Dependence on Conformation of the Site of Proton Transfer from Alkane Radical Cations. Nature of the Octyl Radicals Formed by Proton Transfer from Octane Radical Cations to Octane Molecules in CCl₃F Matrices at 77 K

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A study has been made by EPR spectrometry of octane radical cations and octyl radicals formed by γ-irradiation of octane at various concentrations in CCl₃F. The EPR spectrum at very low concentration (≤ 0.5 mol%) is essentially due to octane radical cations, which are largely in the gauche-at-C-2 conformation with large unpaired-electron density on one in-plane chain-end hydrogen and one in-plane hydrogen attached to C-2. Superimposed on the radical cation spectrum, a low intensity spectrum due to octyl radicals appears above 0.5 mol%. The signal intensity and relative contribution to the paramagnetic absorption of this spectrum increase very strongly with increasing concentration of octane. It is observed that at low octane concentration both primary and secondary octyl radicals are present in irradiated CCl₃F–octane systems, and this is true from the very first appearance of octyl radicals in such systems. At higher concentration, secondary octyl radicals become very much the dominant neutral radical species. The results indicate that: (*i*) primary and secondary octyl radicals are formed by proton transfer from octane radical cations (in the gauche-at-C-2 conformation) to octane molecules; (*ii*) with increasing concentration of octane in CCl₃F, the size of octane aggregates increases gradually from two-molecule to higher-order clusters, resulting in intermolecular radical site transfer with transformation of primary into secondary octyl radicals. The results confirm that the nature of the alkyl radicals formed by proton transfer from alkane radical cations to alkane molecules is related to the structure of the semi-occupied molecular orbital of the parent cation.

The elucidation of the ionic reactions of saturated hydrocarbons and of their characteristics are of fundamental importance for a proper understanding of ionic processes in general. Ionic reactions of alkanes have been extensively studied by mass spectrometry, but such studies often fail to provide structural information. An alternative to mass spectrometry is radiation chemistry which can provide structural information much more easily, but in which it is often difficult to distinguish between the different processes occurring. The radiolysis of alkanes and other classes of compounds has been investigated extensively and yields of stable radiolysis products are known quite accurately for some well-studied systems, but the detailed mechanism of the formation of these products is still open to considerable debate. One general aspect of the radiation chemistry of alkanes is the apparent lack of site-selectivity in the overall radiolytic process. Invariably, the number of different radiolytic products is quite large, giving an impression of more or less random energy deposition, bond scission and reaction. Lack of site-selectivity in the ionic and radical reactions of saturated hydrocarbons, i.e. molecules that contain no functional groups, may intuitively appear natural, especially for the linear alkanes, but there are experimental indications to the contrary. It may well be that the lack of site-selectivity in the radiolysis of alkanes is due much more to the great diversity of reaction processes occurring than to lack of site-selectivity in the individual processes. One ionic reaction, which is probably characterised by a high degree of site-selectivity, is the proton transfer from alkane radical cations to alkane molecules.

The question of whether hydrogen and/or proton transfer between alkane radical cations and alkane molecules takes place widely in the condensed phase radiolysis of higher alkanes has long been an important unsolved problem in radiation chemistry. Conclusive evidence for the occurrence of hydrogen/proton transfer between higher alkanes and their cations has however recently been obtained by X-irradiation of C₄–C₈

n-alkanes adsorbed on synthetic zeolites at 4 K[1] and by γ-irradiation of various alkanes in CCl₃F matrices at 77 K,[2] through observation of the appearance and increasing importance of neutral alkyl radicals with increasing concentration of alkane solute. The relation between the nature of the alkyl radicals formed and the structure of the semi-occupied molecular orbital (SOMO) of the parent cation has been studied for hexane and octane in synthetic zeolites[1] and for heptane in CCl₃F.[3] These studies indicate that reaction (1)

$$RH^{\cdot +} + RH \longrightarrow R^{\cdot} + RH_2^{+} \qquad (1)$$
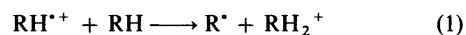
essentially occurs by proton transfer and not by hydrogen abstraction for higher alkanes and point to a dependence on electronic structure of the site of proton transfer from such alkane radical cations. Indeed, the cations in both studies are in the extended conformation with high unpaired-electron density in the carbon–carbon σ bonds as well as the two in-plane chain-end carbon–hydrogen bonds and 1-alkyl radicals are very selectively formed by proton transfer. These results are in agreement with an earlier postulate, stating that a high unpaired-electron density in a particular carbon–hydrogen bond leads to deprotonation at that site, giving rise to a particular alkyl radical.[4b,c] This postulate is essentially based on chemical intuition, but derived some experimental justification at the time of formulation from the fact that the electronic structures of propane and isobutane cations in SF₆ and CCl₂FCF₂Cl are different and that this difference is reflected in the site preference of the cation deprotonation reactions upon warming.

