332
total parent radicals					
spectrophotometric	3.98	4.00	3.95	4.00	3.99
radiochemical	4.02	3.91	3.99	4.05	4.02

[a] Initial yields at ~1 mM I_2.

expected from the parabolic dependencies noted for the higher hydrocarbons (see below). This difference is commented on in the Discussion section.

The Higher Alkanes. The contour plot for nonane in Figure 4S is typical of those observed for the higher normal alkanes. This plot shows that the secondary nonyl iodides are well resolved from the primary iodide. A partial resolution of the secondary iodides is evident. All of the normal iodides from C_2 to C_7 are readily seen in this contour plot. Because methyl iodide and 1-iodooctane are produced only in low yield their signals are extremely weak, with that of the latter buried in the valley between 1-iodononane and 1-iodoheptane. There also is a contribution that appears just after the hexyl iodide peak that absorbs in the 235 nm region but does not appear to interfere with the determination of hexyl iodide at 260 nm. In this figure there are no other obvious contributions that might interfere with the measurements at 260 nm.

The radiochromatogram given for nonane in Figure 5S is very similar to one recorded spectrophotometrically. While there are traces of activity at the positions where the contour plot indicates contributions in the 220 nm region, the radiochromatography shows that these contributions cannot account for more than 0.2% of the total activity, i.e., $G < 0.01$.

Iodides from the Parent Radicals. Chromatograms obtained in the region of the parent iodides produced from octane, nonane, decane, and undecane are illustrated in Figure 11. In these cases the primary and secondary iodides are sufficiently resolved that their individual yields can be determined. These yields are summarized in Table 3. As expected the intensities of the peaks ascribable to the 1-iodoalkanes decrease as the hydrocarbon chain length increases so that the accuracy with which measurements on their yields can be made decreases correspondingly. Similar resolution of the parent iodides was observed in the radiochemical experiments. Because we do not have references for these secondary iodides the radiochemical results are particularly important in determining the yields of the iodides resulting from loss of secondary H-atoms. It is seen in Table 3 that the total yield of parent radicals is similar to that produced from the smaller hydrocarbons.

TABLE 4: Ratios of Yields of Secondary and Primary Iodide Yields[a]

	determined spectrophotometrically	determined radiochemically	per H-atom[b]
pentane	3.36	3.21	3.36/3.21
hexane	4.30	4.19	3.23/3.14
heptane	5.09	5.06	3.05/3.04
octane	6.64	6.48	3.32/3.24
nonane	7.82	7.27	3.35/3.12
decane	8.48	8.36	3.18/3.13
undecane	10.00	10.25	3.33/3.42
dodecane	10.83	11.11	3.25/3.33
spectrophotometric average			3.26 ± 0.11
radiochemical average			3.21 ± 0.12

[a] Of iodides produced by loss of H-atoms from the hydrocarbon. [b] Spectrophotometric/radiochemical.

For these hydrocarbons the secondary iodides are partially resolved into several components, resulting in an increase in the overall width as expected from the increased number of possible products. Interestingly the secondary iodide that is last to elute is separated from the primary iodide by ~1.5 min and decreases in intensity as the length of the hydrocarbon increases. One observes a trend in the overall shape of the secondary iodide peaks that includes a component at increasingly shorter relative elution times. Unfortunately, we have not been able to resolve the observed profiles into components with areas that bear a rational relation to the number of hydrogen atoms at the various positions.

The relative yields of the secondary and primary iodides produced by loss of H-atoms are summarized in Table 4. It is seen that the radiochemical and spectrophotometric results agree extremely well if we assume that the sensitivity ratio at 260 nm is, as noted above for the smaller iodides, 1.12. The ratios divided by the number of H-atoms in the hydrocarbon, given in the last column, show negligible dependence on the length of the hydrocarbon.

