the calculated rate constant of eq 10 stems from the resultant Brønsted β of ≈ 0.8 to 0.9, calculated from the rate constants k_x and k_r. Further studies involving other pyridine aldehyde analogs and aromatic aldehydes are essential to firmly establish the mechanism of this step in the condensation reaction and the reason why aromatic aldehydes apparently undergo the Pictet–Spengler reaction best in acidic media.

This study establishes the condensation reaction of histidine with the pyridoxal analog, 3-hydroxypyridine-4-aldehyde, to proceed through azomethine intermediates. Previous workers have established the presence of azomethines[3,5] but not their essential involvement in the condensation reaction. The inability to obtain condensation products when secondary amines are employed has been interpreted[6] as evidence for the necessity of azomethine intermediates. A criticism of this interpretation is the finding that imines are formed from secondary amines and that said positively charged imines undergo addition with greater facility than the neutral imines formed from primary amines.[17]

Acknowledgment. This work was supported by a grant from the National Science Foundation.

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Selectivity of C–H Bond Rupture by γ Radiolysis and Hot-Radical Attack in Singly Branched Alkane Glasses[1]

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Abstract: Trapped free radicals are produced in singly branched alkane glasses at 77°K by γ irradiation, hot-radical attack, or photosensitization by aromatic solutes. In contrast to similar activation in the gas and liquid phases, there is a high selectivity for rupture of a particular type of secondary C–H bond, as indicated by the esr spectra of the resultant free radicals. All three methods of activation show the same selectivity. For molecules with branching in the 3 or 4 position, the free radicals formed result predominantly from loss of a hydrogen atom from the secondary carbon atom nearest the end of the longest carbon chain. When branching is in the 2 position, detectable amounts of the radical resulting from loss of a tertiary hydrogen are also found. Identification of the trapped radical formed from 3-methylpentane glass has been made by comparing its esr spectrum with the spectra of the four possible 3-methylpentyl radicals. The latter have been produced by radiolysis of the corresponding iodides and the chlorides. Photolysis of 3-methylpentyl iodides in various organic glasses at 77°K produces, with low quantum yield, radicals formed by abstracting hydrogen atoms from matrix molecules, but no radicals formed by rupture of the carbon–iodine bond of the iodide, illustrating the importance of the cage effect in these systems.

When 3-methylpentane (3MP) is cooled in liquid nitrogen, it readily forms a transparent glassy solid and is widely used as a matrix for studying trapped free radicals, ions, and electrons produced at 77°K by irradiation techniques. In such investigations a signal from radicals produced from the 3MP itself often dominates the esr spectrum. Many authors have reported this spectrum (Figure 1A), which appears to arise from one predominate radical species, but there is not agreement on the identity of the radical.

Staples[2] suggested that the radical results from loss of a secondary hydrogen atom, or of the branching methyl group. Others[3,4] have also proposed removal of the branching methyl group, although no signal attributable to trapped CH_3 radicals is observed, and 3MP at 77°K is known to trap CH_3.

Voevodskii and coworkers[5] generated the six-line signal by a benzene-photosensitized decomposition of 3MP at 77°K. They proposed that it is produced by an equal interaction of the unpaired electron with only five of the seven β-hydrogen atoms in the tertiary 3MP radical, one hydrogen on each of the methylene groups being unable to interact significantly as a result of its orientation, relative to the major axis of the electron orbital.

Skelly, Hayes, and Hamill,[6] and Brocklehurst, *et al.*,[7] noted that the spectrum is composed of four central lines having relative intensities in the ratio of 1:3:3:1 or 1:2:2:1, flanked by two much weaker lines, implying the possibility that it might arise from more than one radical.

Photolysis of HI in 3MP at 77°K[7,8] leads to the same sextet of lines as radiolysis of pure 3MP. This argues against rupture of a C–C bond, and on this basis it was again proposed that the radical formed results from abstraction of a secondary or tertiary hydrogen atom.[9]

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[1] This work has been supported in part by U. S. Atomic Energy Commission Contract AT(11-1)-1715 and by the W. F. Vilas Trust of the University of Wisconsin.

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Such ambiguity in the interpretation of esr spectra for radicals in amorphous solids often arises because anisotropic hyperfine coupling of the randomly oriented radicals leads to line broadening, loss of resolution, and distortion of relative line intensities. There may also be unsymmetrical equilibrium configurations of methylene β-protons leading to inequivalent hyperfine interactions.

In the present investigation we have established the identity of the trapped radical produced from 3MP by comparing its spectrum with the spectrum of each of the four different 3-methylpentyl radicals. The latter were prepared by radiolysis of the corresponding chlorides and iodides; other methods tested proved unsatisfactory. The investigations with 3MP have been extended to aid in the interpretation of the esr spectra of radicals produced from a group of closely related branched alkanes. This has led to new generalizations as to selective bond rupture patterns of these compounds when they are radiolyzed or attacked by hot atoms or radicals in the glassy state.