The actual experimental evidence at present available on the relation between the site of deprotonation of alkane radical cations and the electronic structure of these cations is still very limited. Thermal conversion studies of alkane radical cations into alkyl radicals yield quite ambiguous results on this matter.[4]
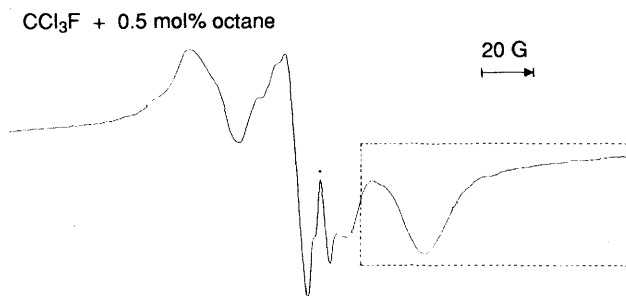
CCl₃F + 0.5 mol% octane

Fig. 1 First derivative EPR spectrum obtained after irradiation of trichlorofluoromethane, containing 0.5 mol% octane; (● indicates a background signal). The dashed line indicates the spectral region in which changes in the spectrum as a result of changes in the octane concentration are most easily detected.
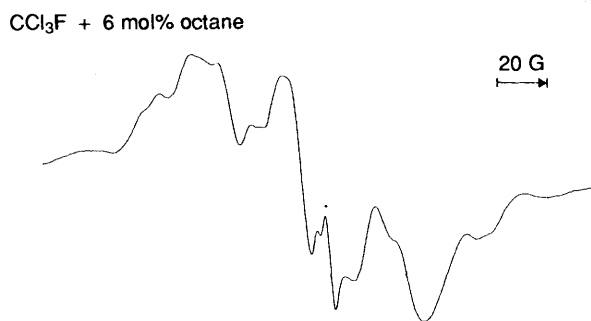
CCl₃F + 6 mol% octane

Fig. 2 First derivative EPR spectrum obtained after irradiation of octane at 6 mol% in trichlorofluoromethane; (● indicates a background signal)

Significant yields of secondary alkyl radicals have repeatedly been observed upon thermal conversion of alkane radical cations in the extended conformation. In specific instances, secondary radicals are exclusively observed. It has been suggested[3] that the transformation of alkane radical cations into alkyl radicals in such instances is not the result of proton transfer to neutral alkane molecules, but results from neutralisation, e.g. reaction (2).

$$RH^{\cdot +} + Cl^- \longrightarrow R^{\cdot} + HCl \qquad (2)$$
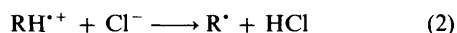
It is quite plausible that the site of deprotonation in such processes would depend on the overall charge distribution in the alkane radical cation, as the anions would be attracted to the position of maximum charge density. For linear alkane radical cations, secondary alkyl radicals would thus be formed preferentially by this process, as the charge density increases towards the cationic centre.[4a] Since reaction (2) is also a deprotonation reaction, it appeared necessary to reformulate the postulate quite specifically in terms of proton transfer to alkane molecules.[3] In its present form it states: 'The nature of alkyl radicals formed by proton transfer from alkane radical cations to alkane molecules is related to the structure of the semi-occupied molecular orbital of the parent cation. A high unpaired-electron density in a particular carbon–hydrogen bond leads to proton transfer from that site, giving rise to a particular alkyl radical'. All experimental results, for which the transformation of alkane radical cations into alkyl radicals can be unambiguously attributed to proton transfer to alkane molecules, are consistent with this statement. At present, experimental evidence only exists, however, for linear alkane radical cations in the extended conformation. It is the purpose of the present paper to extend such evidence to other conformations of n-alkane radical cations.

