Symmetric and asymmetric proton transfer from heptane and octane radical cations to heptane molecules in γ-irradiated n-C₇H₁₆–n-C₈H₁₈–2-C₆H₁₃Cl crystals: structural disorder in mixed alkane crystals

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A study has been made of the isomeric composition of secondary chloroheptanes formed upon γ-irradiation at 77 K and subsequent melting of heptane containing 1 mol% 2-chlorohexane and various concentrations of octane. It is observed that the relative importance of 2-chloroheptane increases as a result of the presence of octane in the crystallites. This increase is attributed to selective proton transfer from ground state heptane radical cations to penultimate C–H bonds in heptane molecules. The proton transfer is induced by (partial) dislocation of heptane molecules adjacent to octane solute molecules, which brings the penultimate heptane C–H bonds into close contact with planar chain-end C–H bonds in heptane radical cations. Proton transfer from extended all-*trans* octane radical cations (on which the positive hole temporarily resides) to heptane molecules may also contribute to the observed effect. The results have important implications with respect to the molecular packing in binary *n*-alkane crystals. In binary *n*-alkane crystals, in which the shorter component is predominant, molecules of the longer component cannot be fully accommodated in one molecular layer of the crystal, even with a chain length mismatch of only one methylene unit; instead (at least partial) dislocation of adjacent molecules of the shorter component takes place. Such dislocations do not extend indefinitely over the crystal, however, and crystal order is restored by squeezing, deformation and changes in conformation of the appropriate molecules, including molecules of the shorter component.

Introduction

Information on donor site selectivity in symmetric proton transfer from *n*-alkane radical cations to *n*-alkane molecules has been obtained from EPR studies on the nature of the alkyl radicals in irradiated SF₆–*n*-alkane (upon annealing),[1] zeolite–*n*-alkane[2] and CCl₃F–*n*-alkane[3,4] systems at cryogenic temperatures. The experiments point to a strict relationship between the electronic structure of the *n*-alkane radical cations and the site of proton donation (intrinsic donor site selectivity). In fact, all experimental data that can unambiguously be attributed to the proton-transfer process indicate that such transfer takes place selectively from planar C–H bonds, *i.e.*, C–H bonds coplanar to the planar or planar part of the C–C skeleton, in *n*-alkane radical cations in the extended all-*trans* and *gauche*-at-C2 conformation, respectively, because of the high unpaired-electron and positive-hole density in those bonds. An EPR study on the nature of the octyl radicals formed by γ-irradiation of pentane-*d*₁₂–octane at 77 K has confirmed the donor site selectivity with respect to the (asymmetric) proton transfer from extended all-*trans* octane radical cations to pentane molecules.[5]

Information on (intrinsic) acceptor site selectivity in symmetric proton transfer from *n*-alkane radical cations to *n*-alkane molecules has been gathered from γ-irradiated frozen CCl₃F–*n*-alkane solutions by gas chromatographic analysis of the appropriate chloroalkanes after melting.[6,7] The proton acceptance appears restricted to C–H bonds at secondary carbon atoms (no proton transfer to C–C bonds nor to C–H bonds at primary carbon atoms), with a preference for the penultimate position and mutually equal (but considerably lower relative to the penultimate site) transfer to the different interior positions. Selective transfer to penultimate C–H bonds

has also been observed in asymmetric proton transfer, *viz.*, in the proton transfer from heptane radical cations to decane molecules in γ-irradiated heptane–decane–1-chloroheptane crystals, by chromatographic analysis after melting.[8]

Crystals are structurally highly organized and as a consequence selectivity with respect to the site of proton donation may lead to selectivity with respect to the site of proton acceptance; (structurally determined acceptor site selectivity). This may lead to additional selectivity with respect to the site of proton acceptance in irradiated mixed *n*-alkane crystals. Structurally determined acceptor site selectivity in γ-irradiated heptane–decane–1-chloroheptane has been observed with respect to protonation of the inner positions of decane and can be explained on the basis of structural diagrams that depict the packing in heptane crystals containing decane molecules.[8] Another system, *viz.* γ-irradiated heptane–octane–1-chlorohexane, is also of great interest because, in this system, penultimate C–H bonds in octane, which for reasons of energetics have the greatest propensity to act as proton acceptors, are also structurally greatly favored over the interior C–H bonds as proton acceptors from planar chain-end C–H bonds in the heptane radical cations. The combined preference for the penultimate C–H bonds due to structural and thermodynamic factors in this system results in very high (almost exclusive) acceptor selectivity with respect to these bonds.[9]

All experiments on structurally determined acceptor site selectivity at present relate to asymmetric proton transfer from matrix radical cations to solute molecules. In order to demonstrate the universality of the phenomenon and the correctness of the explanation presented, it appeared of great interest to extend the experimental evidence to symmetric proton transfer from matrix radical cations to matrix molecules. This is accomplished in the present work by studying the effect of the

concentration of octane on the isomeric composition of the secondary chloroheptanes formed by γ-irradiation of n-C_7H_{16}–n-C_8H_{18}–2-C_6H_{13}Cl crystals at 77 K and subsequent melting. The results obtained are of further interest to solid-state chemists because they also provide information on the packing in mixed n-alkane crystals and on the crystal imperfections that originate from the chain-length mismatch due to the presence of a longer-chain (solute) n-alkane in a mixed n-alkane crystal.

