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# Radical Yields in the Radiolysis of Branched Hydrocarbons: Tertiary C−H Bond Rupture in 2,3-Dimethylbutane, 2,4-Dimethylpentane, and 3-Ethylpentane

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Gel permeation chromatography has been applied to iodine scavenging studies of the distribution of radicals produced in the radiolysis of symmetrically branched hydrocarbons 2,3-dimethylbutane, 2,4-dimethylpentane, and 3-ethylpentane. The principal iodides observed are those expected as a result of simple bond rupture. In the case of 2,3-dimethylbutane all five expected iodides are readily resolvable and it is shown that the loss of H from a tertiary position is favored over loss from a primary position by a factor of ∼10. A similar ratio is also observed for 2,4-dimethylpentane. The higher ratio of 15 observed for 3-ethylpentane indicates a dependence on the number of tertiary sites on the alkane. The relative yield of ∼3.3 for the loss of secondary and primary H atoms from 2,4-dimethylpentane and 3-ethylpentane is similar to that for normal alkanes, indicating a negligible effect of the adjacent tertiary carbon. In all three cases the rupture of terminal C−C bonds is relatively infrequent with C−C rupture occurring preferentially at the bonds adjacent to the tertiary carbon.

## Introduction

In a previous study of the radical yields in the radiolysis of normal alkanes, it was shown that secondary C−H bonds are ruptured ∼3 times more frequently than primary bonds.[1] To provide for a comprehensive discussion of the radiolysis of branched alkanes, information is also needed on the relative frequency of rupture of tertiary C−H bonds. The radical sampling experiments of Holroyd[2,3] have indicated that in the cases of isopentane, 2,4-dimethylpentane, and 2,2,4-trimethylpentane the loss of H from a tertiary position is, respectively, 8.4, 5.5, and 10.1 times greater than from a primary position.[4] However, the application of radical sampling is complicated in that it requires information on the disproportionation/combination ratio of the reactions between the radicals. Also, one has to carry out such studies under high dose rate conditions to minimize additional complications from radical transfer reactions. Whereas Holroyd's studies show that the loss of tertiary H atoms is of considerable importance in the radiolysis of branched alkanes, quantitative information available from such radical sampling experiments is very limited.

Radical scavenging experiments[5] provide a more direct approach. Of the scavengers that have been used to date, molecular iodine appears to be the simplest. Because alkyl radicals react with iodine at diffusion-controlled rates,[6] scavenging occurs at millimolar iodine concentrations on the microsecond time scale and is more rapid than radical transfer processes. As a result, the radical yields are represented by the yields of the iodides produced. The yields of methyl radicals produced in the radiolysis of a number of branched alkanes have, for example, been determined in radiochromatographic studies using iodine as the scavenger.[7] That study demonstrated that the rupture of a given $CH_3$−C bond is inversely proportional to the square of the number of C−C bonds and is strongly affected by the presence of additional methyl groups on the adjacent carbon atom. Only a few iodine scavenging studies have been devoted to a more general determination of the distribution of radicals produced in the radiolysis of branched alkanes.[8−11] Of these, the gas chromatographic study of Castello, Grandi, and Munari[10] on 2,3-dimethylbutane is the most relevant to the present study. In addition to the expected iodides, they found small yields of iodides other than those that would result from simple bond rupture. However, because of the relatively high temperatures required for the separation of the tertiary iodides and their fragility, gas chromatography is generally unsuitable for the quantitative determination of their yields.

As indicated previously,[1] gel permeation chromatography (GPC) provides a particularly attractive alternative to the approaches used in previous studies because many of the iodides of interest can be separated at room temperature. In the present study, we have used GPC to examine the distribution of iodides produced in the radiolysis of 2,3-dimethylbutane, 2,4-dimethylpentane, and 3-ethylpentane containing millimolar iodine as a radical scavenger. These hydrocarbons have been chosen as examples because the number of radicals expected from simple bond rupture is limited by their symmetry. The approaches used are essentially the same as those used in the previous study on normal alkanes.[1] The application of 3-D spectrophotometric detection provides information that is valuable to the positive identification of the individual iodides. Chromatograms recorded spectrophotometrically or radiochemically provide the quantitative information needed for the determination of the individual radical yields.

Although the present results on 2,3-dimethylbutane differ in detail with those reported by Castello et al.,[10] they demonstrate that, as they concluded, the loss of H occurs preferentially at a tertiary position and that the rupture of the carbon backbone occurs mainly at the central C−C bond. In the present study, these conclusions are further generalized by the results on 2,4-

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dimethylpentane and 3-ethylpentane, for which scavenging data do not currently exist in the literature. The results presented here provide a quantitative basis for future discussions of the radiation chemistry of branched hydrocarbons.

## Experimental Section

The experimental arrangements and spectrophotometric and radiochemical methods used in this study have been described previously in considerable detail.[1]

**Hydrocarbons.** Samples of 2,3-dimethylbutane were obtained from Aldrich, Phillips, and Merck, AG; 2,4-dimethylpentane, from Aldrich and Phillips; and 3-ethylpentane, from TCI and Merck, AG. As received, all exhibited significant absorption below 300 nm, indicating the presence of olefinic impurities. After passing them through columns of silica gel and silver nitrate on alumina, the absorbance at 220 nm was less than 0.1. A chromatographic analysis of the resultant samples did not indicate the presence of any impurities that would interfere with the chromatographic analysis.

**Sample Preparation and Irradiation.** For the spectrophotometric studies, the samples were outgassed using freeze−thaw methods after the addition of ∼1 mM $I_2$. The irradiation cells had a quartz cuvette attached that permitted the iodine concentration to be monitored. Irradiations were at room temperature in a $^{60}$Co irradiator at a dose rate of ∼200 krads/h. Doses were 50 to 300 krads. At these doses, 15 to 50% of the iodine was consumed. In the radiochemical experiments, the dose rate was ∼100 krads/h. Freshly prepared samples containing 1 mM $^{125}I_2$ were purged of oxygen as described previously[1] and analyzed immediately after the irradiations. In the following text, radiation chemical yields are given as values of G in units of molecules per 100 eV of absorbed energy.

