

Nature of the Undecyl Radicals Formed by γ -Irradiation of CCl_3F /Undecane at 77 K. Evidence on the Physical State of Alkane Aggregates in CCl_3F

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A study is made by EPR spectroscopy of the nature of the undecyl radicals formed by γ -irradiation of CCl_3F /undecane at 77 K. It is observed that at low undecane concentration (e.g., 1 mol %) primary undecyl radicals are very prominent. With increasing undecane concentration, the (relative) contribution of primary undecyl radicals to undecyl formation decreases as a result of intermolecular radical site transfer and at 4–6 mol % undecane in CCl_3F primary undecyl radicals are essentially absent. With further increases in undecane concentration primary undecyl radicals regain some of their prominence in the EPR spectra but only to a limited extent, contributing an estimated 5–10% to the total undecyl radical concentration at for instance 20 mol % undecane. In view of the documented dependence of intermolecular radical site transfer on the molecular alignment in *n*-alkane crystals (Iwasaki, M.; Toriyama, K.; Fukaya, M.; Muto, H.; Nunome, K. *J. Phys. Chem.* **1985**, 89, 5278), the results allow us to conclude that (quite unlike neat undecane) undecane aggregates in CCl_3F do not assume the orthorhombic crystalline structure at cryogenic temperatures, with exception of some aggregates at the highest concentrations investigated. Taking into account general crystallization characteristics of *n*-alkanes, it can be deduced that as a rule undecane aggregates in CCl_3F are in all likelihood amorphous and this conclusion can reasonably be extended to all *n*-alkanes with $n_{\text{C}} \leq 11$ for concentrations below 20 mol %. Thermodynamic as well as kinetic factors are cited as causes for this general absence of crystallization.

Introduction

Trichlorofluoromethane containing various solutes has been used extensively for the formation and trapping of solute radical cations by γ -irradiation at cryogenic temperatures, allowing the study of these cationic intermediates by EPR spectroscopy.¹ In combination with theoretical calculations, such studies have yielded detailed information on the electronic structure of the radical cations concerned. In a separate development it was observed that *n*-alkanes form small aggregates in CCl_3F , aggregates to which positive-hole transfer still takes place efficiently, thus allowing the study of the reaction of *n*-alkane radical cations with their parent molecules.² Such studies provided unambiguous evidence for the occurrence of proton transfer from alkane radical cations to alkane molecules. Moreover, they clearly indicated that in specific cases (viz., for *n*-alkane radical cations in the extended all-trans conformation) the proton transfer is characterized by very pronounced (essentially absolute) donor-site selectivity and that quite in general a clear correlation exists between the electronic structure of the radical cation and the site of proton donation,³ in agreement with previous studies in irradiated SF_6 /alkanes⁴ and zeolite/alkanes⁵ as well as with subsequent studies in γ -irradiated *n*- C_5D_{12} /*n*- C_8H_{18} mixed crystals.⁶ Gas chromatographic analyses on CCl_3F /decane and CCl_3F /undecane after γ -irradiation at 77 K and subsequent melting, on the other hand, have provided quite intriguing information on intrinsic acceptor site selectivity in the proton transfer from alkane radical cations to alkane molecules.⁷ From such studies, it has been concluded that protonation of *n*-alkanes (from alkane radical cations) results in selective formation of secondary C–H protonated alkanes

(essentially no C–C and primary C–H protonation occurs) with a clear preference for protonation of penultimate C–H bonds, an experimental observation that nicely matches the thermodynamic stability (energetics) of the corresponding pentacoordinated alkyl carbonium ions. The preference for penultimate over interior C–H bonds has been confirmed by a study of γ -irradiated heptane/decane/1-chloroheptane crystals.⁸ This study as well as (and in particular) EPR spectroscopic and gas chromatographic investigations of γ -irradiated *n*- C_7H_{16} /*n*- C_8D_{18} and *n*- C_7H_{16} /*n*- C_8H_{18} /1- $\text{C}_6\text{H}_{13}\text{Cl}$ mixed crystals led to the introduction of the concept “structurally determined acceptor site selectivity”,⁹ i.e., acceptor site selectivity resulting from donor site selectivity in combination with structural effects due to the orderly positioning of molecules in the mixed crystals, thus highlighting the role of the crystalline structure in the proton-transfer process. In view of this and of the prominent role irradiated CCl_3F /alkane systems play in the elucidation of the protonation process, information on the physical state of alkane aggregates in CCl_3F appears to be of paramount importance.

Ample information is available on the crystalline structure of neat *n*-alkanes.^{10,11} The *n*-alkanes with carbon numbers $6 \leq n_{\text{C}} \leq 9$ have a triclinic crystal structure and higher *n*-alkanes with an odd number of carbon atoms have an orthorhombic mode of packing. With respect to *n*-alkanes with an even number of carbon atoms, those with carbon numbers C_{10} – C_{24} have a triclinic structure whereas from C_{28} the monoclinic mode of packing is the stable low-temperature form. Both a triclinic and a monoclinic form have been observed with hexacosane. In addition to these structures, many of the *n*-alkanes both odd and even have been reported to exhibit a hexagonal phase just

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below the melting point. The regular alternation of the crystalline structure of long chain *n*-alkanes ($n_C \geq 10$) reflects itself in many properties of these substances in the solid state. From a radiation-chemical point of view, the most important are that the total yield of trapped alkyl radicals in *n*-alkanes irradiated at 77 K also exhibits marked even–odd alternation and that the radical distribution is fundamentally different as evidenced by the corresponding EPR spectra.¹² Even–odd alternation at 77 K of EPR spectra of a series of irradiated *n*-alkanes starting from C₁₀ has been found to be due to prominent chain-end alkyl radical stabilization in the odd members of the series.¹³ The origin of the striking even–odd alternation of the 1-alkyl yield at 77 K has been traced to secondary reactions of alkyl radicals formed by irradiation in the crystalline *n*-alkanes.¹⁴ As a matter of fact, the alternation is due to intermolecular radical site transfer and the marked difference in importance of this process between even and odd *n*-alkanes ($n_C \geq 10$) arises from differences in alignment of neighboring chains in the crystal, resulting from the alternation in crystalline structure. Interchain radical site transfer with radical transformation takes place only in the even homologues (triclinic crystalline structure) resulting in the conversion of chain-end alkyl radicals to (mainly) penultimate radicals, whereas in the odd homologues (orthorhombic mode of packing) this process is prohibited.

It occurred to us that, as a result of the effect of crystalline structure on intermolecular radical site transfer, information on the physical state of alkane aggregates in CCl₃F could possibly be obtained by EPR investigation of the undecyl radicals formed by γ -irradiation of CCl₃F/undecane at 77 K. It has been observed previously that at low (e.g., 1 mol %) undecane concentration the contribution of primary undecyl radicals to undecyl radical formation is quite considerable.^{2b} If these primary undecyl radicals persist at high undecane concentration, then undecane aggregates in CCl₃F can definitely be concluded to have the orthorhombic mode of packing in common with neat undecane. Massive transformation of primary into secondary undecyl radicals by intermolecular radical site transfer with increasing undecane concentration, on the other hand, would rule out an orthorhombic structure.

Experimental Section

Products used in this study, viz. CCl₃F and 1- and 2-bromooctane from Fluka, undecane and *cis*-decalin-*d*₁₈ (99.5 atom % D) from Janssen Chimica, and 3-bromooctane from K&K, were of the highest purity commercially available. Undecane was purified by passing through a column containing silica gel, which had been activated immediately prior to use by heating at 250 °C for 24 h. Solutions, prepared by conventional techniques, were contained in small (3-mm-i.d.) cylindrical tubes made of quartz of Suprasil grade. Samples were deoxygenated by bubbling with argon for 10 min at 0 °C, after which they were carefully sealed and rapidly cooled to 77 K by immersing in liquid nitrogen. Irradiations were performed with ⁶⁰Co γ -rays to a dose of 7.5×10^{19} eV g⁻¹.