Experimental

Products used in this study were heptane (≥99.7%) from Rathburn, octane (>99.0%) from Janssen Chimica and 2-chlorohexane (>97%) from Fluka. Heptane and octane were purified by passage through a column containing silica gel, which had been activated immediately prior to use by heating at 250 °C for 24 h. The activation procedure removed possible non-paraffinic impurities in the alkanes that might have a disproportionate effect on the radiolytic process.

Solutions, prepared by conventional techniques, were contained in large (11 mm i.d.) cylindrical tubes with a narrow orifice made of borosilicate glass. Argon was bubbled through the solutions for 30 min to remove oxygen. After deoxygenation, samples were carefully sealed and rapidly cooled to 77 K by immersion in liquid nitrogen. All samples were irradiated with [60]Co γ-rays to a dose of 7.5×10^{19} eV g^{-1}. The procedure used in the chromatographic analyses was largely as described before,[9b] except that no internal standards were added because no absolute yield values were determined. The separations were performed at a column temperature of 30 °C. Quantitative data (relative yields) were obtained on the basis of peak heights and (adjusted) retention times according to a method developed previously.[10a] Individual peak heights for 2- and 3-chloroheptane were obtained by deconvolution, in which the (real) peak height of the adjacent overlapping peak at the elution maximum of the other was subtracted from its (apparent) maximum value and vice versa until conversion to within (on average) 3% occurred (seven iterations). Peak widths and shapes required for this process were derived from the elution profile of 4-chloroheptane, which was enlarged in accordance with the linear variation of peak width with (adjusted) retention time.[10b,c] Because of the partial overlap of the peaks of 2- and 3-chloroheptane, quantitative values (even of relative yields) are prone to some error. The discussion can, however, be solidly based on the evolution of relative yields with octane concentration, which especially for 2- vs. 3-chloroheptane gives a quite straightforward indication because of the nearness in chromatographic elution time and radiolytic yield at low octane concentration. In fact, a major observation (viz., the increase of the yield of 2- vs. 3-chloroheptane with increasing octane concentration) can be discerned directly on the respective chromatograms.

Results

The relevant part of the chromatogram showing the analysis of the secondary chloroheptanes formed upon γ-irradiation at 77 K and subsequent melting of heptane containing 1 mol% 2-chlorohexane and various concentrations of octane, is shown in Fig. 1. Different radiolysis products are present in the chromatographic region where 1-chloroheptane elutes, which interfere with the analysis of this product; also, data on the chain-end isomer are not essential to the discussion as primary C–H bonds are not effective as proton acceptors from ground-state alkane radical cations[6,7] and its analysis was therefore not pursued. With respect to the secondary chloroheptanes, the results at zero octane concentration indicate about equal formation of 2- and 3-chloroheptane (with a small bias towards the formation of 3-chloroheptane) and consider-
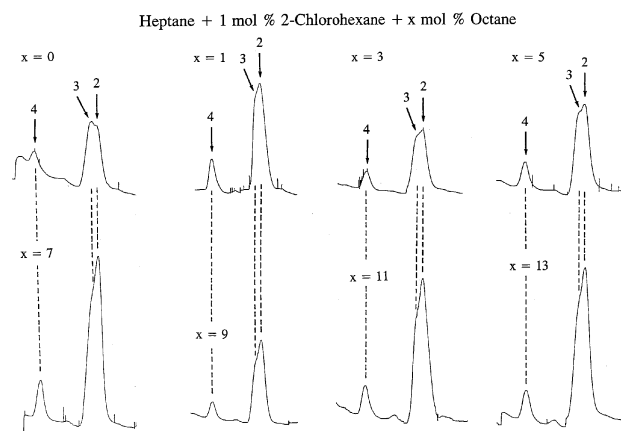
Fig. 1 Relevant part of the chromatograms showing the analysis of the secondary chloroheptanes formed upon γ-irradiation at 77 K and subsequent melting of heptane containing 1 mol% 2-chlorohexane and various concentrations of octane. The number above the arrows indicates the position of the chlorine atom in the chloroheptane isomers.