**Gel Permeation Chromatography.** In most experiments, two Phenomenex 300 mm × 7.8 mm Phenogel 5$\mu$ 50-Å columns were used in series for the separation of the product iodides. Three columns were used where additional resolution was desired. After irradiation, a 50- or 200-$\mu$L sample was introduced into the eluent stream using a loop injector. At the flow rate used (0.5−0.7 cm$^3$/min), these volumes correspond to injection times of 5 and 20 s. The smaller volume is comparable to the detector volume and was used where maximum resolution was desired. Because the peak widths were inherently at least 30 s, this volume did not broaden the peaks significantly, and the peak profiles were essentially Gaussian in shape. Experiments with an injection volume of 20 $\mu$L did not improve peak shape or resolution.The hydrocarbons used for elution were *n*-hexane containing ∼15% hexane isomers (Fisher), chromatographic-grade isopentane (Aldrich), cyclopentane (Aldrich), or cyclohexane (Fisher). The use of saturated alkanes and cycloalkanes as eluents allowed spectrophotometric recordings down to 200 nm. As shown in the Results and Data Analysis section, the resolution of components that have similar elution times critically depends on the eluting system used. In particular, we find that the addition of isopentane to hexane selectively increases the elution times of the primary iodides. Appropriate mixtures were used to optimize the resolution.

**Spectrophotometric Studies.** Absorption spectra of the column effluent were recorded every second in 3-D format with a Waters 996 diode array detector and Waters Millennium software. These recordings allowed the data to be examined in the form of contour plots that provide considerable insight into the identity of the individual peaks and possible contributions from non-iodine-containing products. Where reference samples were available (methyl-, ethyl, isopropyl, and isobutyl iodides and 3-iodopentane), spectra extracted at the chromatographic peaks and the elution times provided positive identification. A reference sample of 2-iodo-3-methylbutane was prepared by iodine trapping of the radicals produced in the radiolytic reduction of 2-bromo-3-methylbutane. Because tertiary iodides absorb at somewhat longer wavelengths (∼267 nm) than the primary (∼256 nm) and secondary iodides (∼261 nm), spectra extracted from the 3-D data provide identification where reference samples were not available.

Most chromatograms were displayed at 260 nm where all saturated alkyl iodides exhibit significant absorption.[1,12−14] These chromatograms provided quantitative data for the determination of the iodide yields. The areas under the chromatographic peaks were determined with Waters Millennium or Origin 6.1 software as described previously.[1] Where chromatographic peaks were only partially resolved, the various contributions were determined using the Gaussian analysis program in Origin 6.1.

Quantitative analysis of the spectrophotometric recordings requires information on the sensitivities of the various iodides such as that given in Table S1 of ref 1. Most normal iodoalkanes have similar extinction coefficients of ∼470 M$^{-1}$ cm$^{-1}$ at 260 nm. Methyl and ethyl iodide, however, have extinction coefficients of only 341 and 423 M$^{-1}$ cm$^{-1}$, respectively, and sensitivities that are correspondingly lower.[12] The extinction coefficients of the secondary iodides at 260 nm are 500−540 M$^{-1}$ cm$^{-1}$, so their sensitivities are ∼10% higher than those of the primary iodides.[12] Where extinction coefficients were available, the relative yields of the different iodides were determined using their corresponding sensitivities. In the other cases, approximate yields were determined using sensitivities of similar iodoalkanes. In the cases of the tertiary iodides, the sensitivities were assumed to be that of *tert*-butyl iodide, which at 260 nm is comparable to that of isopropyl iodide (i.e., 7% higher than that of the primary iodides). A comparison of the approximate relative yields determined with this approach with the results obtained in radiochemical measurements shows that the yields determined spectrophotometrically are accurate to better than 10%.

**Radiochemical Studies.** Analogous radiochemical studies were carried out with $^{125}I_2$ labeled iodine as the scavenger. The chromatography was essentially the same as in the spectrophotometric studies. The resolution was similar except that the peaks were somewhat broadened by the loop in the radioactivity detector. Activity in the eluting stream was recorded in ASCII format, and areas under the chromatographic peaks were determined by Gaussian analysis. Elution was also followed spectrophotometrically at 265 nm. The determination of the relative yields of the different iodides from their areas in the radiochromatograms is quite straightforward because the radiochemical sensitivities of all monoiodides are identical. The yields of the individual iodides were determined assuming a total yield of 5.6. The Discussion section that follows is based on the yields determined in these radiochemical studies. Normalization of the spectrophotometric signals to those determined radiochemically provides information on the extinction coefficients and corresponding sensitivities of the iodides where samples are not available for direct measurement.

## Results and Data Analysis

Before proceeding with a detailed analysis of the data, it is helpful to consider the relationships between structure and radical yields noted previously. For example, it has been shown that the methyl radical yields from a wide variety of alkanes are low and can be correlated by a relation that takes into

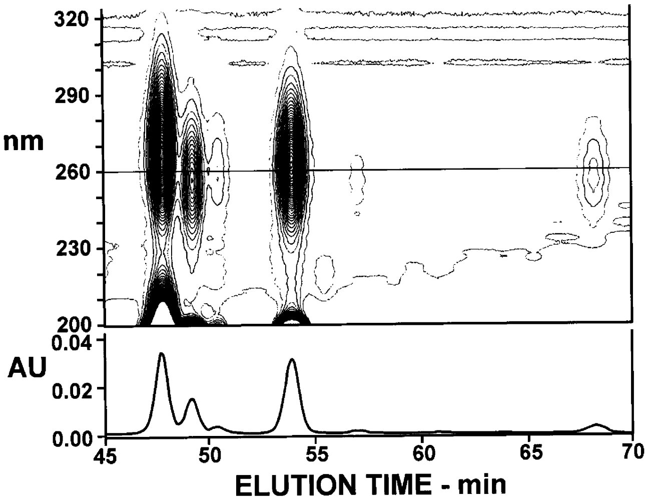

**Figure 1.** Contour plot for 2,3-dimethylbutane containing 1 mM $I_2$ irradiated to a dose of 100 krads. Elution was with hexane containing 25% isopentane. Contours are given in increments of 0.001 AU (absorbance unit). The chromatogram extracted at 260 nm is displayed below the contour plot. In order of elution, the five most intense peaks are identified as 2-iodo-2,3-dimethylbutane, 1-iodo-2,3-dimethylbutane, 1-iodo-3-methylbutane, isopropyl iodide, and methyl iodide from their retention times and spectra (Figure 2).

account the number and type of methyl groups.[7] Using the generalizations given in that study, the predicted methyl radical yield for 2,3-dimethylbutane is 0.45, for 2,4-dimethyl pentane, 0.31, and for 3-ethylpentane, 0.09. These values compare with experimental yields of 0.34 from 2,3-dimethylbutane and 0.28 from 2,4-dimethylpentane.[7] Because the methyl radical yields are low, one expects the yields of the complementary radicals produced by the scission of a terminal $CH_3$−R bond to be correspondingly low.