The procedure for EPR measurements was largely as described before.¹⁵ Irradiated samples were transferred quickly into a Dewar vessel filled with liquid nitrogen, which was inserted in the cavity of a Bruker ER 200tt EPR spectrometer. EPR absorptions were recorded in the X band of the spectrum at a microwave power of 0.6 mW. The spectra were accumulated 100 times with a BNC-12 minicomputer to improve the signal-to-noise ratio. Spectral simulations were performed with the Bruker WIN-EPR SimFonia program.

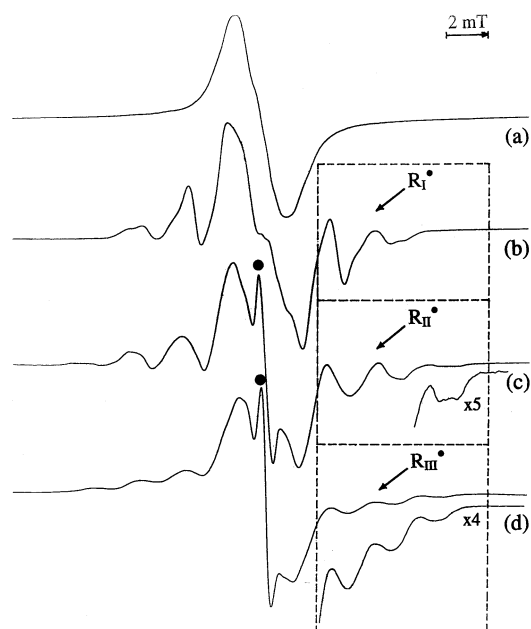


Figure 1. First-derivative EPR spectra obtained after γ -irradiation of neat *cis*-decalin-*d*₁₈ (a) and of *cis*-decalin-*d*₁₈ containing 1 mol % 1-bromooctane (b), 2-bromooctane (c), and 3-bromooctane (d). The dashed rectangles contain spectral features that are highly typical for chain-end (R_I^*), penultimate (R_{II}^*), and interior (R_{III}^*) alkyl radicals, respectively; ● indicates a background absorption.

Results

The nature of the undecyl radicals formed by γ -irradiation of CCl₃F/undecane at 77 K is derived from the appropriate EPR spectra, making use of powder spectra of “authentic” alkyl radicals for spectral analysis. Neutral alkyl radicals derived from *n*-alkanes can be separated into three distinct classes with respect to their EPR spectrum, viz., chain-end ($\cdot\text{CH}_2\text{—CH}_2\text{—CH}_2\cdots$), penultimate ($\text{CH}_3\text{—}\cdot\text{CH—CH}_2\cdots$), and interior ($\cdots\text{—CH}_2\text{—}\cdot\text{CH—CH}_2\cdots$). Powder spectra of authentic chain-end, penultimate, and interior alkyl radicals can be obtained from γ -irradiated *cis*-decalin-*d*₁₈ containing appropriate chloro- and bromoalkanes. The EPR spectrum obtained after γ -irradiation of neat *cis*-decalin-*d*₁₈ consists of a broad unresolved band, which extends over a relatively restricted spectral region as a result of spectral contraction due to deuteration (see Figure 1a). The addition of chloro- and bromoalkanes before irradiation results in a considerable distortion of this unresolved absorption and in the appearance of very characteristic additional EPR absorptions in the lateral regions of the spectra. The additional EPR absorptions are solely due to very specific (solute-dependent) alkyl radicals; these radicals are formed through a process of dissociative electron attachment by the solute chloro- and bromoalkanes.¹⁶ Hole trapping by these compounds is excluded because of the low ionization energy of decalin. Chromatographic analyses have shown that alkyl radicals formed by γ -irradiation of chloro- and bromoalkanes in *cis*- and *trans*-decalin are characteristic for the haloalkane solute and explicitly rule out the occurrence of radical isomerization.¹⁷ The identity of the alkyl radicals observed is thus unambiguously determined by the choice of the chloro- and bromoalkane solutes. The lateral parts of the spectra obtained from γ -irradiated *cis*-decalin-*d*₁₈ containing 1 mol % 1-, 2-, and 3-bromooctane, which are shown in Figure 1b–d, can thus fully be attributed to chain-end (R_I^*), penultimate (R_{II}^*), and interior (R_{III}^*) alkyl radicals, respectively.

The possibility of cancellation of the anisotropic interactions of α -hydrogens is highly relevant with respect to the powder

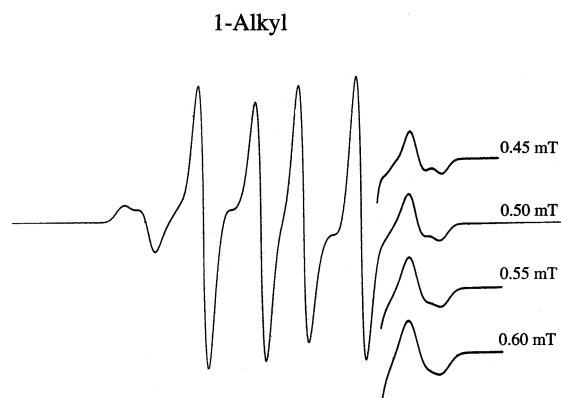


Figure 2. Spectrum of 1-alkyl radicals simulated on the basis of hyperfine coupling constants of ref 13. The spectrum is simulated using the Gaussian type line shape function, with $\Delta H_{\text{ms}} = 0.5$ mT; the effect of different line widths on the outermost anisotropic transition is also shown.

EPR spectra of alkyl radicals. Such annulment is possible for chain-end radicals, but not for penultimate and interior radicals. In alkyl radicals both the isotropic and anisotropic hyperfine interactions with the α -protons are “extensive”, i.e., they affect the paramagnetic absorption to an extent that can clearly be discerned in the powder EPR spectra; in contrast, there is only a large isotropic interaction with the β -protons (anisotropic interactions with the β -protons are much smaller in value). When in 1-alkyl radicals the two α -proton spins are antiparallel, the hyperfine anisotropy largely cancels and relatively sharp intense hyperfine lines result, which are easily discernible in an EPR spectrum. Another specific characteristic of the powder EPR spectrum of 1-alkyl radicals is the outermost transition, which is severely anisotropically broadened because the α -proton spins are parallel and which manifests itself in a first-derivative spectrum as a slightly double-humped curve; (more centrally located anisotropic absorptions are not clearly observable due to spectral interference by the “isotropic” lines). Both features, i.e., the relatively narrow (largely isotropic) lines and the double-humped curve, make the powder EPR spectrum of 1-alkyl radicals easily recognizable;^{18,19} they are clearly discernible in the lateral parts of the spectrum obtained from γ -irradiated *cis*-decalin- d_{18} containing 1 mol % 1-bromooctane (see Figure 1b). The overall appearance of the powder spectrum of 1-alkyl radicals is apparent from the simulated spectra shown in Figure 2. All EPR absorption bands of penultimate and interior n -alkyl radicals are strongly anisotropically broadened because cancellation of the anisotropic hyperfine interaction with the α -proton cannot take place. Unambiguous information on the band shape of the (lateral parts) of the EPR absorption of penultimate and interior alkyl radicals is provided by the spectra of γ -irradiated *cis*-decalin- d_{18} containing 2- and 3-bromooctane (see Figure 1c,d). As is evident from these spectra and from the simulated spectra of penultimate alkyl radicals shown in Figure 3, all absorption bands in these radicals are rather broad. The EPR absorption of interior alkyl radicals is less well resolved than that of penultimate alkyl radicals (see Figure 1c,d); as a result, equally weighted combinations of the experimental powder spectra of authentic penultimate and interior alkyl radicals rather tend to correspond to the spectrum of penultimate radicals and quite considerable fractions of interior radicals may be “hidden” under that of penultimate radicals without seriously affecting the composite spectrum. The spectrum of penultimate and interior alkyl radicals extends over a wider spectral region than that of chain-end radicals, making them detectable in the