ably lower formation of 4-chloroheptane, which can (at least partly) be explained on purely statistical grounds. With increasing concentration of octane, the importance of 2-chloroheptane increases with respect to that of 3-chloroheptane as is quite evident from Fig. 1; already at 1 mol% octane the relative importance of the two isomers is reversed. The effect is further illustrated in Fig. 2, in which the relative yield of the two
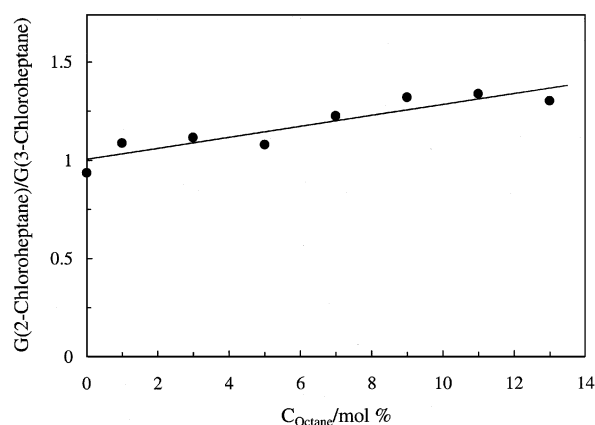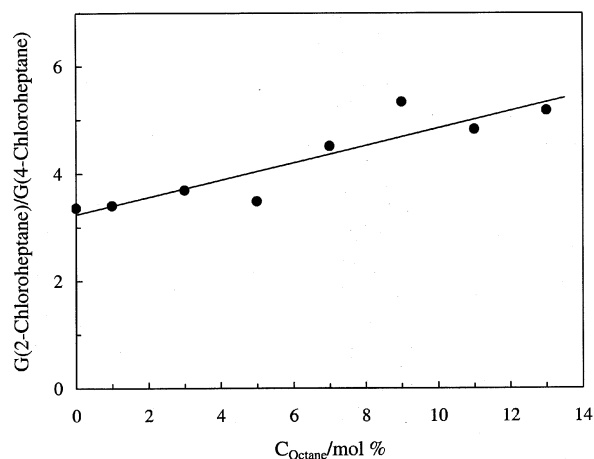

Fig. 2 Ratio of the radiolytic yield of 2- to 3-chloroheptane (based on non-deconvoluted peak heights) vs. octane concentration, upon γ-irradiation at 77 K and subsequent melting of heptane containing 1 mol% 2-chlorohexane and various concentrations of octane.

products (based on non-deconvoluted peak heights) is plotted as a function of the concentration of octane. An increase in importance is also observed for 2- vs. 4-chloroheptane, as is evident from Fig. 3 in which the ratio of the yield of 2- to 4-chloroheptane (based on non-deconvoluted peak heights) is shown as a function of the concentration of octane. Similar conclusions are obtained from graphs in which the relative yield of the respective products (based on deconvoluted peak heights) is plotted as a function of the concentration of octane, but the observed effects are considerably more pronounced, especially with respect to the yield of 2- vs. 3-chloroheptane (see Figs. 4 and 5).

Discussion

### Mode of formation of chloroheptanes in γ-irradiated heptane–2-chlorohexane

The interaction of the ionizing radiation in the heptane–2-chlorohexane system mainly takes place with the major

Fig. 3 Ratio of the radiolytic yield of 2- to 4-chloroheptane (based on non-deconvoluted peak heights) *vs.* octane concentration, upon γ-irradiation at 77 K and subsequent melting of heptane containing 1 mol% 2-chlorohexane and various concentrations of octane.
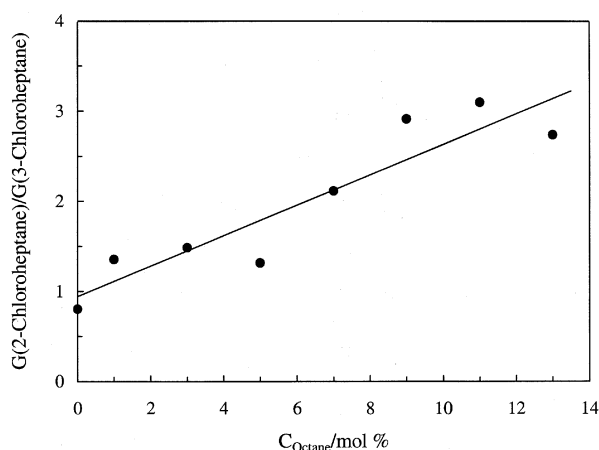
Fig. 4 Ratio of the radiolytic yield of 2- to 3-chloroheptane (based on deconvoluted peak heights) *vs.* octane concentration, upon γ-irradiation at 77 K and subsequent melting of heptane containing 1 mol% 2-chlorohexane and various concentrations of octane.
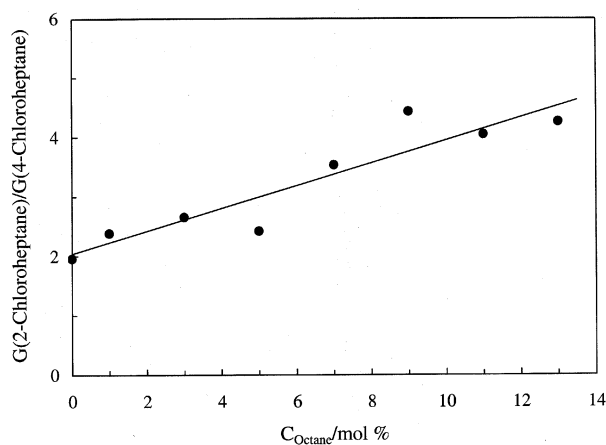
Fig. 5 Ratio of the radiolytic yield of 2- to 4-chloroheptane (based on deconvoluted peak heights) *vs.* octane concentration, upon γ-irradiation at 77 K and subsequent melting of heptane containing 1 mol% 2-chlorohexane and various concentrations of octane.
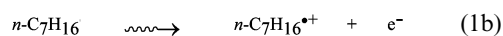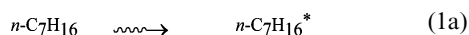
component, which is heptane, and results in its excitation and ionization [eqns. (1a) and (1b)].