Experimental Section

Materials. The four 3-methylpentyl iodides and four 3-methylpentyl chlorides were prepared[10] by treating the corresponding alcohols with 50% aqueous HI, gaseous HCl (for the primary chloride), or $SOCl_2$. Purification was by gas chromatography or trap-to-trap distillation on a vacuum manifold. The products were characterized by gas chromatography or uv absorption spectroscopy, or both, and stored at 77°K. The absorption maxima, determined in this work, are summarized in Table I. The only similar determination we have found in the literature is for 1-iodo-3-methylpentane (1I3MP), for which a value of 2570 Å is given for the wavelength of maximum absorption.[11]

Table I. Absorption Maxima of 3-Methylpentyl Iodides

Iodide	λ_{max}, Å In liquid 3MP	Gas phase
1-Iodo-3-methylpentane	2565 ± 3	
3-Iodomethylpentane	2558	2554 ± 3
2-Iodo-3-methylpentane	2618	2618
3-Iodo-3-methylpentane	2668	

Phillips Pure Grade 3MP and 2-methylpentane (2MP) were further purified to less than 10^{-6} mf impurities by passage through a 4-ft column of freshly activated silica gel. Hydrogen iodide was generated by allowing frozen 50% aqueous HI (J. T. Baker Co.) to warm in the presence of P_2O_5 on the vacuum line. The dry HI was stored at 77°K. Other compounds were analyzed by gas chromatography to verify the absence of gross impurities and were employed without further purification, following drying over P_2O_5 and degassing on the vacuum line. These included American Petroleum Institute Standard Samples (99.98 ± 0.01 mole % stated minimum purity) of 4-methylheptane and 3-methylheptane; methyl iodide, benzophenone, and N,N,N′,N′-tetramethyl-*p*-phenylenediamine dihydrochloride from Eastman Organic Chemicals (White Label); resublimed naphthalene from Baker and Adamson; perfluorodimethylcyclohexane from Halogen Chemicals; 1,2,2-trifluorotrichloroethane from DuPont Organic Chemicals; Fluorochemical O-75 (perfluorinated octanes and cyclic perfluorinated ethers) from Minnesota Mining Corp.; and QF-1 (fluorinated silcone oil) from Varian-Aerograph.

During the degassing of samples on the vacuum line, considerable quantities of vapor were removed from above the sample in the liquid state to ensure removal of CO_2.

Irradiations. Photolyses were conducted in the esr cavity, with the sample in sealed 3- or 4-mm o.d. Suprasil esr tubes under liquid nitrogen in a Varian quartz dewar, using a quartz-jacketed GE AH4 (or AH_6) mercury arc. Radiation from the lamp, focused on the sample with a quartz lens, was passed through a Corning 9-54 filter to remove wavelengths shorter than 2300 Å.

^{60}Co γ irradiations were performed with the samples under liquid nitrogen at a dose rate of approximately 2×10^{18} eV g^{-1} min^{-1}; a total dose of 1.7×10^{19} eV g^{-1} was normally used.

Esr Measurements. Esr measurements were made with a Varian 4500 electron spin resonance spectrometer with 100-Kc modulation at a modulation amplitude of *ca.* 8 G, using a power of 1.5 mW, which was sufficiently low to avoid loss of resolution due to saturation-induced line broadening. All spectra were examined at a variety of detection sensitivities in order to look for underlying structure and additional lines in the spectral extremities.

Results

Radicals Produced from 3MP. A six-line esr spectrum with splittings of 23 G is obtained from 3MP glass radiolyzed at 77°K (Figure 1A). At 77°K it is stable in shape for weeks following radiolysis, and it shows no additional lines when observed at 80-fold higher sensitivity. On warming, it decays without change in shape. These facts indicate that only one, or predominantly one, paramagnetic species is present. The line-intensity distribution agrees with that of theoretically computed, partially resolved spectra[12] for the binomial distribution of 1:5:10:10:5:1, expected from equal coupling of an unpaired electron with five protons.

The same spectrum, slightly better resolved, has been obtained in the present work by the photolysis of dilute solutions (10^{-2} mf) of any one of the four isomeric 3-methylpentyl iodides in 3MP at 77°K. The fact that each of the isomers yields the same spectrum in 3MP, and that photolysis of the isomers in other hydrocarbon glasses produces only the radical from the matrix compound, indicates that the stabilized radicals are produced by abstraction of H from the matrix by hot radicals from the iodide, rather than by the trapping of radicals from the iodide. Similar spectra have been observed from the photolysis of HI,[7,8] Cl_2,[13] CH_3I,[14] C_2H_5I,[14] and benzene[5] in 3MP at 77°K. The fact that the radical can be produced by attack of photolytically produced hot H atoms, Cl atoms, or radicals on 3MP indicates that it must result from C–H rather than C–C bond rupture.

Radicals Produced from 3-Methylpentyl Iodides and Chlorides. It has been shown[15,16] that the predominant radical trapped in organic halide glasses following radiolysis at 77°K is the radical produced by rupture of the carbon–halogen bond. The spectra observed in the present study (except for those from the tertiary halides of 3MP) are consistent with this conclusion. Therefore, to ascertain the identity of the radical responsible for the spectrum of Figure 1A, we have compared the latter with the spectrum of each of the four 3-methylpentyl radicals obtained from radiolysis of the four iodides and chlorides of 3MP at 77°K.