CCl₃F–alkane systems are ideally suited to study proton transfer from alkane radical cations to alkane molecules. In CCl₃F matrices at cryogenic temperatures, alkane solutes form

small aggregates to which hole transfer still occurs efficiently upon γ-irradiation.[2] Moreover, linear alkane radical cations are not always in the extended conformation in this matrix.[4i] Octane radical cations exist largely in a conformation resulting from one 120° rotation around C-2–C-3 in the extended conformer. Interestingly, the electronic structure of this conformer differs from that of the extended conformer. The gauche-at-C-2 conformer has large unpaired-electron density on one in-plane chain-end hydrogen and one in-plane hydrogen attached to C-2. It appeared of great interest therefore to investigate whether this difference is reflected in the site preference of proton transfer to alkane molecules from such cations. For this purpose, a detailed investigation was made by EPR spectrometry of the nature of the octyl radicals formed by proton transfer from octane radical cations to octane molecules in CCl₃F matrices at 77 K. Special emphasis was placed on observing these octyl radicals at low octane concentration, so as to avoid the complicating effects of intermolecular radical site transfer reactions.

Experimental

Products used in this study were octane from Janssen Chimica and trichlorofluoromethane from Fluka. These products were of the highest purity commercially available and were dried on molecular sieve 4 Å (Aldrich) prior to use. All solutions were deoxygenated in cylindrical Suprasil tubes by bubbling with argon for 15 min after which they were carefully sealed. Irradiations were performed at liquid nitrogen temperature with cobalt-60 γ-rays at the Institute for Radioelements at Fleurus. The absorbed dose was 7.5×10^{19} eV g⁻¹ in all cases. The EPR analysis was largely as described before.[2,5] For the observation of EPR spectra at high sensitivity (spectral enlargements), both the detector signal gain and the number of repetitive scans were increased. All spectra were recorded at 77 K.

Results

The EPR spectrum obtained after irradiation of octane at low concentration (0.5 mol%) in CCl₃F is shown in Fig. 1. The spectrum contains a very prominent absorption, associated with the presence of octane in the system, which extends over ca. 140 G. The central part of this absorption is badly distorted by matrix absorption (i.e. absorption of the irradiated matrix) and by spurious lines from irradiated Suprasil. The left lateral part is also distorted, although to a much lesser extent. The right lateral part, on the other hand, is not distorted to any appreciable extent and changes in the spectrum as a result of changes in the octane concentration are most easily detected in this spectral region.

The EPR spectrum obtained after irradiation of octane at high concentration (6 mol%) in CCl₃F, shown in Fig. 2, indicates the presence of an additional EPR absorption, which extends over a larger spectral region. The right lateral part of this additional EPR absorption is shown in Figs. 3 and 4 at a number of different concentrations of octane in CCl₃F. Two main features, designated A and B, are clearly discernible. The inner feature (A) appears to contain a 'double-humped' curve, typical of 1-alkyl radicals,[3,6] although this structure is not clearly discernible at all concentrations and may be nearly absent at high concentration (9 mol%). The outer feature (B), on the other hand, is a broad unresolved band, which is situated in a spectral region where 1-alkyl radicals show no EPR absorption.

Discussion

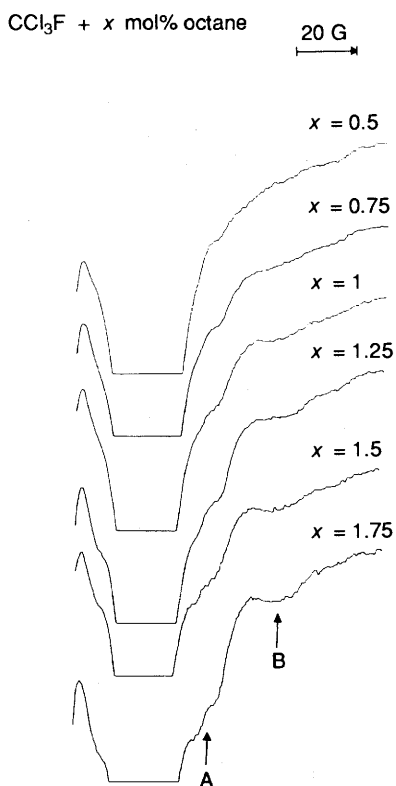The prominent EPR absorption associated with the presence of