$$n\text{-}C_7H_{16} \;\; \wedge\!\!\!\wedge\!\!\!\wedge\!\!\!\longrightarrow \;\; n\text{-}C_7H_{16}^* \qquad (1a)$$

$$n\text{-}C_7H_{16} \;\; \wedge\!\!\!\wedge\!\!\!\wedge\!\!\!\longrightarrow \;\; n\text{-}C_7H_{16}^{\bullet+} \; + \; e^- \qquad (1b)$$

Electrons formed in the ionization process that escape the coulomb attraction of the counter radical cations can migrate through the crystal and have a high likelihood of reacting with 2-chlorohexane, present as additive, by dissociative electron attachment [eqn. (2)].

$$2\text{-}C_6H_{13}Cl + e^- \longrightarrow 2\text{-}C_6H_{13}^{\bullet} + Cl^- \qquad (2)$$
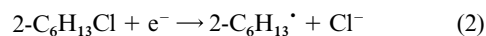
The heptane radical cations formed in the ionization process are usually substantially excited and may be transformed into other cationic species, *viz.* into carbenium ions by dissociation [eqn. (3)]

$$n\text{-}C_7H_{16}^{\bullet+*} \longrightarrow C_7H_{15}^+ + H^{\bullet} \qquad (3)$$
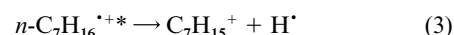
and into carbonium ions by proton transfer to heptane molecules [eqn. (4)].

$$n\text{-}C_7H_{16}^{\bullet+*} + n\text{-}C_7H_{16} \longrightarrow C_7H_{15}^{\bullet} + C_7H_{17}^+ \qquad (4)$$
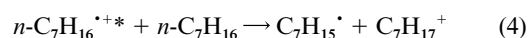
No site selectivity is to be expected in these two reactions, because of the electronic excitation energy on the radical cation. Heptane radical cations that are not transformed by the above processes before substantial relaxation takes place, may contribute to positive-hole migration in the irradiated system. In γ-irradiated neat heptane crystals, positive-hole migration can take place by electron transfer from heptane molecules to adjacent heptane radical cations, the transfer process repeating itself in successive steps [eqn. (5)].

$$n\text{-}C_7H_{16}^{\bullet+} + n\text{-}C_7H_{16} \longrightarrow n\text{-}C_7H_{16} + n\text{-}C_7H_{16}^{\bullet+} \qquad (5)$$
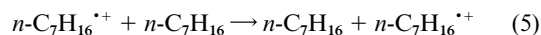
The migration is driven by the coulomb attraction of chloride ions trapped in the vicinity and, if not interfered with, will result in the encounter of these cationic and anionic species leading to charge neutralization.

There are three distinct neutralization processes that may lead to the formation of chloroheptanes in the γ-irradiated heptane–2-chlorohexane system under study. For two of these neutralization and chloroheptane formation is delayed until the sample is warmed and melted after the irradiation, *viz.* the neutralization of heptyl carbenium and heptyl carbonium ions [eqns. (6) and (7)]

$$C_7H_{15}^+ + Cl^- \longrightarrow C_7H_{15}Cl \qquad (6)$$

$$C_7H_{17}^+ + Cl^- \longrightarrow C_7H_{15}Cl + H_2 \qquad (7)$$
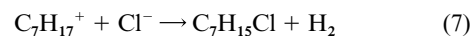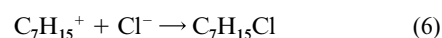
as these cationic intermediates as well as chloride ions are trapped in the crystalline system at 77 K. Positive-hole migration takes place in the irradiated system at 77 K and neutralization of heptane radical cations by chloride ions therefore occurs during γ-irradiation. The exact nature of this neutralization process is unknown at present and is currently under study in our laboratory.

Origin of the increase in the prominence of 2-chloroheptane relative to other secondary chloroheptanes upon addition of octane

The results obtained indicate that addition of octane to the heptane–2-chlorohexane system results in a considerable increase in the prominence of 2-chloroheptane relative to other secondary chloroheptane isomers. This can be attributed to site-selective proton transfer from heptane radical cations in their electronic ground state to heptane molecules, with either the radical cation or the neutral molecule being dislocated in the crystal due to the presence of octane [eqn. (8)].

$$n\text{-}C_7H_{16}^{\bullet +} + n\text{-}C_7H_{16} \longrightarrow 1\text{-}C_7H_{15}^{\bullet} + 2\text{-}C_7H_{17}^{+} \qquad (8)$$
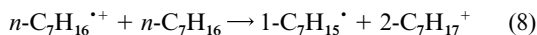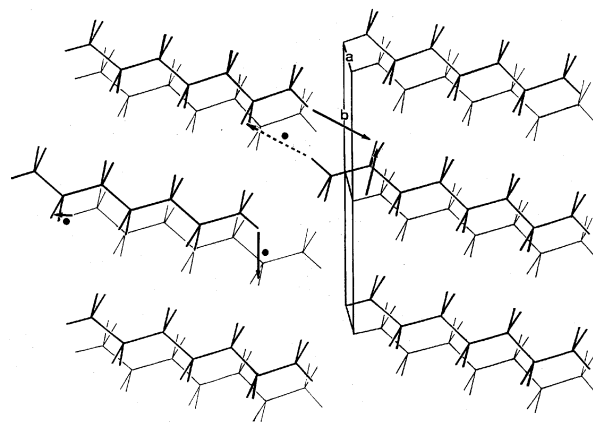
In this process, proton transfer takes place selectively from planar chain-end C–H bonds in heptane radical cations to penultimate C–H bonds in heptane molecules. The reaction undoubtedly also contributes to the previously observed increase in the prominence of 1-heptyl radicals due to the presence of octane in γ-irradiated $n\text{-}C_7H_{16}$–$n\text{-}C_8D_{18}$.[9] Details on the dislocations induced by octane solute molecules in $n\text{-}C_7H_{16}$–$n\text{-}C_8H_{18}$ crystals and on the site selective proton transfer they induce are presented below.