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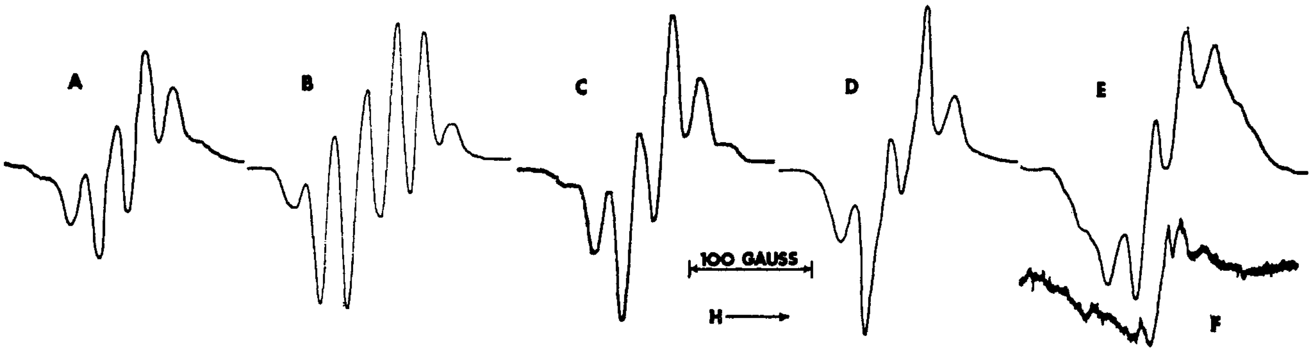

Figure 1. Esr spectra of γ-irradiated glasses at 77°K: (A) 3-methylpentane; (B) 1-iodo-3-methylpentane; (C) 2-chloro-3-methylpentane; (D) 3-chloromethylpentane; (E) 3-chloro-3-methylpentane, signal level 63; (F) after decay of E at 117°K, signal level 800.

The 3-methylpentyl iodides and chlorides all form glasses at 77°K. For each type of halide (primary, secondary, or tertiary) the radical produced by radiolysis of the chloride is the same as that from the iodide, with the esr line widths from the chlorides being slightly narrower. The radicals are stable for weeks at 77°K. The spectra are shown in Figure 1 and discussed below.

(a) 1-Iodo-3-methylpentane (1I3MP). The relative line intensities from the six-line hyperfine pattern obtained from γ-irradiated 1I3MP (Figure 1B) are distinctly different from the binomial distribution of lines produced from 3MP. Their ratio is close to 1:3:4:4:3:1, as shown by comparison with computed spectra.[12] This spectrum is characteristic of primary radicals of the type $RCH_2\dot{C}H_2$.[14,15] The observed structure is accounted for[15] by assuming that the two α-protons and one β-proton have equal hyperfine coupling constants of about one-half that of the other proton. Figure 1B is therefore attributed to the expected 3-methylpentyl radical, $CH_3CH_2CH(CH_3)CH_2\dot{C}H_2$.

(b) 2-Iodo-3-methylpentane (2I3MP) and 2-Chloro-3-methylpentane (2Cl3MP). The secondary chloride and iodide of 3MP yield six-line spectra with 23-G splittings (Figure 1C). These spectra decay without qualitative change at temperatures above 77°K. The intensity distribution is consistent with the binomial distribution of 1:5:10:10:5:1 as determined by comparison with computed spectra.[12] The signal of Figure 1C is attributed to the expected *sec*-3-methylpentyl radical, $CH_3CH_2CH(CH_3)\dot{C}HCH_3$, where the one α- and four β-protons are equally coupled to give the observed six lines.

(c) 3-Iodomethylpentane (3IMP) and 3-Chloromethylpentane (3ClMP). Radiolysis of 3IMP and 3ClMP at 77°K gives four-line esr spectra (Figure 1D) with splittings of 23 G. When the temperature of such a sample is raised, the spectral resolution improves at about 119°K concurrently with the onset of rapid radical decay, but there is no change in splittings or structure. The quartet of lines may be interpreted as resulting from equal interaction (within the resolvable line width) between the two α-protons on the methyl group and the tertiary β-proton in the radical $CH_3CH_2CH(\dot{C}H_2)CH_2CH_3$. The observed line intensities are consistent with[12] the ratio 1:3:3:1 predicted for equal coupling of three protons. The spectrum is independent of whether the matrix is the chloride or iodide and it does not change qualitatively with temperature.

It is of interest that the $CH_3CH(\dot{C}H_2)CH_3$ radical observed in radiolyzed isobutyl halides,[15] and also produced by photoionization of TMPD in 3MP containing isobutyl chloride,[14] has five lines, indicating that the β-proton has an interaction with the unpaired electron of twice that of each α-proton, in contrast to the equal interaction in the $CH_3CH_2CH(\dot{C}H_2)CH_2CH_3$ radical. The relative orientation of the tertiary proton to the orbital of the unpaired electron in the two compounds must be different. Also, unlike the isobutyl radical,[17,18] this primary 3-methylpentyl radical shows no evidence of isomerization to the tertiary radical.