CCl$_3$F + x mol% octane   20 G

x = 0.5

x = 0.75

x = 1

x = 1.25

x = 1.5

x = 1.75

B

A

Fig. 3 Right lateral part of the (enlarged) first derivative EPR spectrum obtained after irradiation of octane at various concentrations in trichlorofluoromethane (low-concentration region). The symbols A and B point to important spectral features.
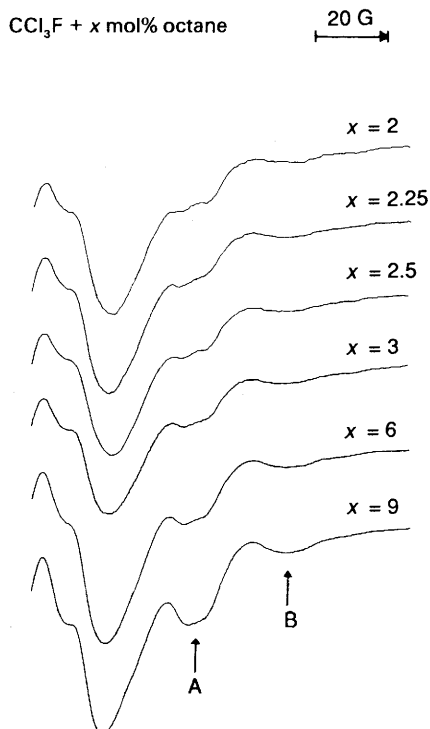
CCl$_3$F + x mol% octane   20 G

x = 2

x = 2.25

x = 2.5

x = 3

x = 6

x = 9

B

A

Fig. 4 Right lateral part of the first derivative EPR spectrum obtained after irradiation of octane at various concentrations in trichlorofluoromethane (high-concentration region). The symbols A and B point to important spectral features.

octane, which is obtained by irradiation of octane at low concentration (e.g. 0.5 mol%) in CCl$_3$F, is due to octane radical cations. These cations are formed as a result of positive hole
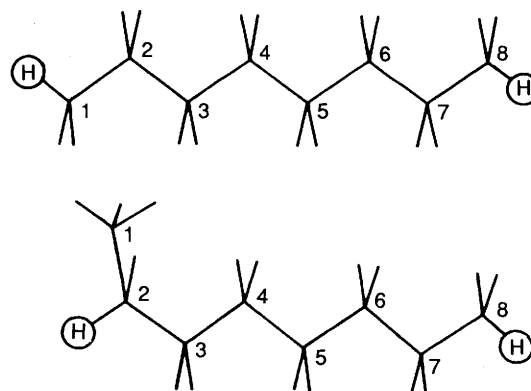

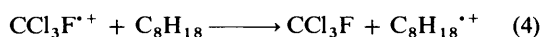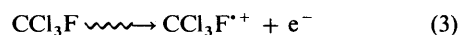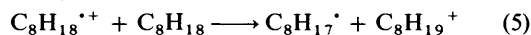**Fig. 5** Extended (all-*trans*) and gauche-at-C-2 conformers of n-C$_8$H$_{18}$$^{·+}$

transfer from radiation-produced matrix cations to solute octane molecules. The additional EPR absorption at high

$$CCl_3F \rightsquigarrow CCl_3F^{·+} + e^- \qquad (3)$$

$$CCl_3F^{·+} + C_8H_{18} \longrightarrow CCl_3F + C_8H_{18}^{·+} \qquad (4)$$

octane concentrations (e.g. 6 mol%), which is clearly discernible in the lateral parts of the spectrum, corresponds with the EPR absorption of irradiated neat octane and is due to octyl radicals. These octyl radicals are formed as a result of proton transfer from octane radical cations to octane molecules, occurring in small octane aggregates, which are increasingly present with

$$C_8H_{18}^{·+} + C_8H_{18} \longrightarrow C_8H_{17}^· + C_8H_{19}^+ \qquad (5)$$

increasing octane concentration in CCl$_3$F. Alternative mechanisms may be ruled out as a major source of octyl radicals on various grounds.[2,3]

The discussion below centres mainly on the nature (primary vs. secondary) of the octyl radicals formed and on its relation to the electronic structure of octane radical cations in CCl$_3$F, which is itself related to the conformation of this cation.