In n-alkane crystals (in the low temperature phase), alkane molecules are in the extended all-*trans* conformation as indicated by X-ray diffraction[11] and infrared spectroscopy.[12] This also applies to alkane radical cations formed as a result of ionization by ionizing radiation in n-alkane crystals, as has been demonstrated by fluorescence detected magnetic resonance (FDMR) experiments.[13] EPR and FDMR experiments as well as theoretical calculations show that in extended n-alkane radical cations the unpaired electron and associated positive hole is delocalized over the C–C σ-bonds as well as the two chain-end C–H bonds that are in the plane of the C–C skeleton.[13,14] There is now very substantial evidence that proton donation (at least to neutral alkane molecules) takes place from such planar C–H bonds,[1–5] which appears quite reasonable in view of the weakening of these bonds and the presence of positive-charge (hole) density on the respective hydrogen atoms. Structural diagrams clearly show that in *neat* heptane crystals the planar chain-end C–H bonds only come into close contact with primary C–H bonds in other heptane molecules. We will now consider the consequences if, in mixed heptane–octane crystals, the presence of octane effects (at least partial) dislocation of adjacent heptane molecules. With such dislocation, planar chain-end C–H bonds in heptane radical cations would be in close contact with secondary C–H bonds at the penultimate position in adjacent heptane molecules as is evident from Figs. 6 and 7. Due to the much higher proton affinity for protonation at a secondary than at a primary C–H bond (see Fig. 8), proton transfer from heptane radical cations (that are in their electronic ground state) to heptane molecules would therefore be substantially enhanced, simply as a result of the physical presence of octane in the
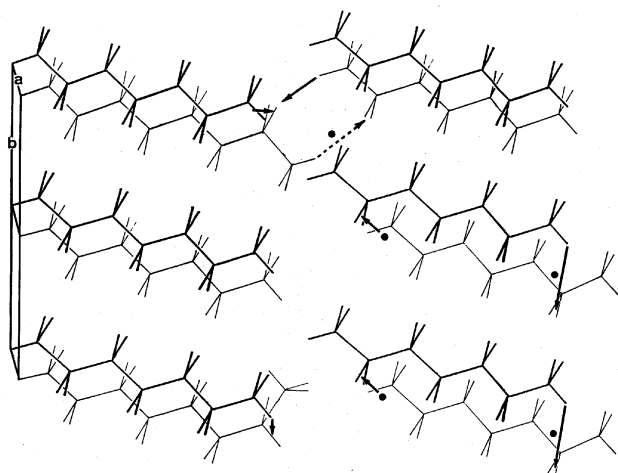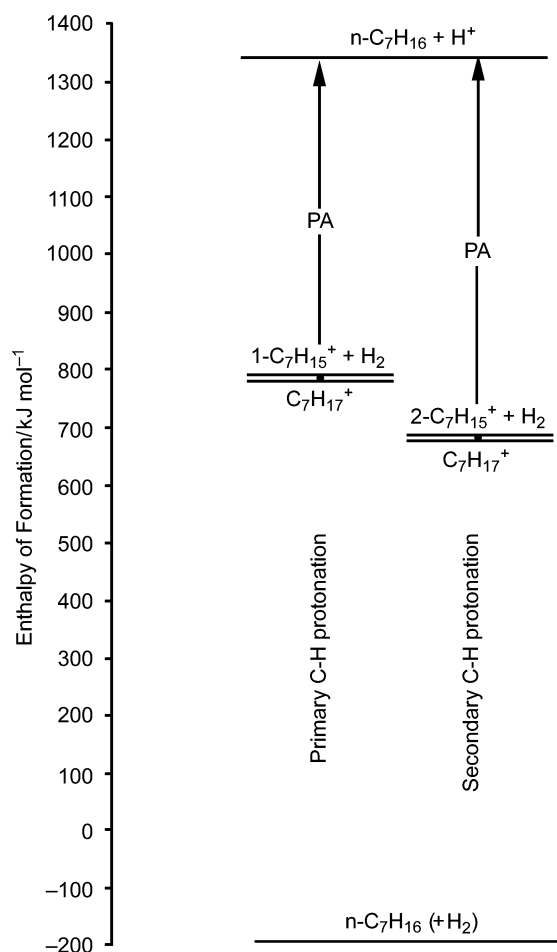

Fig. 6 Structural diagram showing the packing in heptane crystals containing octane molecules in the extended all-*trans* and *gauche*-at-C2 conformation, in which the chain-length mismatch causes a methyl group of octane to protrude at the right hand side into the intermolecular boundary region; (packing without strain or deformation and with full dislocation in adjacent layers). Potential sites of proton transfer from planar chain-end C–H bonds in heptane radical cations to penultimate C–H bonds in heptane and octane molecules are indicated by solid arrows; potential transfer sites from octane radical cations are indicated by dashed arrows; ● specifically indicates transfer to heptane molecules.