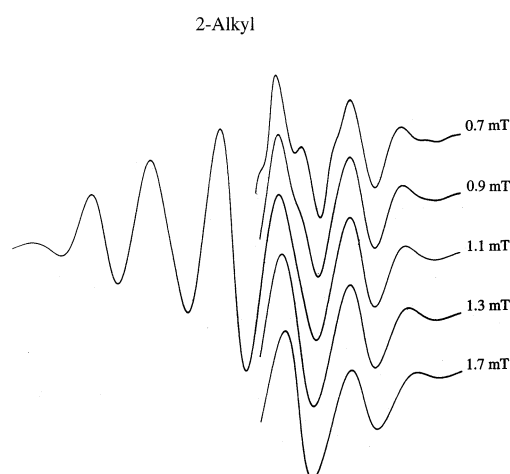


Figure 3. Spectrum of 2-alkyl radicals simulated on the basis of hyperfine coupling constants of ref 13. The spectrum is simulated using the Gaussian type line shape function, with $\Delta H_{\text{ms}} = 1.1$ mT; the effect of different line widths on the right lateral part of the spectrum is also shown.

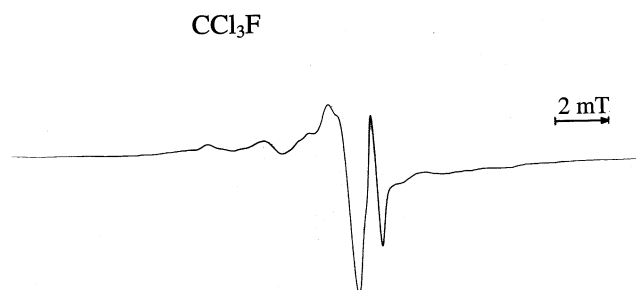


Figure 4. First-derivative EPR spectrum of γ -irradiated neat CCl_3F ; (the main spectral features, i.e., the central asymmetric absorption and “isotropic” line are (largely) due to irradiated Suprasil).

presence of these radicals by careful examination of the region next to the double-humped curve; the overall appearance of convoluted spectra may also provide indication of the presence of secondary alkyl radicals.

The first-derivative EPR spectrum obtained after γ -irradiation of neat CCl_3F is shown in Figure 4. It mainly consists of an asymmetric absorption and a rather narrow singlet; both spectral features are actually due to the irradiated Suprasil tube. Some additional EPR absorption due to γ -irradiated CCl_3F itself is also present, mostly at the left-hand side of the spectrum, but this absorption is rather weak. As a matter of fact, very little EPR absorption is present at the right-hand side of the singlet Suprasil line (clearly marked in the CCl_3F /undecane spectra as “background absorption”); for this reason, the information on the nature of the undecyl radicals formed by γ -irradiation of CCl_3F /undecane is derived from this spectral region.

The first-derivative EPR spectrum obtained after γ -irradiation of CCl_3F containing 1 mol % undecane is shown in Figure 5. The outermost lines of the paramagnetic absorption of authentic 1-alkyl radicals obtained by irradiation of 1-bromooctane in *cis*-decalin- d_{18} are also shown (marked “ R_1 ”). From the main spectrum, the presence in the γ -irradiated CCl_3F /undecane system of both undecane radical cations and undecyl radicals can be deduced. In the center, a narrow paramagnetic absorption is present that (if anything) can be described as a badly distorted singlet; this “singlet” can be attributed to undecane radical cations. The right lateral part of the spectrum is due to undecyl radicals, to a large extent 1-undecyl radicals, revealing the double-humped curve and two (of the four) “isotropic” lines.

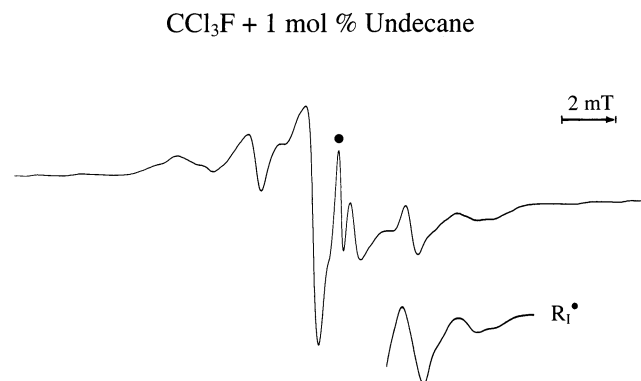


Figure 5. First-derivative EPR spectrum obtained after γ -irradiation of CCl_3F containing 1 mol % undecane. The outermost lines of the powder spectrum of authentic 1-alkyl radicals, obtained by irradiation of *cis*-decalin- d_{18} containing 1 mol % 1-bromooctane, are also shown and marked R_1^\bullet ; ● indicates a background absorption.

The assignment of these features to 1-undecyl radicals can further be confirmed by comparison with the simulated spectrum of 1-alkyl radicals shown in Figure 2. Secondary undecyl radicals cannot clearly be discerned in the spectrum of the γ -irradiated CCl_3F /undecane system, but their presence can certainly not be excluded either.

First-derivative EPR spectra obtained after γ -irradiation of undecane at various (small) concentrations in CCl_3F are shown in Figure 6. The most notable changes with increasing undecane concentration are the appearance of a paramagnetic absorption outside the spectral region of 1-undecyl radicals and a gradual shift of the 1-undecyl radical spectrum away from the baseline, i.e., it becomes superimposed on a broad and (in first-derivative spectral terms and at the right-hand side of the spectra) consistently negative paramagnetic absorption. An additional change is the gradual decrease and disappearance of the spectral absorption attributed to undecane radical cations. From 3 mol %, no clear paramagnetic absorption due to undecane radical cations can be discerned in the spectra; the residual feature at its spectral position correlates nicely in intensity with the narrow singlet background absorption and can thus largely be attributed to irradiated Suprasil.²⁰ The major changes in the spectral characteristics at the right-hand side of the background absorption may be attributed to a gradual increase in importance of secondary undecyl radicals. This is clearly evident from Figure 7a in which the EPR spectrum of γ -irradiated CCl_3F containing 4 mol % undecane is compared with the band shape of the combined paramagnetic absorption of “authentic” penultimate and interior alkyl radicals. As a matter of fact, at this concentration it is hard to point out even a trace of the spectral characteristics of 1-undecyl radicals that were so prominent at lower concentrations; the structure near the center needs not be interpreted as a distortion of the secondary undecyl radical spectrum by the “isotropic” line of 1-undecyl, as it is also present in the simulated spectrum of 2-alkyl radicals (see Figure 7b).