(d) 3-Iodo-3-methylpentane (3I3MP) and 3-Chloro-3-methylpentane (3Cl3MP). These tertiary 3-methylpentyl halides both give a poorly resolved esr pattern with an even-line structure of at least eight components (Figure 1E) with spacings typical of an alkyl radical. The spectral characteristics are independent of dose over a wide range, but change as the signal decays during warming of the sample, giving the spectrum of Figure 1F which has an odd number of lines with 14–16-G spacings characteristic of an allylic radical. It appears probable that both species are present at 77°K, that the alkyl radical decays faster than the allylic on warming, and that superposition of the two spectra accounts for the poor resolution at 77°K.

The alkyl radical is presumed to be the *t*-3-methylpentyl radical since this is the radical to be expected, and because the other 3-methylpentyl radicals have been shown to have fewer than eight hyperfine lines. The *t*-3-methylpentyl radical appears also to be formed during photolysis of HI in 3Cl3MP. In this case, the lines are well resolved and at high sensitivities of observation a total of ten lines are detectable in its esr spectrum, which would be expected for the case where one proton on each of the two methylene groups has a splitting constant about twice that of the other five β-protons. The 20 ± 1 Gauss splittings for these ten lines are significantly smaller than the 23 ± 1 splittings for other radicals reported here, indicative of more delocalization of the electron in the tertiary 3MP radical. The allyl radical signal observed following decay is very likely the center portion of the nine-line spectrum from the radical $CH_3CH{=}C(CH_3)\dot{C}HCH_3$, which is also formed by hot methyl radical attack on 3Cl3MP and will be discussed in another section.

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(e) Identity of Radicals from 3MP. Of the radicals examined above, only the *sec*-3-methylpentyl radical gives the same esr spectrum as the radicals produced by radiolysis of 3MP and hot-atom attack on 3MP. From the excellent agreement of these spectra, it must be concluded that the predominant radical produced by the latter processes is the *sec*-3-methylpentyl radical.

Radicals Produced from Other Branched Alkanes. The high selectivity for rupture of the secondary hydrogen bond in 3MP, noted above, is unexpected. We have, therefore, sought to determine whether radiolysis and hot-hydrogen attack are equally selective in the case of other branched alkane glasses.

(a) 4-Methylheptane (4MHp). Radiolysis of 4MHp glass at 77°K produces an eight-line esr spectrum with a nonbinomial distribution of line intensities close to 1:5:11:15:15:11:5:1. Photolysis of any one of the 3-methylpentyl iodides in 4MHp at 77°K produces the same spectrum, slightly better resolved (Figure 2A). Radicals formed from 4MHp by removal of a primary or tertiary hydrogen atom would be expected to give the same esr signal as the analogous radicals from 3MP. Since the signal (Figure 2A) is different from these (Figures 1B, 1D, 1E), it is presumed to result from radicals formed by loss of H from a 2- or 3-carbon atom. Radicals of the type $RCH_2\dot{C}HCH_3$ have been shown[14,15] to give spectra like Figure 2A, whereas the radical $RCH(CH_3)\dot{C}HCH_2CH_3$ with only four α- and β-protons would not give an eight-line pattern. The spectrum from 4MHp is therefore attributed to the $CH_3(CH_2)_2CH(CH_3)CH_2\dot{C}HCH_3$ radical. The line structure is consistent with a configuration in which one of the methylene β-protons has an interaction with the unpaired electron of approximately twice that of the α-proton and four other β-protons.

(b) 3-Methylheptane (3MHp). Radiolysis of 3MHp or photolysis of a 3-methylpentyl iodide in 3MHp at 77°K gives an eight-line esr spectrum similar to that of Figure 2A for 4MHp. Since the spectrum is different from the six-line spectrum from 3MP, the stabilized radical does not result from cleavage of the C–H bond on a 2-carbon. Loss of H from a 5- or 6-carbon would result in radicals that would be expected to give eight-line spectra[15] with predictably different line intensities. The agreement between the 3MHp spectrum and published spectra from radicals of the type $RCH_2\dot{C}HCH_3$, in addition to the agreement with the spectrum of 4MHp radicals, establishes the octet of lines from 3MHp as due to the radical $CH_3CH_2CH(CH_3)CH_2CH_2\dot{C}HCH_3$.

(c) 2-Methylpentane (2MP). The dominant esr spectrum from γ-irradiated 2MP or photolysis of a 3-methylpentyl iodide or HI[13] in 2MP is an eight-line pattern (Figure 2B) resembling those from 4MHp and 3MHp. By arguments analogous to those above, it is attributed to the $(CH_3)_2CHCH_2\dot{C}HCH_3$ radical. A second radical is indicated by shoulders on the central lines and by additional structure on the wings of the spectrum (observable at high sensitivities). This underlying spectrum appears to consist of at least eight, and possibly ten, lines. Ten lines would result from the *t*-2-methylpentyl radical again assuming that a steric effect on the methylene β-protons results in unequal coupling in the approximate ratio of 1:2. Such coupling is required to explain the ten lines of the similar *t*-pentyl radical, $(CH_3)_2\dot{C}CH_2CH_3$.[13,15]

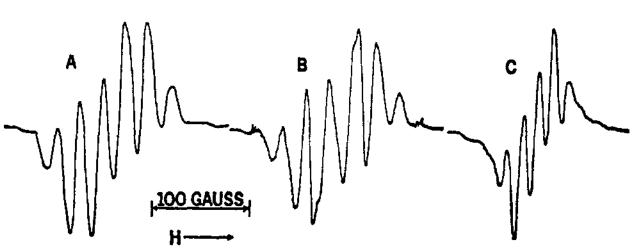

Figure 2. ESR spectra of (A) 4-methylheptane glass containing 1 mole % 1 I3MP photolyzed at 77°K for 44 min with the medium-pressure lamp, signal level 200; (B) 2-methylpentane glass containing 1 mole % 3 IMP photolyzed at 77°K for 1 hr with the medium-pressure lamp, signal level 320; (C) 3-chloro-3-methylpentane glass containing about 1 mole % naphthalene photolyzed at 77°K for 15 min with the high-pressure lamp filtered to remove wavelengths below 2800 Å, signal level 80.