Iodides from the Fragment Radicals. Chromatograms recorded in the region of the iodides produced from the fragment radicals from octane, nonane, and decane are given on an expanded scale in Figure 12. This figure demonstrates very nicely the tendency of C−C rupture to occur near the center of the hydrocarbon chain. It is clear in this figure that methyl radical and its complement are produced only in low yield. In the case of octane a contribution of 1-iodoheptane is manifest just after the peak of 1-iodooctane and is sufficiently intense that a yield can be reasonably estimated using the Gaussian fitting routine. In the case of nonane a small contribution from 1-iodooctane is also manifest even though it is not apparent in the contour plot. For nonane and the higher hydrocarbons one can only estimate upper limits to the yields of the iodides which complement methyl iodide. It is clear that these yields are very small. The chromatograms recorded for these systems in the radiochemical experiments are, as in the case of nonane, very similar to those obtained spectrophotometrically and do not indicate any significant contributions from iodides other than

TABLE 5: Yields of the Iodides Produced from the Fragment Radicals[a]

	octane	nonane	decane	undecane	dodecane
C_1	0.073	0.044	0.053	0.041	0.048
C_2	0.189	0.165	0.133	0.103	0.092
C_3	0.254	0.186	0.148	0.123	0.128
C_4	0.265	0.256	0.204	0.173	0.154
C_5	0.252	0.262	0.240	0.195	0.180
C_6	0.208	0.205	0.205	0.191	0.168
C_7	0.060	0.179	0.163	0.160	0.166
C_8		(0.040)[b]	0.139	0.135	0.134
C_9			(0.046)[b]	0.113	0.101
C_{10}				(0.043)[b]	0.076)[b]
C_{11}					(0.050)[b]
Total fragment	1.30	1.34	1.33	1.28	1.30

[a] Initial yields at ~1 mM I_2; weighted average of spectrophotometric and radiochemical results. [b] Signals not resolved; rough estimate included to account for total products but not in determining the parabola of Figure 14.

those expected. The yields of the iodides produced from the fragment radicals are summarized in Table 5.

Discussion

This study shows very directly that the only radicals produced in significant yield are those expected from simple bond rupture. The overall mechanism is complicated and involves excited states and ions in a variety of primary processes. Ultimately radicals are produced by loss of H from the hydrocarbon and by C−C bond rupture. As pointed out in the Introduction, radicals react with iodine at diffusion-controlled rates[24,44,45] so that at millimolar iodine concentrations scavenging occurs on the 100 ns time scale. Processes involving ions or excited states will have been completed at much shorter times. In the absence of scavenger the steady-state radical concentrations at the dose rates used here are below 10^{-7} M so that second-order reactions between homogeneously distributed radicals occur only at millisecond times and will be unimportant when scavenger is present. Reactions between radicals within spurs, where their concentration is relatively higher, occur on the nanosecond time scale so that interference with spur processes requires much higher scavenger concentrations.[44] As a result these scavenging studies focus on the radicals that diffuse out of the radiation track and undergo homogeneous reactions in the bulk hydrocarbon. The trends for the dependence on chain length appear to be rather straightforward. The present results provide quantitative details on these trends.

Radicals Produced by Loss of H. Parent radicals can be produced directly by C−H scission of excited radicals or ionic precursors

$$RH^* \rightarrow R\bullet + H\bullet \qquad (7)$$

and indirectly by abstraction of H in secondary radical processes.

$$RH + H\bullet \rightarrow R\bullet + H_2 \qquad (4)$$

In the absence of scavenger radical transfer reactions of the type

$$R'H + R\bullet \rightarrow R'\bullet + RH \qquad (8)$$

can be of importance.[7,46,47] Because the rate constants for most radical transfer reactions are relatively low, Reaction 8 is not expected to be important when iodine is present. The relative yields of iodides should, therefore, represent the distributions of fragment radicals produced in the radiolysis. Other processes that produce parent radicals without the intervention of H-atoms, such as,

$$RH^* + RH \rightarrow 2R\cdot + H_2 \qquad (9)$$

must also be included in any overall mechanism.

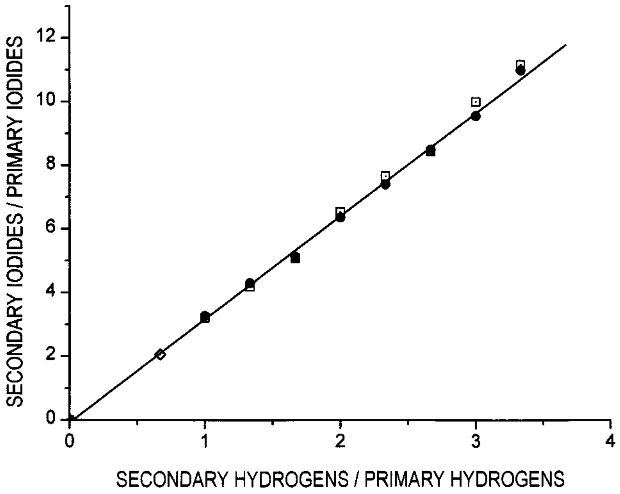

Figure 13. Dependence of the relative yields of secondary and primary radicals on the ratio of secondary and primary H-atoms: (●) spectrophotometric results and (□) radiochemical results. The slope of the linear dependence is 3.24. The ratio previously reported for liquid butane (ref 19) is given by the open diamond.