First-derivative EPR spectra obtained after γ -irradiation of undecane at various (medium and high) concentrations in CCl_3F are shown in Figure 8. The most striking change with increasing undecane concentration is the gradual reappearance of the “isotropic” lines due to 1-undecyl radicals. These lines are even more evident in the EPR spectrum of γ -irradiated CCl_3F containing 20 mol % undecane shown in Figure 9; at this concentration, primary undecyl radicals contribute an estimated 5–10% to the total undecyl radical concentration. It is evident thus that there is a tendency to evolve back to a situation in which primary undecyl radicals constitute an important fraction of the undecyl

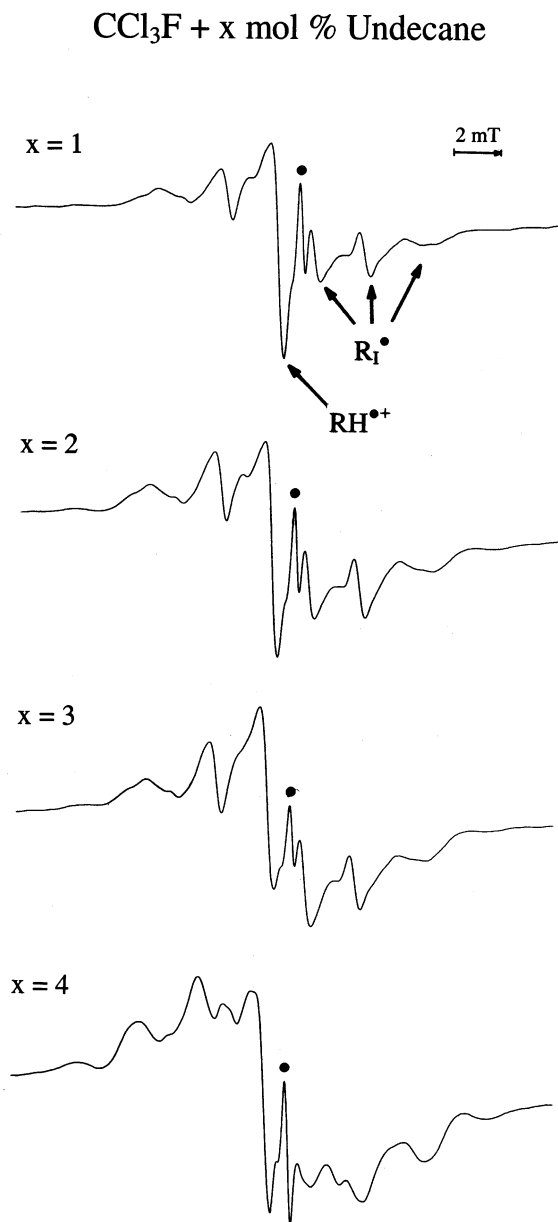
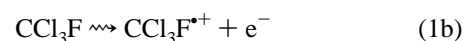


Figure 6. First-derivative EPR spectra obtained after γ -irradiation of undecane at various (small) concentrations in CCl_3F . Spectral features due to undecane radical cations and primary undecyl radicals are, respectively, indicated by $\text{RH}^{\bullet+}$ and R_1^\bullet ; ● indicates a background absorption.

radicals present, which is the case at low concentrations of undecane in CCl_3F and which also applies at the opposite end, i.e., for irradiated neat undecane (see Figure 10).

Discussion

1. Mechanism of Formation of Undecyl Radicals. *a. At Low Undecane Concentration in CCl_3F .* At low concentrations of undecane in the binary CCl_3F /undecane system, absorption of ionizing radiation mainly occurs by trichlorofluoromethane resulting in its excitation and ionization,



leaving the solute alkane largely unaffected as far as direct interaction with the ionizing radiation is concerned. As a result

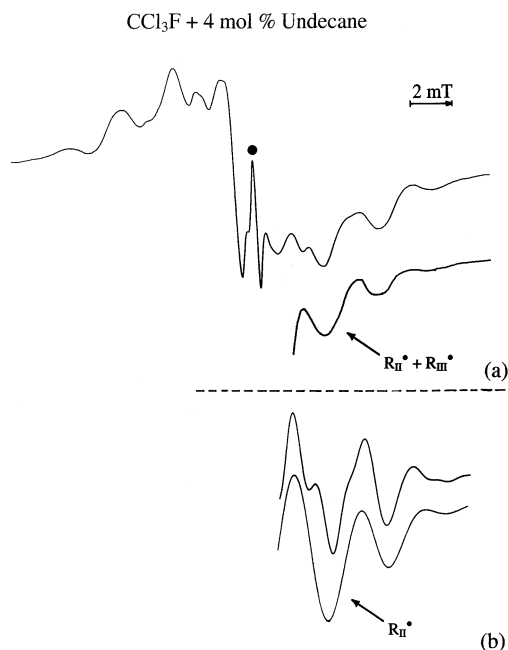


Figure 7. (a) First-derivative EPR spectrum obtained after γ -irradiation of CCl₃F containing 4 mol % undecane. The outermost lines of the composite powder spectrum of authentic penultimate and interior alkyl radicals are also shown and marked R_{II}* + R_{III}*; ● indicates a background absorption. (b) Right lateral part of the spectrum of 2-alkyl radicals simulated on the basis of hyperfine coupling constants of ref 13 using the Gaussian type line shape function with $\Delta H_{ms} = 0.7$ mT and $\Delta H_{ms} = 1.7$ mT, respectively.

of long-range electron tunneling, the positive hole is transferred efficiently from trichlorofluoromethane radical cations to the undecane solute, however, resulting in the neat and selective formation of undecane radical cations.



Though gas-phase ionization energies of CCl₃F and undecane are quite different ("evaluated" ionization energies of 11.68 and 9.56 eV have been reported, respectively),²¹ the excess energy imparted to undecane radical cations may be much lower than this difference suggests because of the possibility of dimer cation formation in irradiated trichlorofluoromethane.²² The stabilization energy due to (CCl₃F)₂^{•+} dimer cation formation is unknown, but it is likely to be similar to that of (CH₃Cl)₂^{•+} dimer cation formation for which a value of 164.7 kJ mol⁻¹ has been reported.²³ Similar stabilization of undecane radical cations by radical cation adduct formation to CCl₃F and by dimer cation formation can be ruled out on the basis of the relative inaccessibility of the semi-occupied molecular orbital (SOMO) in undecane radical cations and (for the adduct formation) by the great difference in ionization energy between CCl₃F and undecane. EPR spectra of alkane radical cations in CCl₃F clearly are incompatible with both adduct and dimer cation formation.

At cryogenic temperatures, undecane radical cations are stable when fully isolated in the CCl₃F matrix, because electrons formed in the ionization process react with trichlorofluoromethane by dissociative electron attachment. It is now well established, however, that alkanes form small aggregates in CCl₃F, aggregates to which positive-hole transfer still occurs efficiently.² The degree of aggregation increases with increasing alkane concentration and at a specific concentration increases quite strongly with increasing chain length of the alkane solute.

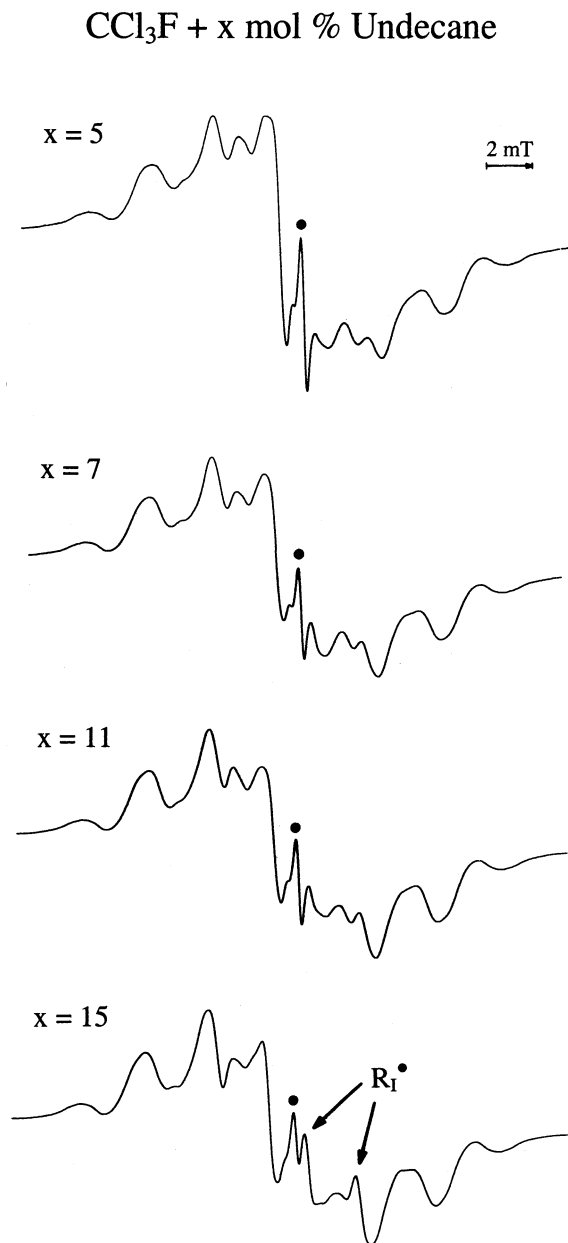
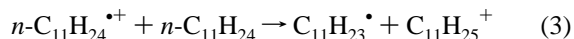


Figure 8. First-derivative EPR spectra obtained after γ -irradiation of undecane at various (medium and high) concentrations in CCl₃F. Spectral features due to primary undecyl radicals are marked R_I*; ● indicates a background absorption.