The study of the distribution of radicals produced in the radiolysis of the normal alkanes[1] has shown that radical production is dominated by the loss of H atoms, with the rupture of a secondary C−H bond being 3.2 times more likely than for a primary C−H bond. That study also showed that the scission of the carbon backbone preferentially occurs near the center of the alkane and is asymmetric, with the yield of the smaller fragment being somewhat greater than that of the larger fragment.

**2,3-Dimethylbutane.** Because 2,3-dimethylbutane contains only two types of C−H bonds, two types of C−C bonds, and no secondary H atoms, this branched alkane represents the simplest of the three examples under consideration. Only five radicals are expected as the result of simple bond rupture: the primary and tertiary radicals produced by C−H scission, the isopropyl radical produced by the rupture of the central C−C bond, and the methyl radical and its complement, the 3-methyl-2-butyl radical, by the rupture of a terminal $CH_3$−C bond. In the contour plot of Figure 1, all five iodides resulting from iodine scavenging of these radicals are well resolved. As is typical of GPC, these iodides elute in order of decreasing molecular weight. The spectra extracted at the chromatographic maxima are given in Figure 2. The first iodide to elute (at 47.7 min) has an absorption maximum at 267 nm and also absorbs strongly at 210 nm, as is characteristic of tertiary iodides.[14] It is readily identified as 2-iodo-2,3-dimethylbutane produced as a result of scavenging of the radicals resulting from the loss of a tertiary H atom. The second peak (at 49.2 min) has an absorption maximum at 256 nm and is assigned as the primary iodide, 1-iodo-2,3-dimethylbutane. These are followed by 2-iodo-3-methylbutane at 50.3 min, isopropyl iodide (2-iodopropane) at 53.7 min, and methyl iodide at 68.1 min. The latter three are identified by a comparison of their spectra and retention times with authentic samples. As expected from the generalization discussed above, the contributions of methyl iodide and 2-iodo-3-methylbutane are low. Other than the minor contribution at 57.0 min, which has an absorption maximum at 257 nm and is attributable to 1-iodopropane, no other iodide is apparent in the contour plot. There is no evidence that any unsaturated iodides are produced.

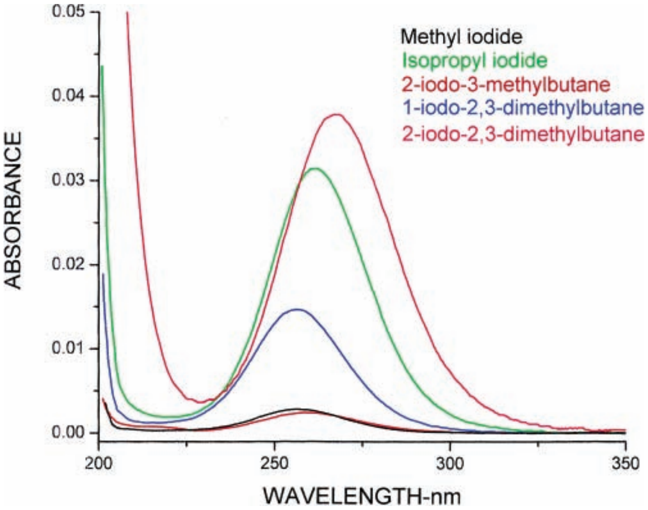

**Figure 2.** Absorption spectra at the chromatographic maxima in Figure 1. The peaks at 47.7 and 49.2 min have absorption maxima at 267 and 257 nm that are typical of tertiary and primary iodides. They are identified as 2-iodo-2,3-dimethylbutane and 1-iodo-2,3-dimethylbutane. The 261-nm absorption maxima of the peaks at 50.3 (2-iodo-3-methylbutane) and at 53.7 min (isopropyl iodide) are typical of secondary iodides. Methyl iodide, observed at 68.1 min in Figure 1, has an absorption maximum at 256 nm. The latter three iodides have spectra and elution times identical to those of reference samples.

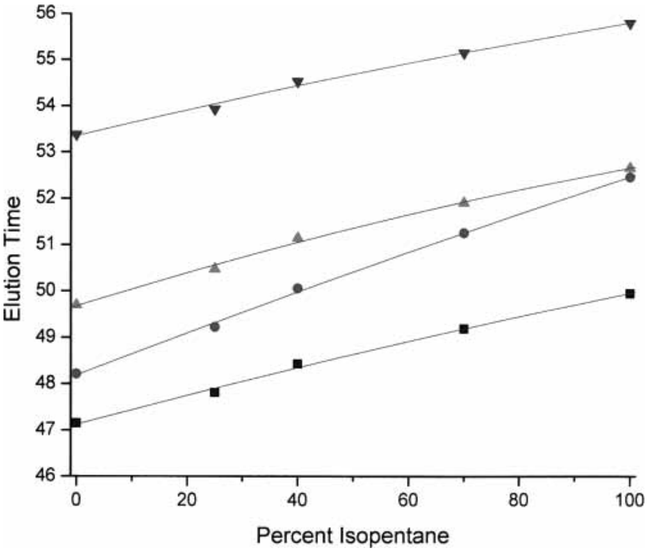

**Figure 3.** Dependence of the retention times of (■) 2-iodo-2,3-dimethylbutane, (●) iodo-2,3-dimethylbutane, (▲) 1-iodo-3-methylbutane, and (▼) isopropyl iodide on the composition of hexane−isopentane eluents. Methyl iodide elutes at 68−72 min and is not shown.

The dependences of the elution times on the eluent composition are given in Figure 3. It is seen that with increases in the isopentane content in the eluent, 1-iodo-2,3-dimethylbutane is delayed more than the other iodides. As is found in the other studies reported below, isopentane selectively increases the

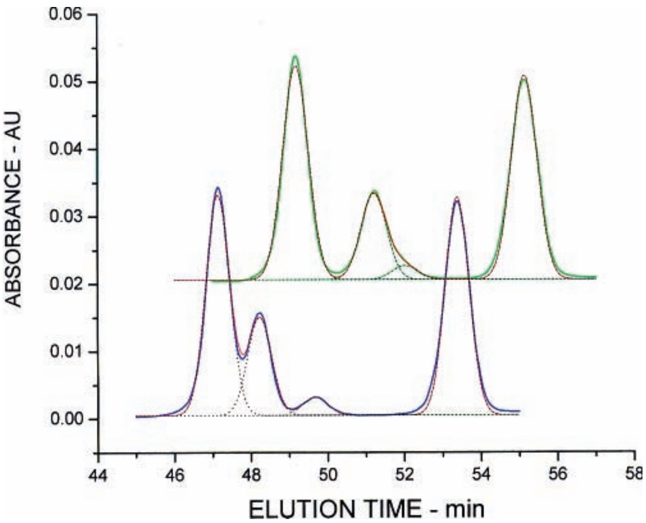

**Figure 4.** Chromatograms at 260 nm for elution with (A) 75:25 (blue) and (B) 25:75 (green) mixtures of *n*-hexane and isopentane. The dotted curves represent Gaussian fits to the observed chromatograms, and the red curves, the sum of the Gaussians.