Reaction 4 is a radical transfer reaction so it does not directly affect the total yield for iodine consumption but is of considerable importance because its rate is estimated to be greater than 10^7 M^{-1} s^{-1}.[53,54] Hydrogen abstraction will occur on the 10 ns time scale and will effectively compete with scavenging at iodine concentrations below millimolar. As indicated by the observed material balance, the total yield of organic iodides accounts for most of the iodine consumed so that almost all of the H-atoms must be converted to alkyl radicals. As a result the total yield of parent radicals can be up to twice those produced directly in the radiolysis. Consideration of the fate of the H-atoms is of considerable importance because the ratios of the yields of the secondary and primary iodides measured in these scavenging studies represent the weighted average of the contributions from Reactions 4, 7, and 9. The data given in the tables show that, in general, parent radicals are produced in a total yield of ~3.98 and represent ~75% of the bond scission.

Relative Yields of Primary and Secondary Radicals. The most striking result of these scavenging studies is the relatively low yields of primary radicals as compared to those of secondary radicals (cf. Table 3). In Figure 13 we display the ratios of the yields of secondary and primary parent radicals as a function of the ratio of the numbers of secondary and primary H-atoms in the hydrocarbon. The dependence is linear with a slope of 3.23 ± 0.15. The value of this ratio for butane, measured much earlier by McCauley and Schuler,[19] also falls on this linear dependence. The fact that H-atoms are lost 3.2 times more rapidly from the secondary positions is also indicated in column 4 of Table 4.

Assuming that this ratio is general and that the total yield of primary and secondary radicals is 3.98, the yield of radicals produced by loss of a terminal H-atom will be given by

$$G(\text{primary parent radical}) = 3.98/(1+1.08\,(N-2)) \qquad (10)$$

where N is the number of carbon atoms in the alkane. This relation predicts that the yield of primary parent radicals will drop from 0.94 for pentane to 0.31 for dodecane. The standard deviation of the differences between the measured and predicted yields for the eight alkanes from C_5 to C_{12} is 0.02. In a study of the radiolysis of hexadecane, Falconer and Salovey[55] have reported a yield of primary hexadecyl radicals of 0.2, in reasonable agreement with the yield of 0.25 predicted by eq 10. It is clear that for long-chain hydrocarbons elimination of a terminal H will be relatively unimportant.

One, of course, expects that H-atoms will preferentially abstract H from the lower-energy secondary positions.[56] However, the observed preferential production of secondary radicals cannot be explained solely by Reaction 4 because this reaction accounts for less than 50% of the parent radicals. It seems likely that the preference for elimination of H from the secondary positions in the initial processes is similar to that resulting from the H-atom abstraction reactions. However, further studies are required to determine the relative importance of the different reactions responsible for the formation of the parent radicals.

The linearity of the plot in Figure 13 and the corresponding constancy of the ratio of secondary and primary radical yields relative to the corresponding number of H-atoms in the hydrocarbon (column 4 in Table 4) indicate that loss occurs approximately equally from all secondary positions. As discussed earlier, the results on pentane show directly that loss of H from its 2- and 3- positions occurs statistically. We conclude that there is little selectivity in the loss of H from the different secondary positions, i.e., that loss of secondary H-atoms will be essentially statistical. This conclusion, and the fact that elimination of terminal H-atoms is infrequent, is particularly important to discussions of the radiolytic cross-linking of polymers such as polyethylene.

Radicals Produced by C−C Rupture. First we note that secondary reactions appear to be unimportant when scavenger is present, indicating that the radicals produced by C−C scission result entirely from primary processes. As a result the distribution pattern observed should be insensitive to the concentration of scavenger or other experimental parameters.