As a result, proton transfer will take place from undecane radical cations to undecane molecules yielding undecyl radicals and protonated undecanes (undecyl carbonium ions).



Quite in general, the extent of the transformation of alkane radical cations into alkyl carbonium ions by the proton-transfer process increases with increasing alkane concentration. In the case of undecane, this transformation is already substantial at fairly low concentrations, for instance at 1 mol %, as is evidenced by the presence of undecyl radicals at such concentrations. The proton-donor site in the proton transfer from alkane radical cations to alkane molecules has been studied in γ -irradiated CCl₃F/alkane systems and a very high degree of site selectivity has been discovered with respect to this reaction. EPR studies on the nature of alkyl radicals formed at the very

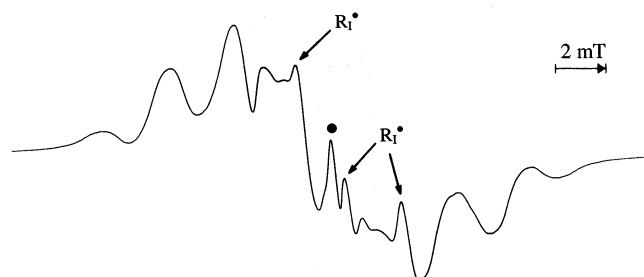
CCl₃F + 20 mol % Undecane

Figure 9. First-derivative EPR spectrum obtained after γ -irradiation of CCl₃F containing 20 mol % undecane. Spectral features due to primary undecyl radicals are indicated by R₁•; ● indicates a background absorption.

Undecane

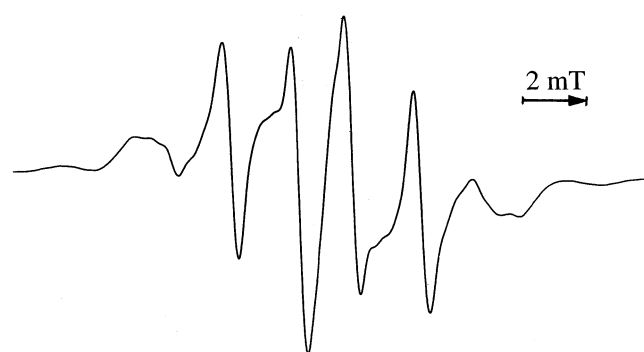
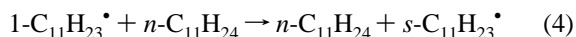


Figure 10. First-derivative EPR spectrum obtained after γ -irradiation of neat undecane.

onset of alkane aggregation clearly indicate that a strict relation exists between the proton-donor site and the electronic structure of the alkane radical cations.³ In the present system, proton transfer leads to extensive formation of primary undecyl radicals, as is evidenced by the prominence of these radicals at low (e.g., 1 mol %) undecane concentration. The relation of this to the electronic structure of the undecane radical cations cannot further be elaborated from the present results, however, because the spectrum of undecane radical cations (observable at low undecane concentration) is badly distorted and thus quite uninformative.

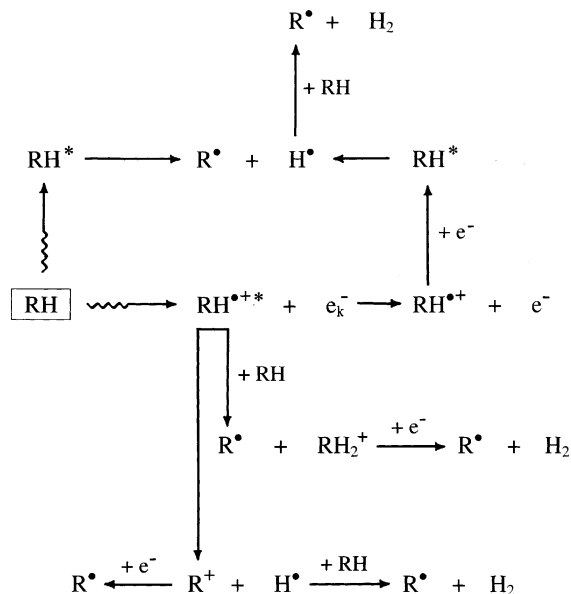
Quite in general, radical transformations become increasingly important with increasing alkane concentration in γ -irradiated CCl₃F/alkanes as a result of intermolecular radical-site transfer, as the alkane aggregates increasingly contain a multitude of alkane molecules. In the present system, primary undecyl radicals are converted into secondary undecyl radicals by this process,



which explains the changes in the observed EPR spectra and the gradual increase in prominence of secondary undecyl radicals as the undecane concentration increases.

b. In Neat Undecane. The formation of neutral alkyl radicals in the radiolysis of solid neat alkanes is depicted in Scheme 1. As indicated by Iwasaki et al.,¹⁴ there are three major *primary* channels for the formation of alkyl radicals in the radiolysis of solid neat alkanes: (i) dissociation of excited alkane radical cations into alkyl carbenium ions and hydrogen atoms, followed

SCHEME 1: Reaction Processes Leading to the Formation of Alkyl Radicals in the Radiolysis of Solid Neat *n*-Alkanes



by neutralization of R⁺ with electrons; (ii) proton transfer from excited alkane radical cations to adjacent alkane molecules with formation of neutral alkyl radicals and alkyl carbonium ions (protonated alkanes) that by electron neutralization are transformed into neutral alkyl radicals and molecular hydrogen;²⁴ and (iii) geminate recombination of alkane radical cations with electrons leading to the formation of electronically excited alkane molecules that dissociate into R• and H•. Electronically excited molecules are also formed by direct interaction of alkane molecules with the ionizing radiation. In analogy with cyclohexane radiolysis, formation of neutral alkyl radicals from electronically excited molecules with energies below the ionization threshold can be expected to be minor, however, as the branching ratio is strongly in favor of molecular (H₂ elimination) rather than radical (H• formation) dissociation at such energies.²⁵ A very important *secondary* channel for formation of neutral alkyl radicals results from the formation of hydrogen atoms in the first and third primary channel, that can abstract a hydrogen atom from neutral alkane molecules.

The proposition by Iwasaki et al.¹⁴ that primary alkyl radicals are mainly formed in the primary channels and secondary alkyl radicals in the secondary channel, though very appealing, must be considered a misconception and is therefore not retained. Indeed, analysis of EPR spectra of irradiated isotopic mixtures of protiated/perdeuterated *n*-alkanes that form orthorhombic crystals have clearly shown that hydrogen atoms produced at the chain end also tend to react at the chain end, i.e., they produce *primary* alkyl radicals by hydrogen abstraction.²⁶ In tridecane-*d*₂₈ containing as little as 2 mol % of the protiated counterpart the ratio of protiated alkyl radicals to total alkyl radicals amounts to about 0.36, which has been attributed to selective H abstraction by D atoms; protiated alkyl radicals present after irradiation of this system are mainly formed by this process. EPR spectral analysis has shown that around 80% of these protiated radicals are chain-end radicals, clearly indicating that (the substantial amounts of) deuterium atoms that migrate do so through the intermolecular boundary region and react mainly in that region. This indicates that the formation of primary alkyl radicals by the secondary process (hydrogen abstraction) is very substantial in irradiated solid *n*-alkanes that

have the orthorhombic crystalline structure and implies that its counterpart, i.e., the formation of secondary alkyl radicals by the primary processes must also be substantial, as the content of chain-end alkyl radicals after irradiation at 4 and 77 K of neat protiated odd *n*-alkanes ($n_C > 10$) amounts to "only" about 35–40 and 40–45%, respectively, regardless of chain length.¹⁴ (The content of chain-end alkyl radicals in corresponding neat protiated even alkanes after irradiation at 4 and 77 K is much lower, viz., 20–25% and about 5–8% respectively; these lower contributions have been attributed to intermolecular radical site transfer).