(d) Other Branched Alkanes. Radiolysis of 2-methylbutane (2MB) at 77°K[2,19] or photolysis of HI in 2MB[13] gives a mixture of two paramagnetic species whose spectra are consistent with the two 2-methylbutyl radicals $(CH_3)_2CH\dot{C}HCH_3$ and $(CH_3)\dot{C}CH_2CH_3$.

Other results from our laboratory show that photolysis of a dilute solution of HI in 3-methylhexane (3MHx) glass at 77°K gives an eight-line esr spectrum,[13] identical with the spectra from 3MHp and 4MHp, and attributable to $CH_3CH_2CH(CH_3)CH_2\dot{C}HCH_3$. Radiolysis of glassy 3-ethylpentane (3EP) at 77°K[20] yields a sextet of lines like that found from 3MP, except that the resolution is poorer. The $(CH_3CH_2)_2CH\dot{C}HCH_3$ radical must be formed. Radiolysis of glassy 3-methyloctane (3MO) produces a poorly resolved eight-line resonance,[20] consistent with formation of the $CH_3CH_2CH(CH_3)(CH_2)_3\dot{C}HCH_3$ radical. A predominant eight-line spectrum is also obtained from radiolyzed glassy 2-methyloctane (2MO) similar to that from 3MO, but there is an indication of underlying structure on the high-field side. The trapped radicals may be $(CH_3)_2CH(CH_2)_4\dot{C}HCH_3$ and $(CH_3)_2\dot{C}(CH_2)_5CH_3$.

Tests of Radical Production from 3-Methylpentyl Iodides. In seeking to obtain authentic examples of the esr spectra of the four 3-methylpentyl radicals, we have tested different methods for preparing the radicals by rupturing the C–I bond in the corresponding iodides. These include γ radiolysis and photolysis of the pure glasses, radiolysis and photolysis of solutions of the iodides in hydrocarbons, dissociative electron capture by electrons produced by the photoionization of TMPD, and photosensitization using aromatic sensitizers. Only γ radiolysis of the pure halides produced well-resolved spectra of the desired radicals, but tests of the other methods yielded information summarized below.

(a) Photolysis of Iodides in Glassy Matrices. Photolysis of each of the four 3-methylpentyl iodides in any of several hydrocarbon matrices produces the same radical that is produced by γ radiolysis of the pure matrix, and no detectable amount of the radical which would be formed by C–I bond rupture in the iodide. Photolysis of the matrix in the absence of iodides produces no esr signal. The absence of the radical from the iodide was confirmed by photolysis of 0.01 mf of

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(20) W. G. French and J. E. Willard, unpublished.

3I3MP in a matrix of fully deuterated 3MP glass. Only a 50-G-wide unresolved esr singlet, attributable to a perdeuterated 3-methylpentyl radical, appeared. If the protonated tertiary 3-methylpentane radical were present, it would give a spectrum of about 160-G width. No structure was detectable on the wings of the singlet, indicating that the yield of the matrix radical was at least ten times as great as that of any radical originating from the light-absorbing iodide. The assumption[7] that the tertiary radical is formed by photolysis of the iodide is therefore incorrect.

Photolysis of pure 3-methylpentyl iodide glasses at 77°K produced no radicals detectable by esr, although the samples turned yellow,[21] indicating decomposition. Similar negative results have been reported for other alkyl iodides at 77[22] and 4.2°K.[23]

In an attempt to find a chemically inert matrix in which trapped radicals could be photolytically produced from dilute iodide solutes, we have photolyzed the iodides of 3MP at 77°K dissolved in fluorocarbon glasses (perfluorodimethylcyclohexane, 1,2,2-trifluorotrichloroethane, Fluorochemical 0-75, and QF-1). Very broad (*ca.* 1350 G) unresolved esr spectra similar to those from γ-irradiated perfluorocarbons at 77°K[24] indicate that these solvents are decomposed by photolysis of the iodides.

(b) Dissociative Electron Capture. Simple alkyl radicals may be generated by dissociative electron capture by subjecting their dilute solutions in 3MP at 77°K to γ irradiation or photoionization of dissolved TMPD.[6,14,25] These techniques proved unsatisfactory for the present purpose because the detail of the spectra of the several 3-methylpentyl radicals cannot be resolved from the *sec*-3-methylpentyl radical signal resulting from γ irradiation of the matrix or from the $TMPD^+$ signal resulting from the photoionization of TMPD.