The yields of fragment radicals, summarized in Table 5, show that C−C scission preferentially occurs near the center of the hydrocarbon chain. This preference is illustrated quite well for the higher alkanes by the chromatograms in Figure 12 but breaks down somewhat for the smaller alkanes. Figure 10 shows that the relative yield of propyl radicals from hexane is ~0.1 less than expected from the parabolic dependence applicable to the higher hydrocarbons (see below). Fragmentation of neutral excited molecules also should result in equal yields of complementary radicals i.e., C−C scission should be symmetrical. In the case of pentane the yield of methyl radical is considerably greater than that of butyl radical. These exceptions show that for the smaller hydrocarbons decomposition is somewhat more complicated than simple C−C cleavage. Ionic reactions, such as have been observed in mass spectrometers, have been suggested to contribute to radical formation.[57−59] Mass spectrometric studies show that the charge remains with the larger fragment on dissociation of cations so that some of the larger fragments may be lost before neutralization. However, as is indicated by the chromatograms in Figure 12, distribution of radicals produced by C−C bond scission of the longer alkanes is rather symmetrical. Since ionic fragmentation is generally endothermic, it usually occurs from vibrationally excited ions.[60] With increasing carbon number the endothermicity increases so that with increasing chain length ionic decomposition is expected to decrease in importance.

The data of Table 5 provide the basis for a general description of C−C scission in the radiolysis of the normal alkanes. In Figure 14 it is seen that the yields of fragments exhibit a parabolic dependence on their position in the hydrocarbon chain expressed as F_c, the fraction of the length of the chain ($F_c = N_c/N$ where N_c and N are the number of carbon atoms in the radical and in the alkane). The ordinate in this figure has been normalized by a factor $(N - 1)$ to take into account the increased number of fragments as the length of the alkane increases. It is seen that the data for the C_8 to C_{12} alkanes can be fitted by a quadratic having a dependence of the form

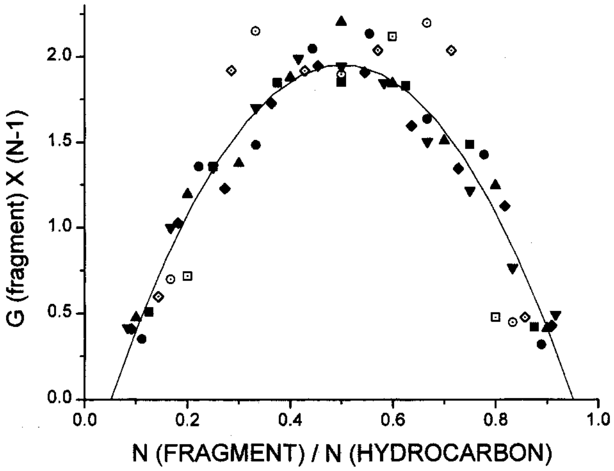

Figure 14. Normalized plot of fragment yields for (□) pentane, (○) hexane, (◇) heptane, (■)-octane, (●)-nonane, (▲)-decane, (◆)-undecane, and (▼)-dodecane. The abscissa, F_c, is the ratio of the number of carbon atoms in the fragment (N_c) to the number in the hydrocarbon (N). The ordinate is the product of $(N - 1)$ and the fragment yield. The parabolic dependence corresponds to eq 11, with $A = -0.44$, $B = 9.67$, and $C = 9.73$, is given by the solid curve.

$$(N - 1)G(\mathrm{R}\bullet) = A + BF_c - CF_c^2 \tag{11}$$

where the empirical parameters A, B, and C have the values −0.44, 9.67, and 9.73. This parabola centers at $F_c = {}^1/_2 B/C = 0.497 \simeq 0.5$, demonstrating the symmetry in the fragmentation.

Because C ~ B the yields of fragment radicals can be approximated by eq 12:

$$G(\mathrm{R}\bullet) = (A + BF_c(1 - F_c))/(N - 1) \tag{12}$$

The standard deviation of the differences of the 40 yields measured for the C_8 to C_{12} alkanes from those predicted by eq 12 is 0.01. Thus eq 12 serves as a general expression that describes the yields quite well up to dodecane. Because eq 12 gives negative value for $F_c < 0.05$ and > 0.95 it must break down for the small and large fragments produced from alkanes much larger than dodecane.