The fact that a considerable fraction of the secondary alkyl radicals are formed in the primary reaction channels must not be considered surprising. As a matter of fact, all three reaction channels are likely to yield secondary radicals.

(i) Dissociation of vibrationally excited alkane radical cations that are in their electronic ground state may well mainly yield primary alkyl carbenium ions, but a quite different dissociation pattern in all likelihood applies to electronically excited cations. In alkane radical cations a number of electronically excited states exist, which may originate from the transition of an electron from a lower-lying molecular orbital to the semi-occupied molecular orbital (SOMO), which is the highest-occupied molecular orbital (HOMO) in the ground-state ion. Such transitions are at the origin of the electronic absorption of alkane radical cations in the visible and near-infrared.²⁷ The removal by irradiation of an electron in alkanes from lower-lying molecular orbitals clearly also results in the formation of such electronically excited radical cations. For obvious reasons, many of the lower-lying molecular orbitals will contribute to C–H bonding at various sites in the molecule and removal will result in unpaired-electron and positive-hole density at those sites²⁸ allowing dissociation at and proton transfer from such positions.

(ii) Proton transfer to adjacent alkane molecules from alkane radical cations that are in their electronic ground state is not very efficient in neat *n*-alkane crystals.⁹ This results from the fact that in such crystals planar chain-end C–H bonds in alkane radical cations, in which appreciable unpaired-electron and positive-hole density resides, are in close contact to primary C–H bonds in alkane molecules only and from the fact that the proton affinity for primary C–H protonation is much lower than that for secondary C–H protonation. Proton transfer from electronically excited alkane radical cations to and from penultimate and interior positions appears a much more efficient process and this results in formation of secondary alkyl radicals, both directly by the proton-transfer process and by neutralization of the pentacoordinated carbonium ions by electrons. It should be mentioned at this point that it has been argued before that proton-transfer involving ground-state radical cations is too slow to compete with geminate radical cation–electron recombination and that evidence has been presented for a rapid proton-transfer reaction involving excited radical cations.^{29,30}

(iii) Radical dissociation of electronically excited alkane molecules is likely to result mainly in the formation of secondary alkyl radicals. As clearly shown by the photolysis of liquid pentane at 147 nm, the radical dissociation process with formation of hydrogen atoms yields mainly secondary alkyl radicals, in accordance with the order of the homolytic bond dissociation energies of the respective C–H bonds.³¹

c. At Medium and High Undecane Concentration in CCl₃F. The radiolysis of undecane at medium and high concentration in CCl₃F differs from that at low concentration in two important aspects. (i) As the concentration of undecane increases, direct interaction of the ionizing radiation with undecane becomes

more important relative to positive-hole transfer from CCl₃F^{•+}. As a result, the excess energy imparted upon ionization of undecane will on average undoubtedly increase. (ii) Increases in undecane concentration are most likely associated with increases in the size of the undecane aggregates. As the size of the clusters increases, electrons formed by direct ionization of undecane are more likely to be thermalized before they escape the cluster and enter the CCl₃F matrix. As a consequence, the importance of geminate electron recombination (with undecane radical cations and undecyl carbenium and carbonium ions) will increase relative to electron trapping (as chloride ions) by reaction with the CCl₃F matrix. Overall, the radiolysis of CCl₃F/undecane (with respect to undecyl formation) will with increasing undecane concentration start to resemble that of neat undecane, while still partly retaining the typical characteristics of the (low concentration) CCl₃F/undecane system. Any change in radical distribution resulting from the changes in the fundamental radiolytic mechanism of CCl₃F/undecane with increasing undecane concentration is masked, however, by the intermolecular radical-site transfer-process that transforms primary into secondary undecyl radicals and is therefore not observed experimentally.

2. Origin of the Difference in Undecyl Radical Distribution between CCl₃F/Undecane (medium and high undecane concentration) and Neat Undecane. It is observed that at low undecane concentrations (e.g., 1 mol %) the contribution of primary undecyl radicals to undecyl radical formation is quite extensive. With increasing undecane concentration, the prominence of primary undecyl radicals decreases as a result of intermolecular radical site transfer (reaction 4) and at medium and high concentrations of undecane in CCl₃F primary undecyl radicals are either essentially absent after irradiation (i.e., at 4–6 mol %) or present only as a small fraction of the total undecyl radical yield (e.g., about 5–10% at 20 mol % undecane). In contrast, in irradiated neat undecane they constitute a very large fraction of the undecyl radical yield as is evident from Figure 10. It has been estimated that the R_p[•] content in odd *n*-alkanes irradiated at 77 K amounts to about 40–45% of trapped alkyl radicals, irrespective of the chain length of the *n*-alkane.¹⁴

The difference in radical distribution between γ -irradiated CCl₃F/undecane and neat undecane cannot be due to differences in the fundamental radiolytic mechanism, but must result from differences in the physical state of the undecane aggregates vs. neat undecane that affect the radical distribution in a very specific way. Indeed, it can easily be argued that from a purely radiolytic point of view formation of secondary undecyl radicals is favored for neat undecane compared to CCl₃F/undecane. The two systems differ basically in two important ways. (i) In neat undecane direct interaction of the ionizing radiation with undecane molecules is paramount, whereas in CCl₃F/undecane (at low undecane concentration) positive-hole transfer from CCl₃F^{•+} to undecane is the main initiator of chemical reactions leading to the formation of undecyl radicals. The latter mechanism results in much softer ionization, with much less excess energy being imparted upon ionization. (ii) In CCl₃F/undecane electrons are trapped (as chloride ions) by reaction with the CCl₃F matrix whereas in neat undecane they are not, resulting as a rule in geminate electron recombination (with undecane radical cations and undecyl carbenium and carbonium ions). Though with increasing undecane concentration the radiolysis of CCl₃F/undecane (with respect to undecyl formation) more and more resembles that of neat undecane, it most certainly still partly retains the typical characteristics of the (low concentration) CCl₃F/undecane system. From the above discus-

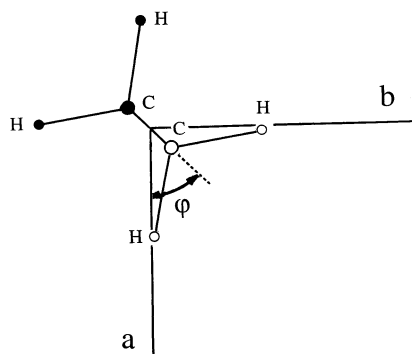


Figure 11. Angle of inclination of the molecular plane to the *ac*-plane of the crystal.

sion on the radiolytic processes, it is evident that the two fundamental radiolytic differences between undecane and CCl_3F /undecane are conducive to a greater prominence of secondary undecyl radicals in neat undecane. Quite the contrary is observed experimentally. It is obvious therefore that it is not the intrinsic radiolytic mechanism but rather the physical state of the respective systems under the conditions of the irradiation, that must be at the origin of the greater prominence of primary undecyl radicals in neat undecane vs in CCl_3F /undecane at medium and high undecane concentration.