Electronic Structure of Octane Radical Cations in CCl$_3$F.— Information on the electronic structure and conformation of octane radical cations in CCl$_3$F can be derived from EPR spectra and from INDO calculations. The EPR spectrum obtained after irradiation of octane at low concentration in CCl$_3$F contains two lateral bands which are separated by ca. 65 G. The central part of the spectrum appears to be very weak and is badly distorted by matrix absorption and spurious lines, so that the absorption of octane radical cations cannot be clearly discerned in this region. Quite similar spectra of octane radical cations in CCl$_3$F have been reported by Toriyama et al.[4c] and by Dolivo and Lund.[4i] The spectrum extends over a considerably larger spectral region than the triplet spectrum of extended octane radical cations, which is observed in e.g. CCl$_2$FCF$_2$Cl[4c] and in CCl$_3$CF$_3$,[2b] and must therefore be attributed to a different conformer. On the basis of EPR simulations and INDO calculations an assignment has been made to a gauche conformer,[4c,i] obtained by one 120° rotation around C-2–C-3 in the extended conformer (see Fig. 5). This gauche conformer possesses two non-equivalent in-plane protons, which may give extensive hyperfine coupling, resulting in a four-line spectrum with equal intensities. The central region of the spectrum is very weak as a result of mutual cancellation of the different (first derivative) EPR lines and is consequently largely obscured by matrix absorption and spurious lines. Coupling constants of $a_1 = 41$ G (1 H) and $a_2 = 22$ G (1 H) were obtained for the

major hyperfine interactions. INDO calculations indicate that the largest coupling must be assigned to the in-plane hydrogen atom attached to C-2 at the folding position of the carbon chain. This assignment has been confirmed by the experimental spectrum of [1,1,1,8,8,8-²H₆]octane radical cations in CCl₃F,[4i] which contains a doublet with a hyperfine splitting of 41 G. Indications are that there is some contribution in the central part from the extended conformer of octane radical cations; it has been estimated that ca. 20% of octane cations in CCl₃F are in this conformation.[4i]

The same type of gauche conformation (in addition to the extended conformation), has been observed for pentane and hexane radical cations in CCl₂FCF₂Cl.[4c] The EPR spectra are hardly distorted by matrix absorption and spurious lines in this case. Also, hyperfine coupling constants are considerably larger, because the carbon chain is shorter than in octane, resulting in much less mutual cancellation of the different first derivative EPR lines in the central region. Experimental spectra could be very neatly simulated by superposition of a 1:1:1:1 quartet on a 1:2:1 triplet. Assignment of the quartet spectrum to a gauche conformer with the folding position at C-2 instead of C-3 could unambiguously be made from spectra of [2,2,5,5-²H₄]hexane and [3,3,4,4-²H₄]hexane radical cations in CCl₂FCF₂Cl.[4i]

The EPR bands in the spectrum of octane radical cations in CCl₃F are quite broad, much broader than the bands of the triplet spectrum of extended octane radical cations in other chlorofluorocarbon matrices[2b,4c] and of extended heptane radical cations in CCl₃F.[2,3] This indicates that other conformations, e.g. a conformation obtained by one 120° rotation around C-3–C-4 in the extended conformer, may also be present, though to a much lesser extent. In such a conformation there is also large unpaired-electron density on one primary and one secondary carbon–hydrogen bond, but hyperfine coupling constants may be expected to be larger as the planar carbon chain is shorter and the unpaired-electron delocalisation is less extensive. No such conformation is observed for hexane in CCl₂FCF₂Cl, as is evidenced by EPR spectra of [2,2,5,5-²H₄]hexane and [3,3,4,4-²H₄]hexane radical cations in this matrix,[4i] but this does not exclude its occurrence for octane in CCl₃F. It is to be noted that absorption bands in the EPR spectra of the extended and gauche conformers of hexane radical cations in CCl₂FCF₂Cl have about the same width, i.e. the nature of the conformation does not affect the spectral band width. Increases in band width may, on the other hand, quite well result from the presence of different gauche conformers, exhibiting different hyperfine interactions, as a result of overlapping of the respective EPR absorptions.

Nature of the Octyl Radicals formed by Proton Transfer from Octane Radical Cations to Octane Molecules.—Information on the nature (primary vs. secondary) of the octyl radicals formed by proton transfer from octane radical cations to octane molecules in CCl₃F matrices at 77 K may be derived from the right lateral part of the EPR spectrum of irradiated CCl₃F–octane systems (see Figs. 3 and 4) with the aid of powder spectra of authentic alkyl radicals. Such spectra have been obtained by irradiation of bromoalkanes in cis-[²H₁₈]decalin.[3] Features in these spectra, which are relevant to the present discussion, are (i) that secondary alkyl radicals extend over a wider spectral region than primary alkyl radicals, the outermost feature corresponding with feature B in the spectrum of irradiated CCl₃F–octane and (ii) that the outermost feature in the spectrum of primary alkyl radicals, which corresponds in spectral position with feature A in irradiated CCl₃F–octane, consists of a 'double-humped' curve, whereas the absorption curves of secondary alkyl radicals exhibit no such structure.