For rupture of the central bond of the even-numbered hydrocarbons, the factor $F_c\ (1 - F_c)$ is ~0.25. From the coefficients given above, eq 12 predicts that the yields of the fragment resulting from rupture of a central bond should be given by $1.98/(N - 1)$. For octane, decane, and dodecane the yields predicted by this relation, 0.282, 0.220, and 0.180, agree with the respective averages of 0.265, 0.240, and 0.168 reported in Tables 2 and 5 to better than 7%. For the odd-numbered hydrocarbons the factor is only slightly less for the fragments produced by rupture of the bond adjacent to the central atom. Their yields should be equal and given approximately by $1.94/(N - 1)$. The predicted yields of 0.323, 0.243, and 0.194 for the complementary fragments produced from heptane, nonane, and undecane agree extremely well with corresponding averages of 0.328, 0.259, and 0.193 reported in the tables. Thus, eq 11 and the relations derived from it describe the yields for rupture of most central bonds quite well. However, in the case of pentane and hexane there are discrepancies from the predictions of eq 11 that, as noted above, point to the importance of processes other than simple bond cleavage.

As one approaches the end of the hydrocarbon chain, A becomes more important and the factor F_c $(1 - F_c)$ decreases. As a result, the dependence of the yields for rupture of bonds near the chain ends is more strongly dependent on the alkane length than in the middle. While eqs 11 and 12 are empirical, they go a long way toward explaining the fact that, as indicated by the work of Schuler and Kuntz,[26] the methyl radical yield depends strongly on the number of carbon atoms in the alkane. One, of course, expects an increase in the number of C−C bonds to result in a corresponding decrease in the fraction of chain rupture that results in methyl radical production. However, this decrease is exaggerated by the steepness of the parabola in the region where $F_c < 0.2$. According to eq 12 the yield for rupture of a terminal C−C bond should be $A/(N - 1) + B/N^2$. However, this relation gives methyl radical yields larger than observed here and about twice those reported by Schuler and Kuntz, who suggested an inverse dependence on $(N - 1)^2$. Because eq 11 clearly breaks down for fragments having values of $F_c < 0.05$ the dependence of the yields of methyl radical and its compliment on chain length is better described by a relation having a form similar to that suggested by the earlier study.

Comparison with Scavenging by HI. Isildar[13,14,43] used tritium-labeled HI as the radical scavenger to study the fragments produced from the alkanes up to hexadecane. His studies provide information on the distributions of the fragment radicals but not on those produced by loss of H from the primary and secondary positions. In the case of hexane these studies showed that as the HI concentration increased from 0.5 to 7.5 mM there was a large increase in the activity in the hydrogen fraction and a somewhat smaller decrease in the activity in hexane.[43] The relative yields of fragment radicals were, however, not observably dependent on the HI concentration and, as shown in Figure 10, are comparable to those determined in the sampling studies of Holroyd and Klein and in the present study. The independence of yield on HI concentration was taken as an indication that ionic processes are not appreciably involved in the formation of the fragments.[43] However, Figure 10 shows that the yield of propyl radical from hexane is less than expected from the distributions observed from the higher alkanes. As we have already commented, it now appears that the occurrence of bond rupture before neutralization may play some role in determining the relative yields of the fragment radicals, particularly in the case of the lower-molecular-weight hydrocarbons. The similarity of the fragment distributions determined by the three different approaches and the observed lack of dependence on HI concentration makes it clear that up to concentrations of 10 mM HI does not interfere significantly with dissociation of the initial ions.

In Isildar's studies, because only relative yields were available, the total yield of tritiated products (including hydrogen) was normalized to a yield calculated from a model that takes into account ion scavenging by HI. Because of this normalization there appeared to be a decrease in the relative importance of fragmentation as the hydrocarbon chain length increases. However, the present results show that at least up to dodecane the total yield of fragments is essentially constant at 1.3. In Figure 15 the yields determined in the TI scavenging studies are plotted on the scale used in Figure 14 after renormalization to a total of 1.3. The solid parabola in Figure 15 represents the best fit of eq 11 to the data as measured by scavenging with TI and the dotted parabola to the fit given in Figure 14. The two approaches give essentially identical pictures for the distributions of the fragments. As a result there is reasonable assurance that these distributions represent the radicals present after the primary processes are completed.