(c) Aromatic Photosensitization. Aromatic compounds act as photosensitizers for the production of alkyl radicals in glassy matrices containing methyl or ethyl iodide in ethyl alcohol at 77°K, when exposed to 2900–3400-A radiation.[26,27] In the present work photolysis of 10^{-2} *M* solutions of naphthalene or benzophenone in pure 3I3MP or 1I3MP at 77°K failed to generate esr signals, although the glasses turned yellow, indicating decomposition of the iodide.[21] Similar solutions diluted 3:1 with ethanol and photolyzed at 77°K gave poorly resolved spectra with unequal splittings and probably contained radicals from both the iodides and the alcohol.[28]

In contrast to the pure iodides, undiluted 3-methylpentyl chloride glasses produced esr signals when photolyzed with light absorbed by naphthalene or benzophenone solute. With 3Cl3MP the nine-line signal was that of Figure 2C, with allylic-type splittings of 15 ± 1 G and no indication of a *t*-3-methylpentyl radical which would result from C–Cl rupture.

Photolysis of CH_3I and HI in 3-Methylpentyl Chlorides. Photolysis of 10^{-2}–10^{-3} m*F* of methyl iodide or hydrogen iodide in 3ClMP at 77°K yields six-line spectra identical with those obtained from photolysis of an alkyl iodide or hydrogen iodide in 3MP. After 1 week at 77°K these spectra were unchanged. This signal is attributed to the $CH_3CH_2CH(CH_2Cl)\dot{C}HCH_3$ radical, produced by abstraction of a secondary H by a hot methyl radical or hot hydrogen atom. There was no indication of trapped methyl radicals or $CH_3CH_2CH(\dot{C}H_2)CH_2CH_3$ radicals. Neither was there any indication of a radical with a chlorine atom α or β to the orbital of the unpaired electron. Again this emphasizes the preferential rupture of the *sec*-hydrogen bond in the 3MP structure. Of related interest is the fact that hot methyl radicals from the photolysis of methyl iodide in the gas phase have been shown to abstract H in preference to Cl from chloroethanes.[10]

Photolysis of methyl iodide in a 3Cl3MP glass generated a nine-line spectrum with allylic radical splittings identical with that obtained from the aromatic photosensitized decomposition of 3Cl3MP (Figure 2C). The formation of allylic radicals in these systems is surprising since a *t*-3-methylpentyl iodide or chloride must lose three atoms in the process. Inasmuch as the evidence shows that the secondary C–H bond in 3MP and 3ClMP is especially susceptible to cleavage, the initial act is likely to be the rupture of this bond. There is no spectrum attributable to tertiary chloro radicals, $CH_3CH_2CCl(CH_3)\dot{C}HCH_3$; therefore they must be rapidly removed, plausibly by molecular elimination of HCl to give a stable allyl radical, $CH_3CH{=}C(CH_3)$-$\dot{C}HCH_3$. The observed nine-line pattern has a binomial intensity distribution that is attributable to eight equivalent protons in the two contributing resonance structures of the above allylic radical.

Discussion

The results reported above appear to answer without ambiguity the question posed at the start of the investigation, *i.e.*, they indicate that the free radical formed from 3MP glass by γ radiolysis or hot-atom attack is the secondary 3-methylpentyl radical. In addition, they reveal a systematic selectivity of bond rupture for such reactions in a series of related compounds.

Selectivity of Bond Rupture. The esr spectrum of Figure 1A represents predominantly a single radical. It is probable that if as little as 20% of a second radical were present, it would have been detected. Thus the probability, per hydrogen atom, of loss of a hydrogen atom from the 2-carbon atom must be at least as great as for loss of a tertiary H and ten times as great as for loss of a primary H.

In the case of γ radiolysis, hydrogen-atom loss presumably occurs by decomposition of an excited molecule[29] or by proton transfer or hydrogen transfer.

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[21] This color is believed to be due to a charge-transfer complex, probably RI·HI, and not to I_2 formation (T. Lantz, Ph.D. thesis, University of Wisconsin, 1968).

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[24] R. E. Florin, H. W. Brown, and L. A. Wall, *J. Phys. Chem.*, **66**, 2672 (1962).

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[27] V. V. Ryl'Kov, V. E. Kholmogorov, and A. N. Terenin, *Dokl. Akad. Nauk SSSR*, **165**, 356 (1965).

[28] (a) M. V. Alfimov, I. G. Batekha, and V. A. Smirnov, Abstracts, 8th International Symposium on Free Radicals, Novosibirsk, USSR, 1967, p 67; (b) Kh. S. Bagdasaryan, Z. A. Sinitsyna, V. A. Kondratiev, *ibid.*, p 61.

[29] Neutralization of positive ions when *trapped* electrons undergo thermal decay or photobleaching does not generate free radicals[25] but neutralization by prompt geminate recombination may do so.

$$CH_3CH_2CH(CH_3)CH_2CH_3^* \longrightarrow CH_3\dot{C}HCH(CH_3)CH_2CH_3 + H$$

$$CH_3CH_2CH(CH_3)CH_2CH_3^+ + C_6H_{14} \longrightarrow CH_3\dot{C}HCH(CH_3)CH_2CH_3 + C_6H_{15}^+$$

$$CH_3CH_2CHCH_3CH_2CH_3 + C_6H_{14}^+ \longrightarrow CH_3\dot{C}HCH(CH_3)CH_2CH_3 + C_6H_{15}^+$$

Both excitation and ionization occur by nearly random interaction of the Compton and δ-ray electrons with any of the electrons in a 3MP molecule. Consequently either excitation energy, or positive charge, or both, must migrate to secondary C–H bonds, and rupture these with high selectivity, despite the fact that tertiary bonds are weaker and primary bonds are more plentiful, or, if atom transfer is responsible, the secondary bond must be selectively susceptible to this process.