The major observation, on examination of EPR spectra obtained after irradiation of octane at various concentrations in

CCl₃F, is that secondary octyl radicals are present from the very first appearance of alkyl radicals in such systems. This can clearly and unambiguously be deduced from the presence of feature B in these spectra. Primary octyl radicals are also present, as is indicated by the 'double-humped' structure in the EPR absorption (feature A). The prominence of this feature gradually decreases with increasing octane concentration. This can be attributed to intermolecular radical site transfer [reaction (6)] occurring in octane aggregates consisting of more than two molecules.

$$1\text{-}C_8H_{17}\cdot + C_8H_{18} \longrightarrow C_8H_{18} + sec\text{-}C_8H_{17}\cdot \quad (6)$$
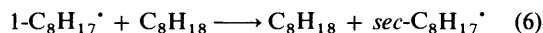
than two molecules. This hydrogen-abstraction reaction is greatly assisted by the excess energy available as a result of the hole transfer process [reaction (4)]. Secondary octyl radicals are preferentially formed by this process,[7,8] because primary C–H bond energies are higher than secondary C–H bond energies.

The observation that both primary and secondary octyl radicals are formed as a result of proton transfer from octane radical cations to octane molecules [reaction (5)] contrasts strongly with that of irradiated CCl₃F–heptane systems, in which at low concentration (≤1.75 mol%) only primary heptyl radicals are observed. The difference can be attributed to differences in conformation and ensuing differences in electronic structure of heptane and octane radical cations in CCl₃F matrices at 77 K. In CCl₃F, heptane radical cations are fully in the extended conformation. In this conformation, the unpaired electron is delocalized over the carbon–carbon σ bonds as well as the two in-plane *chain-end* carbon–hydrogen bonds. This electronic structure correlates with the nature of the heptyl radicals formed by proton transfer from heptane radical cations to heptane molecules, such transfer taking place selectively from the chain-end positions. As indicated above, octane radical cations in CCl₃F are mainly in a gauche conformation, with large unpaired-electron density in the in-plane carbon chain and in-plane carbon–hydrogen bonds at C-2 and C-8 (see Fig. 5). On the basis of INDO calculations and of the EPR spectrum of protiated octane and [1,1,1,8,8,8-²H₆]octane radical cations, it has been deduced[4c,i] that the unpaired-electron density in the in-plane carbon–hydrogen bond at C-2 is considerably larger than at C-8. This electronic structure correlates with the nature of the octyl radicals formed by proton transfer to octane molecules, secondary octyl radicals being quite prominent (relative to chain-end octyl radicals) even at low octane concentration. Chain-end octyl radicals are also present in irradiated CCl₃F–octane systems, as is evidenced by the 'double-humped' structure in the observed EPR spectra (feature A in spectra shown in Figs. 3 and 4). Their formation can be explained by proton transfer from the chain-end positions in the extended conformer, which is present to some extent (ca. 20%), and by proton transfer from the C-8 position in the gauche conformer (see Fig. 5).

Conclusions

The results obtained provide further support for the postulate[3] stating that the nature of the alkyl radicals formed by proton transfer from alkane radical cations to alkane molecules is related to the structure of the semi-occupied molecular orbital of the parent cation. Whereas proton transfer to heptane molecules from extended heptane radical cations, in which there is large unpaired-electron density in the in-plane carbon–hydrogen bonds at the chain-end positions, leads to the selective formation of 1-heptyl radicals,[3] proton transfer from octane radical cations to octane molecules in CCl₃F matrices results in the formation of both primary and secondary octyl radicals, in accordance with the large unpaired-electron density in the in-plane carbon–hydrogen bonds at C-2 and C-8 (gauche-at-C-2

conformation). It thus appears that the high unpaired-electron density in those particular carbon–hydrogen bonds leads to proton transfer from those sites, giving rise to quite specific alkyl radicals.

Acknowledgements

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