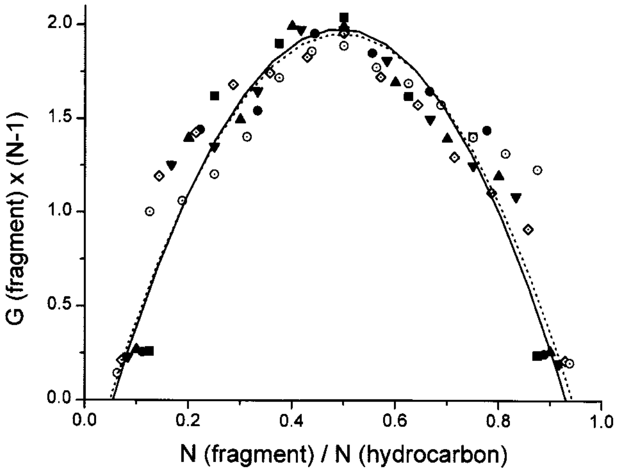

Figure 15. Fragment distributions as determined by scavenging with TI (from ref 43): (■)-octane, (●)-nonane, (▲)-decane, (▼)-dodecane, (◇)-tetradecane, and (○)-hexadecane. Data are renormalized as described in the text. Coordinates are as in Figure 14. Solid parabola is fitted to the closed symbols. The dotted parabola is the fit to the present data given in Figure 14.

General Conclusions

In the radiolysis of liquid normal alkanes, scavengeable alkyl radicals are produced in a total yield ~5.3 of which ~25% represent primary radicals produced by rupture of the hydrocarbon backbone and most of the remainder by loss of H from the primary and secondary positions. Other radicals are produced only in very low yield, i.e., $G < 0.01$. At millimolar iodine concentrations there is no evidence for skeleton rearrangement or other secondary reactions of the alkyl radicals occurring within the time scale of scavenging, i.e., 100 ns. However, at millimolar iodine concentrations H abstraction reactions contribute significantly to the production of parent radicals. For normal alkanes loss of H from a secondary position is favored by a factor of ~3.2 over loss from a primary position with this ratio being essentially independent of chain length up to at least dodecane. This ratio represents the weighted average of radicals produced initially and as the result of H abstraction. The relative frequency for loss of H-atoms from different secondary positions appears to be statistical.

It is found that fragmentation of the hydrocarbon skeleton occurs preferentially in its central region. Elimination of a terminal methyl group occurs relatively infrequently. For the alkanes having 8 or more carbon atoms C−C rupture is essentially symmetrical and is describable by a general expression having the form of a parabola (eq 11). Some asymmetry is observed in the case of pentane. While the pattern observed in the case of hexane is essentially symmetrical the yield of propyl radical is somewhat lower than expected from the generalizations derived from the patterns observed for the higher alkanes. These latter observations are interpreted as indicating that ionic processes that occur before neutralization are of some importance in the radiolysis of the lower-molecular-weight alkanes.

The present results demonstrate that primary radicals represent from 25 to 50% of the total radicals produced. It is important to stress this point because ESR data obtained on solids at low temperatures have been interpreted as indicating that the principal intermediates in the radiolysis of normal alkanes are the penultimate radicals, i.e., those produced by loss of a H from the position adjacent to the terminal methyl group, and that primary radicals are produced only in low yield.[61,62] In the ESR studies the spectra of the primary and other secondary radicals will, of course, be masked by those of the penultimate radicals that exhibit coupling by 6 protons and have a considerably greater overall width. ESR spectra obtained during the irradiation of liquid hydrocarbons, where spectra of the secondary and primary radicals are resolved, exhibit the production of both types.[2]

The present study provides considerable insight into details of the processes involved in the radiolysis of the normal alkanes. Extrapolation of the generalizations indicated by eqs 10 and 11 allows reasonable estimates to be made of the yields of specific radicals for alkanes of modest length. This study also demonstrates the considerable potential for other studies using gel permeation chromatography to examine the products resulting from the scavenging of radicals by iodine. We are currently extending these studies to branched and cyclic hydrocarbons. It is also clear that GPC approaches also can be extended to many other aspects of analysis of hydrocarbons that involve measurements on components that absorb above 200 nm.

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Supporting Information Available: Table 1S reports the extinction coefficients and sensitivities of the alkyl iodides. Figures 1S and 5S are radiochromatograms for pentane and nonane containing 1 mM iodine irradiated to 250 krads. Figure 2S is a contour plot of Figure 4 in the region of ethyl iodide on an expanded scale that illustrates the vinyl iodide contribution. Figure 3S gives chromatograms for hexane and heptane extracted from the 3-D data at 260 nm. Figure 4S is a contour plot for nonane 1 mM in I_2 irradiated to a dose of 200 krads. This material is available free of charge via the Internet at http://pubs.acs.org.

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