**TABLE 1: Alkyl Iodide Yields[a] in the Radiolysis of 2,3-Dimethylbutane**

| | spectroscopic | radiochemical | ref 10 |
|---|---|---|---|
| 2-iodo-2,3-dimethylbutane | 1.95 | 2.00 | 2.66 |
| 1-iodo-2,3-dimethylbutane | 0.91 | 1.18 | 1.60 |
| 2-iodo-3-methylbutane | 0.16 | 0.19 | 0.17 |
| isopropyl iodide | 2.05 | 1.77 | 1.74 |
| methyl iodide | 0.45 | 0.42 | 0.60 |
| (1-iodopropane) | <0.05 | <0.10 | 0.08 |
| (others) | <0.02 | <0.10 | 0.11 |
| tertiary/primary | | 10.2 | |

[a] Radiation chemical yields in units of molecules per 100 eV of absorbed energy.

elution time of the primary iodide relative to those of the secondary and tertiary iodides. As indicated in the Figure, 2-iodo-3-methylbutane and 2-iodopropane are not resolved with isopentane elution. Because of the selective delay of the primary iodide, one can, to a certain extent, tune chromatographic resolution by the judicious choice of the eluent. The dependences of elution times and resolution on eluent composition are very subtle.

Chromatograms obtained with hexane and also with a 30:70 mixture of hexane and isopentane as the eluents are given in Figure 4. The areas of the major components were determined by Gaussian analysis, as indicated by the dotted curves in the Figure. The peak areas obtained with the other mixed eluents are essentially independent of the eluent composition and have a standard deviation on the order of a few percent. In the case where isopentane was used as the eluent, the area of the unresolved composite of 1-iodo-2,3-dimethylbutane and 2-iodo-3-methylbutane agreed with the sum of their areas determined in the other experiments. These spectrophotometric studies demonstrate the excellent reproducibility attainable in these measurements and provide the spectral information needed to identify the individual iodides. The yields obtained from the spectrophotometric experiments based on the assumed sensitivities of the hexyl iodides are given in column 2 of Table 1.

In Figure 5, a typical radiochromatogram is compared with one simultaneously obtained spectrophotometrically, demonstrating that except for the relatively low spectroscopic sensitivity of methyl iodide the spectroscopic sensitivities of the different iodides are very similar. The radiochromatogram of

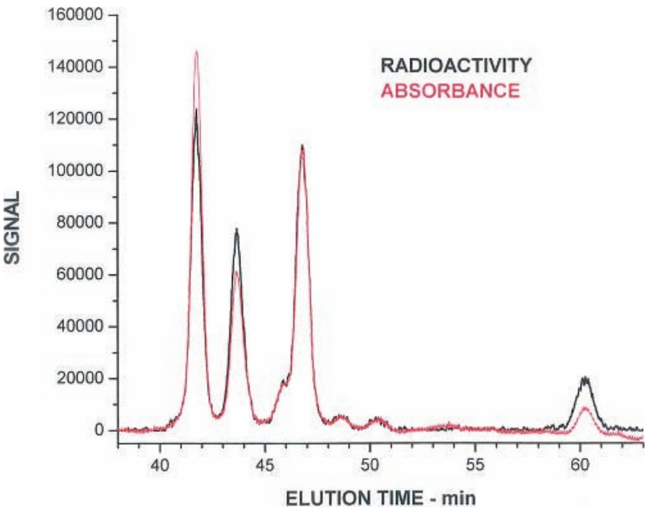

**Figure 5.** Comparison of radiochromatographic and spectrophotometric recordings (at 265 nm) for 2,3-dimethylbutane containing 1 mM $^{125}I_2$ irradiated to a dose of 100 krads. Elution was with 40:60 hexane−isopentane. The isopropyl iodide peak at 46.8 min was used to normalize the chromatograms.

Figure 5 shows that there are no significant yields of iodides other than those noted in the spectroscopic studies. The yields of the individual iodides determined from their relative areas in the radiochromatogram are summarized in column 3 of Table 1. Because reference samples were not available for the hexyl iodides, their yields determined in the radiochemical experiments must be regarded as more accurate than those given by the spectrophotometric studies.

The methyl iodide yield given in Table 1 (0.42) is somewhat higher than that given in ref 7 (0.34) but is similar to the value of 0.45 predicted by empirical relation IV in that reference. It is noted that the yield of the 2-iodo-3-methylbutane, produced as a complement to methyl iodide, is only half the yield of the latter. This difference is in accord with the asymmetric patterns noted previously for the radicals produced in the radiolysis of the low-molecular-weight normal alkanes.[1]

The yields reported by Castello et al.[10] are given in column 4 of Table 1. It is seen that whereas the yields that they reported for the iodohexanes are considerably higher than those determined in the present study the relative yields in the two studies are somewhat similar. The principal difference is the relatively low yield that they give for isopropyl iodide. The overall agreement is, in fact, far better than might be expected considering the differences in the experimental methodologies, the 5-fold higher iodine concentration, and the correspondingly higher doses used in their experiments.

Schrob and Trifunac,[15] using time-resolved ESR, identified the tertiary radical—2,3-dimethyl-2-butyl—and the isopropyl radical as the principal intermediates present 10 $\mu$s after pulse irradiation of 2,3-dimethylbutane at −52 °C. However, the scavenging studies show that there also is an appreciable yield of the primary radical and the radicals produced by the rupture of the C−$CH_3$ bond. These latter radicals are not apparent in the ESR experiments because their ESR spectra involve coupling to only three or four protons whereas the spin couples to seven or six protons in the cases of the tertiary hexyl and isopropyl radicals. As a result, ESR spectra of the latter radicals extend over much broader field region and mask the signals of the other radicals.