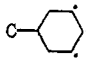
It is tempting to speculate that the observed selective rupture of secondary C–H bonds by different types of processes results from excitation of molecules or radicals to a common excited state which relaxes to the secondary radical as the most stable state. However, it seems improbable that such widely different methods of activation as radiolysis, hot hydrogen atom attack, hot methyl radical attack, and photosensitization by light absorbed by benzene could give this result. Further evidence against the isomerization hypothesis is the fact that each of the four 3-methylpentyl radicals can be formed by γ radiolysis of the corresponding alkyl iodide glass and trapped in the glass at 77°K without isomerizing.

The G value of trapped radicals from the γ radiolysis of 3MP glass is 1.6 (*i.e.*, 1.6 radicals produced/100 ev absorbed), while the total G of ion pairs (assumed to be the same as in the gas phase) is about 3. Thus if all radical formation occurs by proton transfer, about one-half of the positive ions have this fate. The remainder may undergo prompt neutralization in times too short for the proton to transfer. The yield of stably trapped positive charge in the matrix must be equal to that of trapped electrons, and this has been reported as $G(e^-_{tr}) = 0.5 \pm 0.2$[30] and 0.69.[31] There is at present no way of distinguishing radical production by charge transfer from that by excitation.

The fact that the secondary 3-methylpentyl radical is preferentially formed by attack by hot H atoms[8] or hot methyl radicals as well as by γ radiolysis is remarkable because the mechanisms of reaction are necessarily very different. Further, it might be expected that hot atoms and hot radicals, which react because they are born with energies much in excess of the activation energy for reaction with any of the bonds in the molecule, would attack indiscriminately.[32] However, preferential attack on the weaker C–H bonds in gaseous hydrocarbons by hot tritium atoms[33] and on the secondary C–H bonds of gaseous and solid propane by hot CH_3 radicals[32] have been observed. In contrast to the results with 3MP, reported in the present paper, the attack on propane in the solid state is less selective than in the gas. Preferential attack on hydrogen and chlorine bonds in gaseous chlorocarbons[10] by hot methyl radicals occurs in a manner suggesting that it is dependent on the same factors which determine thermal activation energies. The fraction of the hot H or CH_3 which lead to secondary H removal from 3MP at 77°K is significant. For the HI photolysis the quantum yield is 0.1–0.2.[8,34] For attack by hot CH_3 formed by dissociative e⁻ capture ($CH_3I + e^- \rightarrow CH_3 + I^-$), $G(CH_4)$ is 0.3, with G(trapped CH_3) being about 0.8.[25]

Bond-Rupture Rule. The conclusions as to radical structure presented in the Results section and summarized in Table II lead to the following generalizations with respect to the bond rupture which occurs when singly branched alkanes are subjected to γ radiolysis or hot-radical attack in the glassy state at 77°K.

Table II. Electron Spin Resonance Spectra of Branched Alkanes Irradiated at 77°K

Compd	Total no. of lines	Assignment of radicals
2-Methylbutane	10 + (5)	$CC(C)\dot{C}C$ and $C\dot{C}(C)CC$
3-Methylpentane	6	$CCC(C)\dot{C}C$
3-Ethylpentane	6	$(CC)_2C\dot{C}C$
2-Methylpentane	8 + (10)	$(C)_2CC\dot{C}C$ and $(C)_2CCCC$
3-Methylhexane	8	$CCC(C)C\dot{C}C$
3-Methylheptane	8	$CCC(C)CC\dot{C}C$
4-Methylheptane	8	$CCCC(C)C\dot{C}C$
8-Methyloctane	8	$CCC(C)CCC\dot{C}C$
2-Methyloctane	8 + (10)	$(C)_2CCCCC\dot{C}C$ and $(C)_2\dot{C}CCCCCC$
Methylcyclohexane	6	
Cyclohexane	6	

(1) When branching is at the 3 or 4 position, rupture occurs predominantly at a secondary C–H bond of the CH_2CH_3 group of the longest branch of the molecule.

(2) When branching is at the 2 position, major rupture of secondary hydrogens of the CH_2CH_3 group of the longest chain occurs, but a significant yield of rupture at the tertiary hydrogen also occurs.

Simple cyclohexanes show a selectivity of bond rupture similar to that of the branched alkanes. Cyclohexane[2,15,35,36] and methylcyclohexane[37,38] give the same six-line esr spectrum following γ radiolysis in the glassy state at 77°K. Identical spectra are to be expected only if the radical from methylcyclohexane is formed by loss of H from a 3-, 4-, or 5-carbon on the ring. The tertiary H is not lost; a secondary H is lost from a carbon atom at least two removed from the methyl group.