Fig. 7 Structural diagram showing the packing in heptane crystals containing octane molecules in the extended all-*trans* conformation, in which the chain-length mismatch causes a methyl group of octane to protrude at the left hand side into the intermolecular boundary region; (packing without strain or deformation and with full dislocation in adjacent layers). Potential sites of proton transfer from planar chain-end C–H bonds in heptane radical cations to penultimate C–H bonds in heptane and octane molecules are indicated by solid arrows; potential transfer sites from octane radical cations are indicated by dashed arrows; ● specifically indicates transfer to heptane molecules. The potential sites for asymmetric proton transfer are indicated for the sake of completeness only, their importance appearing rather minor.

system. In this transfer process, the penultimate position is strongly favored for proton acceptance over the other secondary positions for structural reasons (see Figs. 6 and 7); it is also the favored site with respect to proton acceptance on energetic grounds.[6–8] The transfer process would therefore result in selective formation of heptane carbonium ions that are C–H protonated at the penultimate position, neutralization of which by chloride ions results in the selective formation of 2-chloroheptane. This hypothetical reaction scheme correlates nicely with the observed increase in the prominence of 2-chloroheptane relative to the other secondary chloroheptane isomers as a result of the presence of octane in the system, which indicates its relevance. The results thus provide evidence for (at least partial) dislocation of heptane molecules adjacent to octane solute molecules in the crystal.

The structural diagrams shown in Figs. 6 and 7 indicate that the proton transfer from heptane radical cations to heptane molecules, induced by the physical presence of octane, takes place predominantly (perhaps exclusively) along the *a*-axis of the crystal. Due to the presence of octane, heptane molecules (and heptane radical cations on passage of the positive hole) are shifted by about one methylene unit, bringing planar chain-end C–H bonds in heptane radical cations into direct contact with secondary (penultimate) C–H bonds in heptane molecules above and/or below the radical cations along the *a*-axis of the crystal (with the single or dual transfer potential depending on whether the reacting heptane molecule or heptane radical cation is shifted in the crystal). Potential proton-transfer sites between heptane radical cations and heptane molecules do not appear to be created along the *b*- and *c*-axis of the crystal by the presence of octane. The structural diagrams further indicate that the dislocation of heptane molecules and the associated selective proton transfer to C–H bonds at the C2 position would for an 'unstrained' crystal occur regardless of the fact that octane is in the extended all-*trans* or *gauche*-at-C2 conformation. The presence of octane puts considerable strain in the crystal, however, which can (to some extent) be relieved by partial squeezing and deformation of appropriate molecules. It is evident that this process is more easily effected with octane molecules that are in a *gauche*-at-C2 conformation than with fully extended octane molecules; the displacement of adjacent heptane molecules and the associated proton transfer will be

Fig. 8 graph:

Enthalpy of Formation/kJ mol^{-1} (y-axis: 1400, 1300, 1200, 1100, 1000, 900, 800, 700, 600, 500, 400, 300, 200, 100, 0, −100, −200)

n-C$_7$H$_{16}$ + H$^+$

PA   PA

1-C$_7$H$_{15}^+$ + H$_2$
C$_7$H$_{17}^+$

2-C$_7$H$_{15}^+$ + H$_2$
C$_7$H$_{17}^+$

Primary C–H protonation   Secondary C–H protonation

n-C$_7$H$_{16}$ (+H$_2$)

Fig. 8 Scheme establishing the energetics of pentacoordinated heptane carbonium ions protonated at either primary or secondary C–H bonds. The enthalpy of formation[20] of the neutral alkane and the heterolytic bond strengths[21] were taken from the literature. The enthalpy of formation of hydride ions was calculated from the commonly available bond strength of H$_2$ and electron affinity of hydrogen atoms. The enthalpy changes associated with the dissociation of primary and secondary C–H protonated heptanes were assumed equal to those for the lower members of the alkane series and were taken from the literature.[22]

affected accordingly, *i.e.*, they are likely to be more extensive in the vicinity of a fully extended octane molecule. Both fully extended and *gauche*-at-C2 conformers of octane may be expected to be present in the system studied, by analogy with the structure of the binary solid nonadecane–henicosane, which was investigated by IR spectroscopy using partially deuterated samples.[15] Such a study has shown that the percentage of henicosane in the *gauche*-at-C2 conformation increases with decreasing henicosane concentration; at for instance 10 mol% henicosane in nonadecane, about 40% of the henicosane molecules are in the *gauche*-at-C2 conformation. It is to be noted that in the present heptane–octane system, the *gauche*-at-C2 conformation appears structurally excluded when the protruding alkyl group is at the 'front' of the molecule (*i.e.* at the left hand side of the molecule as depicted in the structural diagrams), because of the physical strain this would put on the crystal (see Fig. 7).