The source of the small yield of 1-iodopropane in Figure 1 is not obvious. Samples of 2,3-dimethylbutane from different sources gave similar yields, suggesting that the *n*-propyl radical

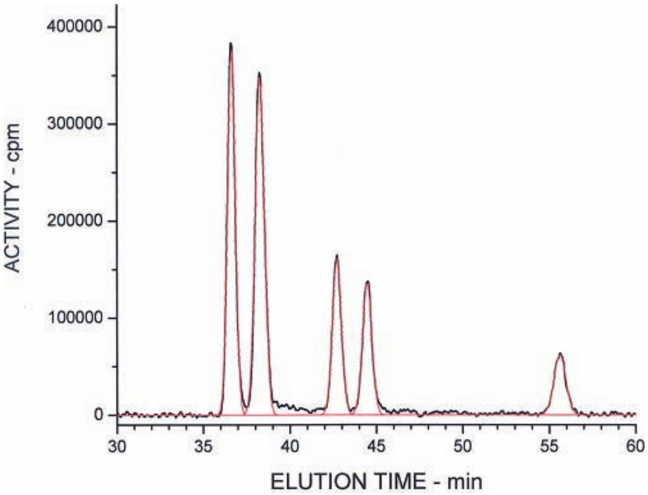

**Figure 6.** Radiochromatogram (black) for 2,4-dimethyl pentane containing 1 mM $^{125}I_2$ irradiated to a dose of 100 krads. The red curves represent Gaussian fits to the five chromatographic peaks. The tertiary 2-iodo-2,4-dimethylpentane elutes first (at 36.6 min) and is followed at 38.3 min by a somewhat broader peak that is a composite of the primary and secondary heptyl iodides and the secondary hexyl iodide that complements methyl iodide (Figure 8). The peaks at 42.5, 44.5, and 55.6 min are attributable to isobutyl, isopropyl, and methyl iodides.

may result from the isomerization of a cation initially produced in the radiation process. However, it is also possible that it is attributable to an impurity in the sample such as 2-methylpentane where propyl and isopropyl radicals are the dominant radicals produced.[16] Neither the normal alkanes previously studied[1] nor the other two hydrocarbons studied here give any indication of significant yields of radicals produced by other than simple bond rupture.

**2,4-Dimethylpentane.** Seven iodides are expected to result from the simple bond rupture of 2,4-dimethylpentane. However, in this case, the analysis is complicated in that only five peaks are apparent in the radiochromatogram of Figure 6 where hexane was the eluent. The first peak is identified as the expected tertiary heptyl iodide, 2-iodo-2,4-dimethylpentane, from its absorption maximum at 269 nm in corresponding spectrophotometric recordings (see below). The third, fourth, and fifth peaks in Figure 6 are identified as isobutyl iodide (1-iodo-2-methylpropane), isopropyl iodide (2-iodopropane), and methyl iodide by comparing their elution times with those of authentic samples. The second peak in Figure 6 is 20% broader than the first and, as shown below, is a composite of contributions from the three remaining expected iodides: the primary and secondary heptyl iodides, 1-iodo-2,4-dimethylpentane and 3-iodo-2,4-dimethylpentane, and the hexyl iodide, 2-iodo-4-methylpentane. A radiochromatogram recorded with cyclopentane elution shows an even broader peak of this composite but does not provide sufficient resolution to allow analysis. No other iodides are evident in the radiochromatogram.

The yields of the various iodides, determined from the radiochromatogram of Figure 6, are given in column 3 of Table 2. The area of the composite peak corresponds to 33% of the iodides produced. The contributions to the composite peak are given in Table 2 on the assumption that their relative yields are in the ratios indicated by the spectroscopic analyses described below.

The contour plot of Figure 7, where elution was with cyclopentane, shows that, as indicated above, the first peak that elutes is the expected tertiary heptyl iodide. This peak is followed by a partially resolved peak at 46.3 min that has a maximum at 256 nm and one at 46.8 min with a maximum at 260 nm. These peaks make up the composite observed in the radiochromatogram. The first of these peaks has an absorption maximum at 256 nm and is identified from its spectrum as the expected primary heptyl iodide, and the second is a composite of the secondary heptyl and hexyl iodides, both of which are expected to have similar spectra with absorption maxima at ~260 nm. The peaks that follow the composite are identified by their spectra and elution times as isobutyl, isopropyl, and methyl iodide (not shown in Figure 7). Because the sensitivities of these three iodides are known, their contributions can be determined readily.

The Gaussian analysis, given in Figure 8b, of the composite observed with cyclopentane elution is particularly important in that it provides a measure of the yield of the primary heptyl iodide. Although cyclopentane elution gave the narrowest peaks and best overall resolution, it did not resolve the contributions from the secondary heptyl and hexyl iodides. We note that 2-iodo-4-methylpentane complements methyl iodide and should be produced in a yield less than 0.4. The peak due to the secondary iodides in Figure 8b must, therefore, be mainly attributed to the heptyl iodide, 3-iodo-2,4-dimethylpentane. With isopentane and cyclohexane elution, the contribution from

**TABLE 2: Alkyl Iodide Yields[a] in the Radiolysis of 2,4-Dimethylpentane**

| | spectroscopic | radiochemical | type |
|---|---|---|---|
| 2-iodo-2,4-dimethylpentane | 1.73 | 1.71 | tertiary |
| 3-iodo-2,4-dimethylpentane | 0.60 | 0.61[b] | secondary |
| 1-iodo-2,4-dimethylpentane | 0.99 | 1.01[b] | primary |
| 2-iodo-4-methylpentane | 0.24 | 0.24[b] | secondary |
| 1-iodo-2-methylpropane | 0.86 | 0.85 | primary |
| isopropyl iodide | 0.78 | 0.76 | secondary |
| iodomethane | 0.40 | 0.42 | primary |
| tertiary/primary | | 10.2 | |
| secondary/primary | | 3.6 | |

[a] Radiation chemical yields in units of molecules per 100 eV of absorbed energy. [b] Total yield of 1.86 distributed among 1-iodo-2,4-dimethylpentane, 3-iodo-2,4-dimethylpentane, and 2-iodo-4-methylpentane in a ratio of 54:33:13, as indicated by the spectrophotometric results.

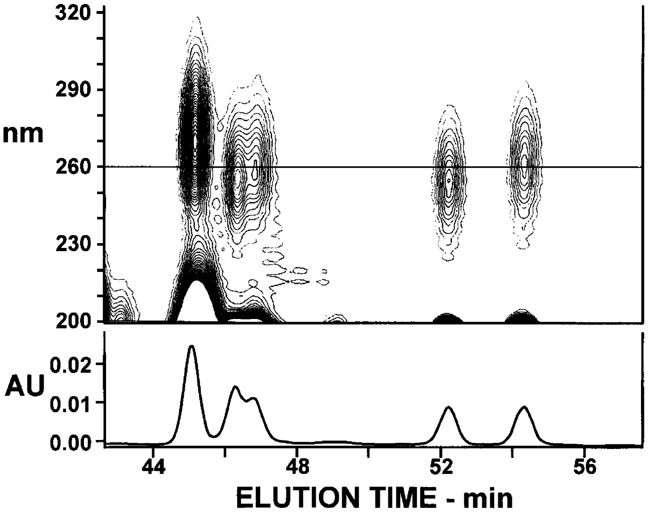

**Figure 7.** Contour plot for 2,4-dimethylpentane containing 1 mM $I_2$ irradiated to a dose of 100 krads. Elution was with cyclopentane containing 15% isopentane. Contours represent absorbance levels at intervals of 0.001 AU. The chromatogram extracted at 260 nm is given below the contour plot. Peak assignments are the same as in Figure 6. The contours of isobutyl and isopropyl iodide illustrate the typical differences between the absorption maxima of primary and secondary iodides.