Neat undecane at 77 K undoubtedly is crystalline. In common with other odd *n*-alkanes with $n_C \geq 11$, undecane crystallizes in the orthorhombic system at low temperature, with the molecular chain axis perpendicular to the *ab*-plane of the unit cell. In orthorhombic *n*-alkane crystals the angle of inclination of the plane of the alkane molecules, which are in the extended all-trans conformation, to the *ac*-plane of the crystal is close to 45° as depicted in Figure 11; (values of $48^\circ \pm 5^\circ$ ^{10a} and 49° ^{11b} have been reported for the angle, ϕ , though a much lower value 23° – 30° is also cited in a much older publication by Müller^{32a}). The molecular packing in neat undecane, as derived from orthorhombic packing arrangements in various *n*-alkanes and *n*-alkane mixtures^{10a,11b,32} and from specific information on the crystalline structure of undecane by Norman and Mathisen,^{10b} is depicted (in an idealized way) in Figure 12. From this *ab*-projection, a structural diagram showing the molecular packing in undecane crystals as a projection on a diametrical plane, *dc*, that forms an angle of 45° with the *ac* and *bc* planes of the crystal, can easily be constructed. This diagram, which gives considerable information on the distances and directional matching of the various bonds and orbitals, is shown in Figure 13.

The molecular packing of undecane is conducive to primary undecyl radical formation and stabilization for two important reasons. (i) Toriyama et al.²⁶ and Muto et al.³³ have clearly shown that hydrogen/deuterium atoms formed in the primary processes tend to migrate preferentially through the intermolecular boundary region and react mainly in that region. In orthorhombic crystals such migrating hydrogen/deuterium atoms mainly abstract *primary* hydrogen atoms (at least for about 80%), despite the fact that bond strengths of primary C–H bonds are considerably greater than that of secondary C–H bonds. The origin of this clearly can be traced back to the much greater accessibility of primary than of secondary C–H bonds from the intermolecular boundary region in such crystals. (ii) Iwasaki et al.¹⁴ have pointed out that intermolecular radical site transfer, which transforms primary into secondary alkyl radicals, depends in a quite decisive way on the alignment of the neighboring chains and that the orthorhombic crystalline structure is not

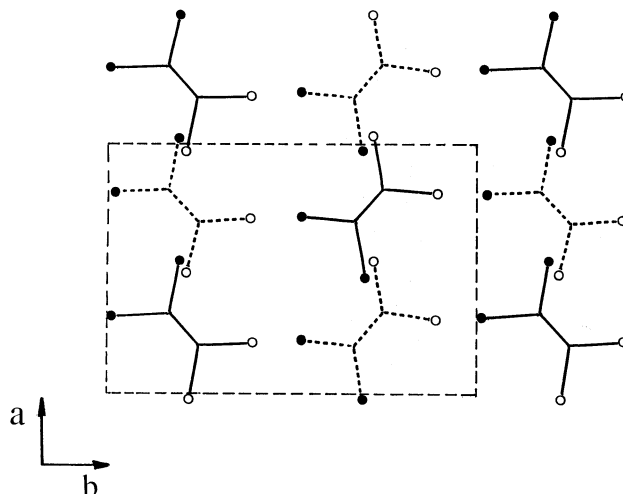


Figure 12. Idealized and highly schematic representation of the molecular packing in neat undecane, depicted as an *ab*-projection. (Solid lines represent upper layer and dashed lines lower layer along the *c*-axis). Adapted according to ref 32b.

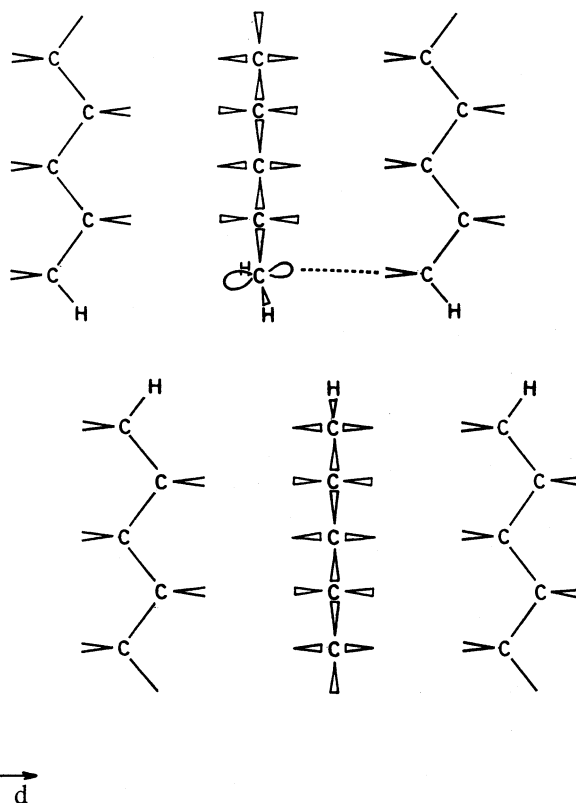


Figure 13. Structural diagram showing the molecular packing in undecane crystals as a projection on a diametrical plane, *dc*, that forms an angle of 45° with the *ac* and *bc* planes of the crystal.

conductive to such transformations. In orthorhombic crystals, the nearest neighboring C–H bond (of adjacent molecules) to a primary radical site belongs to a (chain-end) methyl group as can clearly be seen in Figure 13. Secondary C–H bonds of methylene groups at penultimate positions are situated at a considerably greater distance and thus cannot be considered in direct contact. It has also been argued that the directional matching of the unpaired-electron orbital of a primary radical site to penultimate C–H bonds in the neighboring chain is unfavorable in an orthorhombic crystal.¹⁴ All this undoubtedly affects the rate of the interchain radical site transfer and thus the transformation of primary into secondary radicals.

The major observation in the present work is that at medium and high concentrations of undecane in CCl₃F primary undecyl radicals are either essentially absent (i.e., at 4–6 mol %) or present only as a small fraction of the total amount of undecyl radicals (e.g., about 5–10% at 20 mol % undecane). Intermolecular radical site transfer clearly takes place efficiently in the undecane aggregates, as is evidenced by the transformation of primary into secondary undecyl radicals in the 1–4 mol % concentration range. On the basis of the arguments presented, it can therefore be concluded that at all those concentrations undecane aggregates in CCl₃F as a rule do not crystallize in the orthorhombic system; (a minority of undecane aggregates appears to assume an orthorhombic structure with increasing undecane concentration, very modestly starting from 7 mol %).

A small note should be added on intramolecular radical site transfer (radical isomerization) and its potential role in the radical transformation processes. It has been argued that intramolecular radical site transfer cannot account for transformation of primary into secondary radicals in *n*-alkane crystals, because the directional matching of the unpaired-electron orbital to the adjacent penultimate C–H bonds (within the radical) is unfavorable.¹⁴ EPR results on γ -irradiated CCl₃F/heptane^{3a} and pentane-*d*₁₂/octane⁶ bear this out, as they have clearly shown that primary alkyl radicals when sufficiently isolated do not transform into secondary alkyl radicals. The concentration dependence of the transformation of primary into secondary undecyl radicals in γ -irradiated CCl₃F/undecane at low undecane concentration (1–4 mol %) in the present study is also in clear contradiction with an attribution to an intramolecular transformation process.