The observed increase in prominence of 2-chloroheptane with increasing octane concentration relative to other secondary chloroheptanes is partially due to asymmetric proton transfer from octane radical cations to heptane molecules, which occurs in parallel to the symmetric proton-transfer process described above [eqn. (9)].

$$n\text{-}C_8H_{18}^{\bullet+} + n\text{-}C_7H_{16} \longrightarrow 1\text{-}C_8H_{17}^{\bullet} + 2\text{-}C_7H_{17}^+ \quad (9)$$
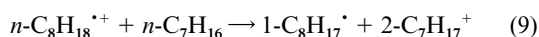
Such a process is restricted to octane radical cations in the extended all-*trans* conformation; planar C–H bonds in octane radical cations in the *gauche*-at-C2 conformation are structurally quite similar to planar chain-end C–H bonds in (fully extended) heptane radical cations and are most certainly *not* in direct contact with secondary C–H bonds in adjacent molecules (see Fig. 6). Also, the reaction appears largely limited to octane radical cations that extend 'at the back side' in the intermolecular boundary region because of unfavorable directional matching of the appropriate bonds in the alternative mode of packing (see Figs. 6 and 7). Asymmetric proton transfer from solute alkane radical cations to matrix molecules has been observed in γ-irradiated n-C$_5$D$_{12}$–n-C$_8$H$_{18}$ crystals by EPR spectroscopy.[5] The importance of the process appears critically dependent on positive-hole trapping by the solute alkane molecule. Hole trapping by the solute alkane greatly increases the lifetime of the solute radical cation in solid systems and apparently makes the proton-transfer process much more effective. This is indicated by the fact that in γ-irradiated pentane-d_{12}–heptane (at 0.5 mol% heptane), in which hole trapping by heptane is very weak, the corresponding proton-transfer process is not important. Clearly, the site selective proton transfer from ground-state alkane radical cations during the migration process of the positive hole does not take place at every opportunity that would appear structurally favorable, *i.e.*, formation of a radical cation in which planar chain-end C–H bonds are in close contact with secondary C–H bonds in adjacent alkane molecules. The actual occurrence of the process in all likelihood depends critically on a suitable matching of the phase of the vibrations of the (donor and acceptor) C–H bonds involved. In the present n-C$_7$H$_{16}$–n-C$_8$H$_{18}$–2-C$_6$H$_{13}$Cl system, hole trapping on octane radical cations is not expected, in view of the limited difference in ionization energy between heptane (9.93 eV) and octane (9.80 eV).[16] An electronic absorption study of γ-irradiated heptane, containing 1 mol% 1-chlorohexane and 1 mol% octane, gave no indication of the presence of trapped octane radical cations.[9b] Asymmetric proton transfer from octane radical cations to heptane molecules is thus not enhanced by hole trapping on octane radical cations in the present system and is thus restricted to the accidental passage of the hole on octane in its migration process through the irradiated system, as it is with heptane in the symmetric transfer process. Its occurrence and relevance to the formation of 2-chloroheptane should not be disregarded, however, especially at the higher octane concentrations, in view of the documented increase of all-*trans* vs. *gauche*-at-C2 conformers of the long-chain component with increasing concentration of this component, which appears to be very considerable.[15]

## Molecular packing in binary *n*-alkane crystals

The results obtained provide important information with respect to the packing of alkane molecules in binary *n*-alkane crystals and the disordering effects of the chain-length mismatch. Asbach *et al.* have introduced two structure models for the crystal imperfections in the border regions between the layers in binary *n*-alkane crystals,[17] which are characterized, respectively, by the creation of voids (packing type A, longer component predominant) and by the presence of end-*gauche* conformers of the longer component (packing type B, shorter component predominant). For intermediate compositions two additional packing schemes have been proposed by Maroncelli *et al.*, involving (i) the interleaving of chains at the layer surface (packing type C) and (ii) the pairwise packing of all-*trans* conformers of the short component with end-*gauche* conformers of the long component (packing type D).[15] In view of the range of concentrations of octane in the systems under investigation, packing type B is anticipated to apply largely in the present study. With such a packing scheme the question arises as to whether molecules of the longer component can be packed fully

in one molecular layer of the crystal (the width being determined by the shorter component), with the excess alkyl group forced into a suitable conformation, and this without any dislocation of adjacent molecules of the shorter component. The structural diagrams shown suggest that such packing without dislocation of molecules in adjacent layers appears improbable. Also, the results of Maroncelli *et al.* indicate that even at relatively small concentrations of the long-chain component (*e.g.*, between 5 and 10 mol%) a substantial fraction of the long-chain molecules in mixed *n*-alkane crystals are in the extended all-*trans* conformation,[15] which makes packing fully within one molecular layer especially problematic. The experimental results of the present study clearly point to dislocation of molecules of the shorter component (in this case heptane) in adjacent layers of the crystallites, as is indicated by the increase in the formation of 2-chloroheptane relative to that of the other secondary chloroheptanes by the physical presence of octane. There must thus be a fair amount of interleaving even at low concentrations of the long-chain component. It is likely, however, that the dislocations do not extend indefinitely through the crystallites, which would result in unequal (and substantial) shifting of the different rows of molecules and thus in complete elimination of structurally related site selectivity in the proton-transfer process. In fact, unlimited interleaving would destroy the layer structure of the crystallites, whereas X-ray diffraction studies show mixed *n*-alkane crystals to be packed in layers analogous to neat *n*-alkanes, with the long spacing varying smoothly with composition.[17,18] The layer structure of the crystallites can be preserved by partial squeezing, deformation and changes in conformation of appropriate molecules, thus allowing the crystal defect to be eliminated and crystal order to be restored in layers (and rows) adjacent to a chain-length mismatch. It is evident that the deformation can be most easily effected in a *gauche* conformation. It is interesting in this regard that the IR study of partially deuterated nonadecane–henicosane mixed crystals has shown *gauche*-at-C2 conformers of nonadecane (the short-chain component) to be present, whereas such conformers are virtually absent in neat nonadecane crystals.[15,19] On the basis of all this, it can be concluded that the molecular packing in mixed *n*-alkane crystals at low and medium concentrations of the long-chain component has characteristics that correspond to both packing type B (deformation, accompanied by formation of end-*gauche* conformers of the long- *and also* of the short-chain component) and packing type C (interleaving of chains at the layer surface, though only partial and restricted to the immediate vicinity of the chain-length mismatch).