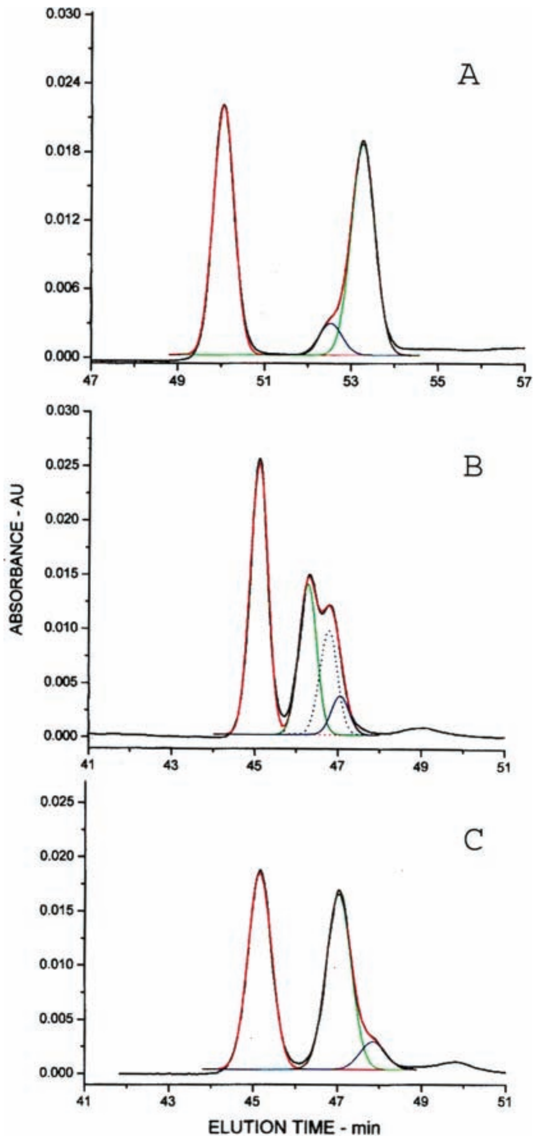

**Figure 8.** Chromatograms at 260 nm for 2,4-dimethylpentane containing 1 mM $I_2$ irradiated to a dose of 100 krads obtained with elution by (A) isopentane, (B) cyclopentane containing 15% isopentane, and (C) cyclohexane. In each case, the tertiary heptyl iodide elutes first. Its peak is fitted very well by a single Gaussian. The solid green and dotted blue Gaussians in B represent the contributions of the primary and secondary heptyl iodides, respectively, to the composite. The dark-blue Gaussians represent a common contribution of 2-iodo-4-methyl pentane to the three chromatograms.

2-iodo-4-methylpentane becomes apparent. With isopentane elution (Figure 8a), this contribution appears as a shoulder before a composite of the primary and secondary heptyl iodides. With cyclohexane elution (Figure 8c), it appears after that composite. Gaussian analysis shows that these shoulders have similar areas that correspond to a yield of about half that of methyl iodide. Although the primary and secondary heptyl iodides are not resolved in Figure 8a and c, the contributions of the secondary heptyl iodide can be determined by subtracting the area of the primary heptyl iodide observed with cyclopentane elution from that of the combined peaks or, alternatively, by constraining the Gaussian analysis of the composite in Figure 8b to that area. Taking into account the higher sensitivity of the secondary iodides, both approaches show that the relative yields of 1-iodo-2,4-dimethylpentane, 3-iodo-2,4-dimethylpentane, and 2-iodo-4-methyl pentane are in a ratio of 54:33:13 with their total corresponding to 33% of the iodides produced, as indicated by radiochemical experiments. Their yields, determined in the spectroscopic experiments, are summarized in column 2 of Table 2.

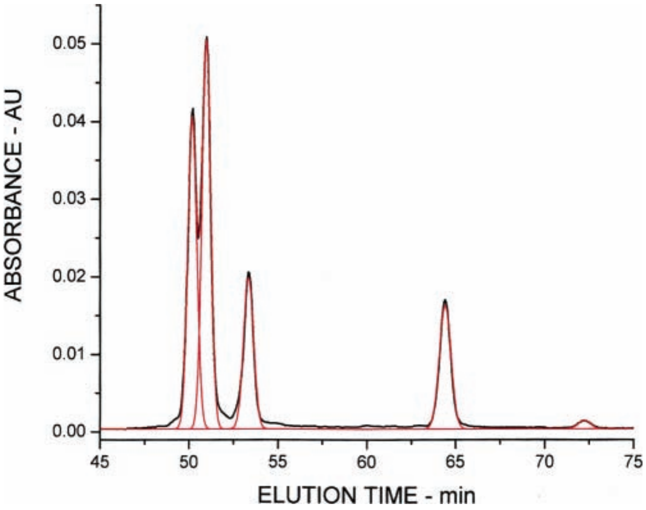

**Figure 9.** Chromatogram recorded spectrophotometrically at 260 nm for 3-ethylpentane containing 1 mM $I_2$ irradiated to a dose of 100 krads. Elution was with hexane. The red curves represent optimized Gaussian fits to the five chromatographic peaks. The first peak is attributed to the secondary heptyl iodide, 2-iodo-3-ethylpentane. (See Figure 10 and text.) The second peak is 20% wider than the first and is the composite of the tertiary and primary heptyl iodides and 1-iodo-2-ethylbutane that complements methyl iodide. These are followed by 3-iodopentane at 53.5 min, its complement ethyl iodide at 64.5 min, and methyl iodide at 72.4 min.