At present there is no satisfactory explanation of the observed selectivity. For the radiolysis it is tempting to assume that it is due to specialized molecular distortion and constraints to vibration and rotation in the glassy state. However, such effects would not be expected to induce selectivity of attack by hot H, Cl, and CH_3. It

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is to be noted that the radical spectra produced by hot fragment attack are better resolved than those produced by radiolysis, and therefore at least as free of contribution from more than one radical.

Comparison with Other Systems. When compounds such as those of Table II are subjected to radiolysis in the gas or liquid, bond rupture is much less selective than in the glassy state.[32,39] It is also of note that the radiolytic radical yield, $G = 1.6$, in 3MP glass is significantly lower than that in liquid 3MP ($G = 7$), which has been demonstrated by scavenger methods.[40] *n*-Alkanes[2,36,41] and doubly branched alkanes such as neopentane,[36] 2,2-dimethylbutane,[2] and 2,3-dimethylpentane,[20] unlike the singly branched compounds discussed in this paper, give rather complex esr spectra following radiolysis at 77°K, suggesting the presence of several radicals.

Radical Production by Iodide Photolysis. The observation that photolysis of any of the 3-methylpentyl iodides in dilute solution in a glassy hydrocarbon produces a radical derived from the hydrocarbon is unexpected. Significant yields of hot-radical abstraction are produced by hot methyl, ethyl, and propyl radicals formed by dissociative electron capture, but these yields decrease with increasing length of the carbon chain.[25] 3-Methylpentyl radicals are sufficiently complex so that it is improbable that they can utilize efficiently either kinetic or vibrational energy for hot processes. Consistent with this expectation, the quantum yield of 2-methylpentyl radicals from the photolysis of a 3-methylpentyl iodide in 2MP is less than 10^{-4}.[42] Possibly this yield results not from hot-radical attack, but from attack by hot H atoms from the photolysis of HI, formed by a disproportionation reaction in the photolysis of $C_6H_{13}I$. The absence of radicals corresponding to the 3-methylpentyl iodide results from caging effects which maximize the recombination of sibling partners.

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Synthesis and Solvolytic Reactivity of 8-Tricyclo[3.2.1.$0^{2,4}$]octane Derivatives[1]

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Abstract: To investigate the stereochemical influence of a cyclopropyl group on carbonium ion formation in a homoallylic position, the four stereoisomers (*i.e.*, *exo-anti*, *exo-syn*, *endo-anti*, and *endo-syn*) of tricyclo[3.2.1.$0^{2,4}$]octan-8-ol were synthesized and their *p*-nitrobenzoates (*p*-NB) or *p*-bromobenzenesulfonates (brosylates) were solvolyzed. Reaction of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene with cyclopropene gave the *endo* Diels–Alder adduct which was dechlorinated with Na-*t*-butyl alcohol and catalytically hydrogenated to give *endo*-8,8-dimethoxytricyclo[3.2.1.$0^{2,4}$]octane. This ketal was hydrolyzed to the *endo* 8-ketone which reduced ($LiAlH_4$ or Pt–H_2) to a mixture of *endo-syn* and *endo-anti* alcohols separated by gas–liquid partition chromatography. The *exo* 8-ketone, available from CuCl-catalyzed addition of diazomethane to 7,7-dimethoxynorbornene followed by hydrolysis, was reduced by $LiAlH_4$ to *exo-syn* alcohol. The kinetics of acetolysis of *endo-syn* brosylate was studied at 165–185° and the *exo-syn* isomer at 95–115°; first-order rate constants at 100° were calculated as 1.9×10^{-7} and 7.0×10^{-5} sec^{-1}, respectively. Products of both compounds were complex and extensively rearranged. As the brosylate of *endo-anti* alcohol was too reactive for isolation, the *p*-nitrobenzoate derivative was solvolyzed in 70% aqueous dioxane and compared to the rate of solvolysis of *anti*-7-norbornenyl *p*-nitrobenzoate; at 100° the rate constants are 2.4×10^{-4} and 1.9×10^{-7} sec^{-1}, respectively. The relative rates for brosylate acetolysis of *exo-anti*, *endo-syn*, *exo-syn*, and *endo-anti* structures are calculated to be 1:10:10^4:10^{12} at 100°, with the *endo-anti* compound 10^3 times more reactive than the already very reactive 7-norbornenyl brosylate. Highly favorable homoconjugative interaction involving considerable σ-type interaction of sp^5-cyclopropyl and *p*-carbonium ion orbitals is demonstrated by these ratios. The two solvolysis products from *endo-anti* *p*-nitrobenzoate (*i.e.*, the rearranged *endo*-tricyclo[3.3.0.$0^{4,6}$]oct-2-yl alcohol and its *p*-nitrobenzoate) correspond, respectively, to stereospecific hydrolysis and ion-pair return of an intermediate ion which shows characteristics expected of a nonclassical 2,4-ethanotrishomocyclopropenyl cation.

The allylic interaction of cyclopropyl ring orbitals with directly adjacent carbonium ion centers, as in solvolysis of cyclopropylcarbinyl derivatives, is well known to result in relatively great chemical reactivities[3] and highly stable cyclopropylcarbinyl cations.[4] Such

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