Considerations on the 'scavenging' role of octane in the system under study

The presence of octane in the n-C_7H_{16}–n-C_8H_{18}–2-$C_6H_{13}Cl$ system under study causes very specific changes with respect to the isomeric composition of the chloroheptanes formed by γ-irradiaton at 77 K and subsequent melting, by way of a mechanism quite distinct to that of conventional scavengers in radiation chemistry. Scavenging is the general term applied for the deliberate addition to a system *before or after* irradiation of a small concentration of a foreign substance, that will react preferentially with a specific reactive intermediate at the expense of the normal reactions of that intermediate. Different types of scavenger (*e.g.*, neutral-radical scavengers, electron scavengers, positive-hole scavengers) have been widely used as an aid in the elucidation of the (always quite complex) mechanism of radiolytic processes by means of the effect they have on the reactive intermediates and/or stable radiolysis products of the irradiated system. Alternatively, novel reactive intermediates and/or stable radiolysis products resulting from the action of the scavenger can be investigated, an approach that appears altogether more useful as it yields more direct information.

Electron, positive-hole and neutral-radical scavengers generally act in the strict sense of the word in that they effectively (though not necessarily fully) cleanse the system of the specific intermediate by transforming it into a stable entity or a (less reactive) intermediate associated with the scavenger. Proton scavengers also can act as scavengers in the strict sense if they interfere with protonated molecules of the system under investigation. The role of octane in the present system is considerably more complicated, however, and can hardly be described as a simple proton scavenger. For a proper understanding it will be useful to outline the triple action it exercises. (i) With respect to the formation of 2-chlorooctane[9b] it acts as a proton scavenger (proton acceptor), but the proton is not transferred from protonated heptane molecules but from heptane radical cations [eqn. (10)].

$$n\text{-}C_7H_{16}^{\bullet+} + n\text{-}C_8H_{18} \longrightarrow 1\text{-}C_7H_{15}^{\bullet} + 2\text{-}C_8H_{19}^{+} \quad (10)$$
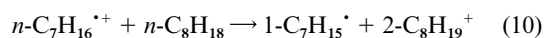
As a result of this scavenging action, only the ionic part of the reactivity is transferred to the scavenger, whereas the radical reactivity remains on a species associated with the system. (ii) With respect to its effects on the isomeric composition of secondary chloroheptanes discussed in the present paper its action is double in nature: (a) it acts as a temporary positive-hole scavenger and the resulting octane radical cations may act as proton donors to heptane molecules; (b) it dislocates heptane molecules in the crystallites and brings penultimate C–H bonds in these molecules into direct contact with planar chain-end C–H bonds in heptane radical cations, causing proton transfer to heptane molecules to take place from heptane radical cations in their electronic ground state. The latter action is quite intriguing (and quite novel) as octane exercises this action without interfering directly with the radiolytic process at all; its action in this regard is purely physical in nature.

Acknowledgements

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present. Three non-planar conformers have been observed, *viz.* 'end-*gauche*', 'kink' and 'double-*gauche*' forms, the first two being dominant. The concentration of non-planar conformers increases markedly with increasing chain length and it has been estimated that for C_{29}, for instance, end-*gauche* defects occur in about 20–30% and kink defects in about 60–70% of the molecules. Some end-*gauche* molecules as well as molecules with kinks may also be present in the low temperature phase *but their concentration is very low*; in the low temperature phase, essentially all molecules are in the extended all-*trans* conformation. In infrared studies on partially deuteriated *n*-$C_{21}H_{44}$, for instance, no end-*gauche* conformers could be detected in the low temperature phase, putting the concentration of such defects below 0.5 mol%. See in this regard: (*a*) R. G. Snyder, M. Maroncelli, S. P. Qi and H. L. Strauss, *Science*, 1981, **214**, 188; (*b*) M. Maroncelli, S. P. Qi, H. L. Strauss and R. G. Snyder, *J. Am. Chem. Soc.*, 1982, **104**, 6237; (*c*) R. G. Snyder, M. Maroncelli, H. L. Strauss, C. A. Elliger, D. G. Cameron, H. L. Casal and H. H. Mantsch, *J. Am. Chem. Soc.*, 1983, **105**, 133.

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