It is expected that the smaller 2-iodo-4-methylpentane should elute after the heptyl iodides, as is observed with cyclohexane elution. The question now arises as to why it elutes ahead of the heptyl iodides with isopentane elution. With this eluent, the delay of the primary heptyl iodide relative to that of the smaller hexyl iodide is similar to the delays noted in Figure 4 for the corresponding peaks in the case of 2,3-dimethylbutane. 3-Iodo-2,4-dimethylpentane is also delayed because of its high symmetry, as is also noted in other cases of highly symmetrical molecules.[16] Apparently, highly symmetrical compounds are selectively delayed in GPC because they are more compact and diffuse more deeply into the gel. (See, for example, the delay of 3-iodo-3-ethylpentane discussed below in the case of 3-ethylpentane.) Although the magnitudes of these delays are small, they are large enough that the observed chromatographic patterns are critically dependent on the eluent. Both the molecular shape of a given component and that of the eluent play significant roles in determining elution times in GPC.

The yield of methyl iodide (0.42) is considerably higher than that reported previously (0.28).[7] Except for the tertiary radical, the radical yields reported by Holroyd[3] are ∼50% lower than those indicated in Table 2. These differences reflect on the difficulties in interpreting the data from the sampling experiments. There are no other measurements of these yields in the literature.

**3-Ethylpentane.** For 3-ethylpentane, seven radicals are also expected: the primary, secondary, and tertiary heptyl radicals produced by the loss of an H atom and methyl and ethyl radicals and their complements produced by C−C rupture. However, the chromatogram of Figure 9, recorded spectrophotometrically with hexane elution, manifests only five iodide peaks. The first peak is identified as the secondary heptyl iodide from its absorption maximum at 261 nm. The second peak has an absorption maximum at 264 nm, indicating unresolved contribu-

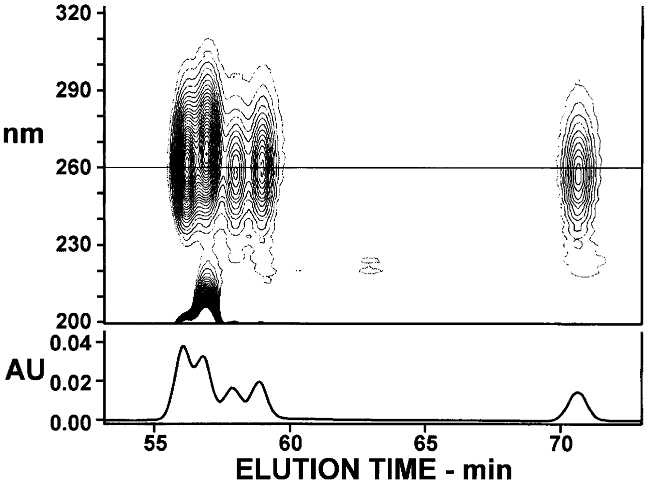

**Figure 10.** Contour plot for 3-ethylpentane containing 1 mM $I_2$ irradiated to a dose of 100 krads. Elution was with isopentane containing 5% cyclopentane. Contours represent absorbance levels at intervals of 0.001 AU. The chromatogram extracted at 260 nm is given below the contour plot. The first peak to elute is the secondary heptyl iodide. This is followed by the tertiary and primary heptyl iodides, 3-iodopentane and ethyl iodide. Methyl iodide is observed as a weak peak at 89 min and is not shown.

tions from the primary and tertiary heptyl iodides. The remaining three peaks are, in order of elution, identified by comparing their elution times and spectra with authentic samples such as 3-iodopentane, ethyl iodide, and methyl iodide. Because their extinction coefficients are known,[1] their contributions are readily determinable. The hexyl iodide produced as a result of the scission of a terminal $CH_3-C$ bond is expected to be produced in very low yield and to elute with and be masked by the other more abundant iodides. It is not apparent in the chromatographic data.

Partial resolution of the heptyl iodides, illustrated in the contour plot of Figure 10, was achieved using isopentane containing 5% cyclopentane as the eluent. As with hexane elution, the component at 54.9 min is assigned as the secondary heptyl iodide, 2-iodo-3-ethylpentane. This peak is followed by one at 56.5 min having an absorption maximum at 267 nm that identifies it as the tertiary iodide, 3-iodo-3-ethylpentane, and by one at 57.8 min that has an absorption maximum at 257 nm, showing it to be the primary iodide, 1-iodo-3-ethylpentane. The peak at 58.9 min in Figure 10 is due to 3-iodopentane that is only poorly resolved from the primary heptyl iodide with cyclopentane elution but well-resolved with hexane elution (Figure 9).

Figure 11 compares the chromatogram of Figure 10 with a radiochromatogram recorded under similar conditions. The spectrophotometric data given in Figure 11a exhibit four peaks that can be resolved by the indicated Gaussian analysis. For completeness, an approximate contribution from the 2-iodo-4-methylpentane that complements methyl iodide is included in this analysis, but its inclusion has only a minor effect on the Gaussian fits. The radiochromatogram given in Figure 11b is considerably noisier than the chromatogram obtained spectroscopically but with appropriate constraints can be analyzed similarly. A comparison of these two chromatograms shows that, as expected, the extinction coefficient of the primary heptyl iodide is relatively less than those of the other iodides. From the areas of the peaks in the radiochromatogram, the yields of the secondary, tertiary, and primary iodides and 3-iodopentane are given in column 3 of Table 3. The agreement between the two sets of results indicates that the sensitivities assumed in the spectroscopic experiments are reasonably accurate.

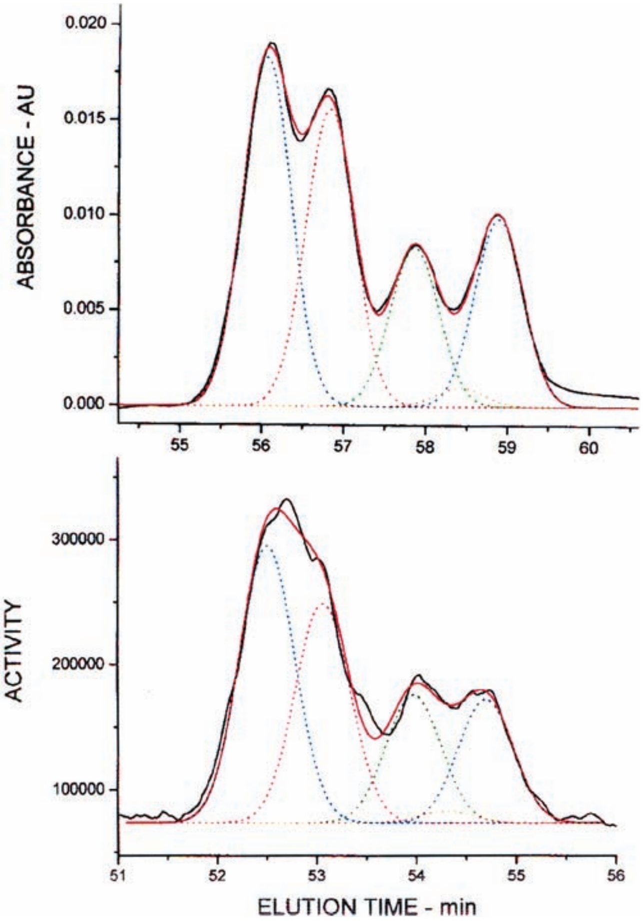

**Figure 11.** Analysis of the chromatograms (upper) extracted from Figure 10 at 260 nm and (lower) recorded in an analogous radiochemical experiment. The five Gaussians represent (blue) the secondary heptyl iodide, (red) the tertiary heptyl iodide, (green) the primary heptyl iodide, (orange) the primary hexyl iodide that complements methyl iodide, and (cyan) 3-iodopentane.