It might intuitively be expected from the above discussion that in liquid *n*-alkanes transformation of primary into secondary alkyl radicals is complete and that during irradiation only secondary radicals are observed. After all, in liquid *n*-alkanes there are no structural factors that favor hydrogen abstraction (by hydrogen atoms) from primary rather than secondary C–H bonds or that hinder the transformation of primary into secondary alkyl radicals by intermolecular radical site transfer. In a time-resolved EPR study of short-lived alkyl radicals in pulse radiolysis of liquid *n*-alkanes no chain-end radicals were observed. Attempts to observe by pulsed EPR chain-end radicals produced photolytically using a well-established method also gave negative results, however. The absence of signals from chain-end radicals in spin-echo spectra has been attributed to rapid T₂ spin relaxation in these species.^{29d} Continuous-wave EPR has been used to observe alkyl radicals in liquid hydrocarbons during irradiation with 2.8 MeV electrons in the classical study by Fessenden and Schuler.^{34a} The general conclusion from this study is that chain-end radicals are present, but that their contribution to the total radical yield is much lower than statistically expected. A similar conclusion is reached from a study by the radioiodine scavenging method on the distribution of radical species produced during radiolysis of liquid butane.^{34b} The reason for the observation of chain-end radicals despite the fact that they are thermodynamically less stable and that there are no structural factors that inhibit their transformation into secondary radicals appears obvious. In studies on alkyl radicals during irradiation of liquid alkanes, kinetic considerations must also be taken into account. The process of radical transformation by intermolecular radical site transfer is not “immediate” and certainly not complete in irradiated liquid alkanes, hence the presence of (statistically less than expected) chain-end radicals during irradiation.

3. Physical State of *n*-Alkane Aggregates in CCl₃F. The results presented in this paper clearly show that over the

concentration range from 1 to 20 mol % (quite unlike neat undecane) undecane aggregates in CCl₃F as a rule do not crystallize in the orthorhombic system. Quite likely, the aggregates are amorphous with no specific structure at all. This generalization can be made on the basis of well-known characteristics of the *n*-alkane crystallization process. A very important point in this regard is the fact that an anomalous crystalline structure has repeatedly been observed for even numbered *n*-alkanes, but never for the odd *n*-alkanes, the anomaly consisting in the fact that even *n*-alkanes assume an orthorhombic crystalline structure instead of the proper triclinic or monoclinic one. It has repeatedly been reported that addition of a few percent of neighboring homologues converts the triclinic and monoclinic forms, observed with even *n*-alkanes, into an orthorhombic form.^{10a,35,36} Even in mixtures of close (near equal chain length) even *n*-alkanes, that both have triclinic or monoclinic crystal structures for the neat alkanes, the crystal structure is orthorhombic over much of the binary composition range.^{30,32b,35} It appears reasonable therefore to accept that the undecane molecules, for which the natural inclination is crystallization into an orthorhombic structure, do not assume a triclinic or monoclinic form as aggregates in CCl₃F as this would be directly against the general trend observed for crystallization of *n*-alkanes. Since the EPR results presented clearly rule out that most or all (depending on concentration) of the undecane aggregates in CCl₃F are present as tiny orthorhombic crystals, the evident conclusion appears that they are amorphous.

The absence of crystallization of alkane aggregates in CCl₃F may reasonably be generalized to all *n*-alkanes with $n_C \leq 11$ in the concentration range below 20 mol %. As the extent of aggregation at a particular concentration increases with increasing chain length of the alkane solute,² aggregates of *n*-alkanes with $n_C \leq 10$ can at a particular concentration reasonably be expected to be smaller than those of undecane. On the basis of this and of the rationalization of the absence of crystallization of alkane aggregates in CCl₃F presented below, an amorphous state is *a fortiori* expected for all *n*-alkane aggregates with $n_C \leq 10$. It is not possible to investigate this by EPR spectroscopy as done in the present work for CCl₃F/undecane, because all neat *n*-alkanes with $6 \leq n_C \leq 10$ have a triclinic mode of packing at cryogenic temperatures, which allows the occurrence of radical transformation by intermolecular radical site transfer in the crystalline state.

Absence of crystallization in alkane aggregates in CCl₃F may have both a thermodynamic and a kinetic origin. To put things into perspective, it seems appropriate to consider first in some detail the crystallization process of neat *n*-alkanes (and of liquids in general). Crystallization commences at one or more nucleation points, termed “nuclei”, as a result of the accidental alignment of a sufficient number of alkane molecules causing a decrease in energy (enthalpy) that more than offsets the decrease in entropy with respect to the free energy (Gibbs free energy) of the system. From the initial nucleation point(s), crystallization proceeds rapidly as adjacent alkane molecules are locked in position by the nuclei, resulting in formation of a monocrystal or of a number of tiny crystallites that constitute a polycrystalline *n*-alkane. As a matter of fact, the art of making monocrystals of *n*-alkanes consists of putting them in a container with a thin capillary tube at the bottom and lowering them very slowly into a cooling bath, so that crystallization proceeds solely from the one nucleus created at the bottom tip.³⁷

The absence of crystallization in alkane aggregates in CCl₃F may have a thermodynamic origin, because the aggregates may lack the critical size for nucleation. The number of alkanes that

must be aligned properly to decrease the energy sufficiently to compensate for the decrease in entropy (and thus the minimal size for the alkane aggregates to allow crystallization) decreases with temperature, but the lowest temperature that matters is not so much the temperature of observation (*in casu* 77 K) as the temperature at which the viscosity of the system reaches magnitudes as to seriously hinder translational and rotational movement of the alkane molecules. At the lower concentrations of alkanes such as heptane and octane in CCl_3F the alkane molecules are essentially monomolecularly dispersed through the system, as is evidenced by the fact that the only paramagnetic species observed after γ -irradiation are the corresponding radical cations.^{2b} EPR results on γ -irradiated CCl_3F /heptane also show that, when it commences, aggregation starts very modestly involving only two or a few molecules; this is evidenced by the fact that at the onset only 1-heptyl radicals are observed, clearly ruling out intermolecular radical site transfer and thus larger aggregates.^{3a} It has clearly been established that aggregation does not only increase with concentration, but that it also becomes more pronounced at a specific concentration with increasing chain length of the alkane solute.² However, even in the present CCl_3F /undecane system undecane radical cations appear to be present at the lowest concentrations and at such concentrations radical transformation by intermolecular radical site transfer is far from complete, as is evidenced by the presence (and prominence) of primary undecyl radicals in the system. In other words, the size of the undecane aggregates at the lowest concentrations (e.g., 1 mol %) must be quite limited (only a few molecules) and may be insufficient for nucleation as the alignment of only a few molecules proportionally does not cause the same lowering in energy as proper alignment of a larger group.

The kinetic origin of the absence of crystallization in alkane aggregates may be put in perspective by comparing the size of the alkane aggregates with that of the crystallites in polycrystalline *n*-alkanes. When the size of the alkane aggregates in CCl_3F is smaller than that of the crystallites in polycrystalline neat *n*-alkanes, which undoubtedly is the case at low concentrations of alkanes in CCl_3F , then a much larger number of nuclei must be created for full crystallization, as each individual nucleus only contributes to crystallization in the aggregate in which it is formed. The creation of these nuclei clearly is the rate-determining step in the crystallization process. It is a well-known fact that liquids may be supercooled much below their freezing point and that crystallization of such liquids proceeds very rapidly once it starts (either spontaneously or by addition of a "seed crystal" of the substance). Nucleation is a random process as it requires the accidental alignment of molecules and will thus occur on vastly different time scales in the numerous alkane aggregates in CCl_3F . As a consequence, only part of them may crystallize upon rapid cooling for kinetic rather than for thermodynamic reasons. The fact that at the higher concentrations of undecane in CCl_3F (e.g., 15 and 20 mol %) primary undecyl radicals start to reappear is clear evidence that some of the aggregates have indeed assumed an orthorhombic structure. The contribution of 1-undecyl radicals to the total undecyl spectrum at such concentrations is still limited, however, constituting an estimated 5–10% of the total at 20 mol % undecane. We favor the thermodynamic origin for the absence of crystallization in alkane aggregates in CCl_3F at the lower concentrations and the kinetic origin at higher concentrations. It appears evident to us that further EPR studies of γ -irradiated CCl_3F containing undecane or some higher odd *n*-alkane, with a systematic study of the effect of the rate of cooling at various

concentrations, could yield valuable fundamental information on the crystallization process.

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