**TABLE 3: Alkyl Iodide Yields[a] in the Radiolysis of 3-Ethylpentane**

| | spectroscopic | radiochemical | type |
|---|---|---|---|
| 3-iodo-3-ethylpentane | 1.33 | 1.34 | tertiary |
| 2-iodo-3-ethylpentane | 1.64 | 1.71 | secondary |
| 1-iodo-3-ethylpentane | 0.80 | 0.81 | primary |
| 1-iodo-2-methylbutane | (0.07)[b] | (0.07)[b] | primary |
| 3-iodopentane | 0.80 | 0.78 | secondary |
| ethyl iodide | 0.85 | 0.80 | primary |
| methyl iodide | 0.11 | 0.09 | primary |
| | | | |
| tertiary/primary | | 14.9 | |
| secondary/primary | | 3.2 | |

[a] Radiation chemical yields in units of molecules per 100 eV of absorbed energy. [b] Estimated from ref 7.

In most cases, tertiary iodides elute before their isomers, so it is quite surprising that in Figure 10 the secondary iodide is observed to elute first. In this case, the elution of 3-iodo-3-ethylpentane is delayed because of its high symmetry and compact structure that allows it to penetrate more deeply into the gel. As a result, it appears after the secondary iodide. It is another manifestation of the delay noted above in the case of the symmetric secondary heptyl iodide, 3-iodo-2,4-dimethylpentane, produced from 2,4-dimethylpentane. These observations demonstrate that the resolution in GPC critically depends on the structure of the molecules under consideration and the eluent being used. We note here that the detailed spectroscopic information available from the 3-D recordings is essential to identify the chromatographic peaks properly. Without this information, it is likely, because tertiary iodides usually elute before their isomers, that one would assume the first peak in the radiochromatogram of Figure 9 to be the tertiary iodide.

## Discussion and Summary

It has previously been shown[1] that in the radiolysis of the normal alkanes the relative yields the for production of secondary and primary radicals are proportional to the number of secondary H atoms in the alkane (i.e., that the relative frequency for the loss of H from a secondary position is independent of the size of the alkane and a factor of 3.24 greater than for loss from a primary position). The yields given in Tables 2 and 3 correspond to similar relative frequencies of 3.6 and 3.1 for the cases of 2,4-dimethylpentane and 3-ethylpentane, respectively. The relative frequency for the production of secondary and primary radicals is clearly not strongly dependent on the structure of the alkane.

The yields of tertiary radicals from the three hydrocarbons studied are high, as expected from the relatively low energy of a tertiary C−H bond.[17] For 3-ethylpentane, the yields of the tertiary and primary radicals are in the ratio of 1.65 so that, taking into account the 9-fold greater number of primary H atoms, the relative frequency for the loss of a tertiary H is 14.9 times that for the loss of a primary H. For 2,3-dimethylbutane and 2,4-dimethylpentane, this relative frequency is somewhat lower—10.2 for each of the two tertiary H atoms—indicating competition between the tertiary positions. Hydrogen atoms should, of course, mainly abstract at the tertiary position and will contribute to the observed selectively. However, because the H-atom yield is estimated to be only ∼1.5,[18] H abstraction alone cannot explain the observed selectivity in the yields of C−H rupture. It is clear that there is considerable selectivity in the initial bond rupture processes.

The yields for radicals produced by the rupture of the central C−C bonds are similar: 1.74 for 2,3-dimethylbutane, 1.61 for 2,4-dimethylpentane, 1.58 for 3-ethylpentane, and somewhat higher than the total yield of 1.3 for C−C scission in the normal alkanes.[1] The rupture of a central C−C bond is only marginally affected by groups that are remote from that bond. For 2,3-dimethylbutane and 2,4-dimethylpentane, the yields for the rupture of a terminal C−C bond are high, as expected from the previous study that showed that methyl radical production was strongly enhanced by the presence of adjacent methyl groups.[5] As a result, fragmentation accounts for 40% of the radicals as compared to 25% in the case of the normal alkanes. For 3-ethylpentane, the methyl radical production is low, as expected from the previous study. In this case, the yield of ethyl radicals is 60% greater than the yield of 0.5 expected from its yield from *n*-heptane.[1] There appears to be a modest effect of the adjacent ethyl groups analogous to the effect of methyl substitution noted in ref 7.

In general, photochemical studies have shown that that excess energy in excited alkanes is highly localized around tertiary carbon atoms and leads to the preferential rupture of C−H and C−C bonds adjacent to the tertiary site.[19,20] Because C−C rupture occurs only as the result of primary processes, the high yields of the radicals produced radiolytically by the rupture of the C−C bonds adjacent to the tertiary site demonstrate that the energy deposited by ionizing radiation is similarly localized at tertiary sites.

We especially note here that 2,4-dimethylpentane is a special case in that the yield of the isobutyl radical is 12% higher than that of its complement, the isopropyl radical (cf. Figure 6). This contrasts with the similar yields of ethyl and 3-pentyl radicals observed in the case of 3-ethylpentane and the relatively low yield of the complement to the methyl radical produced from 2,3-dimethylbutane. For the normal alkanes, the smaller fragments are observed in slightly greater abundance than their complements.[1] Although one expects the yields of complementary fragments to be similar factors, other than simple bond rupture, such as secondary reactions of the ions initially produced, they play some role in determining the yields of radicals that can be scavenged at microsecond times.

In summary, this study shows that in the radiolysis of branched alkanes the loss of H from tertiary positions occurs an order of magnitude more frequently than from primary positions but that competitive effects play a role when there are several tertiary H atoms present. The relative frequency for the loss from secondary and primary positions (3.2) is similar to that observed for normal alkanes. These observations provide the basis for a general understanding of bond rupture in the radiolysis of saturated branched hydrocarbons.

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