PERKIN 2

Proton acceptor site selectivity in the proton transfer from heptane radical cations to decane molecules in γ-irradiated heptane/decane/1-chloroheptane crystals at 77 K

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A study is made of the yield and isomeric composition of chlorodecanes formed by γ-irradiation of heptane/decane/1-chloroheptane crystals at 77 K and subsequent warming. It is observed that in such systems 2-chlorodecane is predominantly formed with smaller yields of the other chlorodecane isomers, in analogy with observations of γ-irradiated CCl_3F/decane. The selective formation of 2-chlorodecane is attributed to proton transfer from heptane radical cations to decane molecules, $(n\text{-}C_7H_{16}^{\cdot +} + n\text{-}C_{10}H_{22} \longrightarrow 1\text{-}C_7H_{15}^{\cdot} + n\text{-}C_{10}H_{23}^{+})$, followed by neutralization of the so-formed protonated decanes by chloride ions upon warming. The results confirm that, when different secondary C–H bonds in neutral *n*-alkane molecules are directly accessible to the planar chain-end C–H bonds in *n*-alkane radical cations from which proton donation takes place, proton transfer occurs preferentially to the penultimate position (intrinsic acceptor site selectivity). Comparison of the isomeric composition of the chlorodecanes in heptane/decane/1-chloroheptane and CCl_3F/decane, on the other hand, clearly points to structurally-determined acceptor site selectivity with respect to the inner C–H bonds of decane in the heptane system.

Introduction

In the proton transfer from *n*-alkane radical cations to *n*-alkane molecules, a clear relationship is observed between the electronic structure of the *n*-alkane radical cation and the site of proton donation (intrinsic donor site selectivity). As a matter of fact, all experimental data available at present indicate that such proton transfer takes place selectively from C–H bonds coplanar to the planar C–C skeleton in *n*-alkane radical cations in the extended all-*trans* and *gauche*-at-C2 conformation, because of the high unpaired-electron and positive-hole density in those bonds (these are referred to as 'planar C–H bonds'). Experimental evidence on this matter can only be obtained in a limited number of carefully selected experiments, but is altogether quite consistent in cases in which formation of alkyl radicals can unambiguously be attributed to proton transfer from alkane radical cations to alkane molecules. The experimental evidence at present comprises EPR studies on the nature of alkyl radicals in irradiated zeolite/alkane,[1] CCl_3F/alkane[2,3] and pentane-d_{12}/octane[4] systems at cryogenic temperatures.

In crystals, which are inherently structurally highly organized, 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). Such studies can also indirectly yield evidence on the dependence of the site of proton donation on the electronic structure of the alkane radical cation. Structurally-determined acceptor site selectivity has been observed in heptane/octane/1-chlorohexane[5,6] crystals; in such crystals, planar chain-end C–H bonds in heptane radical cations are in close contact with chain-end and penultimate C–H bonds in octane molecules only, regardless of the fact that octane is packed in the extended or *gauche*-at-C2 conformation, and selective transfer to the penultimate position is observed. The selectivity in the proton donation to secondary rather than to primary C–H bonds in alkane molecules has a thermodynamic origin, *viz.* the higher proton affinity for protonation at a secondary than at a primary C–H bond.

The role of thermodynamic effects with respect to acceptor site selectivity in the proton transfer from alkane radical cations to alkane molecules certainly deserves further study. More specifically, when different secondary C–H bonds in neutral *n*-alkane molecules are directly accessible to planar C–H bonds in *n*-alkane radical cations from which proton donation takes place, it is of considerable interest to investigate whether some of these bonds will preferentially act as proton acceptors (intrinsic acceptor site selectivity). Recently, information on the relative propensity of different C–H bonds in *n*-alkanes to act as proton acceptors has been obtained from a study of γ-irradiated CCl_3F/alkane systems.[7,8] However, in view of the general complexity of radiolytic processes, this study would clearly benefit from confirmation by investigation of a completely different system. As will be shown in the paper, such confirmation may be obtained by studying the yield and isomeric composition of chlorodecanes formed by γ-irradiation of heptane/decane/1-chloroheptane crystals at 77 K and subsequent warming.

Experimental

Products used in this study were heptane from Rathburn, decane from Janssen Chimica and 1-chloroheptane, 1-chlorodecane and trichlorofluoromethane from Fluka. These products were of the highest purity commercially available. Heptane and decane were 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. The other products were used as received.

Solutions were made by conventional techniques. Samples were contained in large (11 mm id) cylindrical tubes with a narrow orifice made of borosilicate glass. Oxygen was removed by bubbling with argon for 30 min at room temperature (0 °C

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Table 1 Yield [G (number of molecules per 100 eV)] and site-selectivity data (SSD) for the formation of the different chlorodecane isomers by γ-irradiation at 77 K and subsequent warming of heptane containing 1 mol% 1-chloroheptane and 5 mol% decane and site-selectivity data for CCl_3F containing 21 mol% decane

	$G_{heptane}/10^{-2}$	$G_{r,heptane}$	$G_{c,heptane}/10^{-2}$	$SSD_{heptane}$	SSD_{TCFM}
1-Chlorodecane	0.63	0.51	0.03	0.05	0.07
2-Chlorodecane	2.67	2.17	2.07	3.29	1.95
3-Chlorodecane	1.23	1	0.63	1	1
4-Chlorodecane	0.91	0.74	0.31	0.49	1.02
5-Chlorodecane	0.60	0.49	0	0	0.96

in the case of CCl_3F). After deoxygenation, samples were carefully sealed and rapidly cooled to 77 K by immersing in liquid nitrogen. All samples were irradiated with ^{60}Co γ-rays to a dose of 7.5×10^{19} eV g^{-1}.

After irradiation samples were warmed slowly to room temperature. For quantitative analysis, a solution containing a known amount of a suitable internal standard was added to 3 ml of the irradiated sample. All samples to be analyzed were considerably preconcentrated before analysis by controlled blowing of argon over the surface while maintaining the temperature at 80 °C (tests with solutions with known concentration clearly showed that the relative concentration of chlorodecanes is not significantly affected by this process). The analyses were performed on a Sigma 3 gas chromatograph (Perkin-Elmer) equipped with an inlet-splitting capillary injector and a flame ionization detector. A support-coated open tubular (SCOT) glass capillary column (52 m × 0.5 mm id) coated with OV-101 (methylsilicone polymer, a relatively non-polar liquid phase[9]) was employed and helium was used as carrier gas throughout the study. Good separation of the isomeric chlorodecanes was obtained at a column temperature of 75 °C. As internal standard, 1-chlorodecane was used at a concentration that very considerably exceeded its radiolytic formation; the yield of this product (and the minor correction to be applied for its radiolytic formation in its use as internal standard) was determined by a separate analysis in which no internal standard was added. Quantitative data were obtained on the basis of peak heights and (adjusted) retention times,[10a] using the effective carbon number (ECN) method[10b] to estimate the detector response to the different chlorodecane isomers. Radiolytic yields are expressed as the number of molecules formed per 100 eV energy absorbed by the sample (G value).

Results

The relevant part of the chromatogram relating to the analysis of the chlorodecanes, formed upon γ-irradiation at 77 K and subsequent warming of heptane containing 1 mol% 1-chloroheptane and 5 mol% decane, is shown in Fig. 1. G Values with respect to the formation of chlorodecanes in heptane/1-chloroheptane/decane crystals are given in Table 1 under the heading $G_{heptane}$. From these results it is clearly evident that 2-chlorodecane is predominantly formed, with considerably smaller yields for the other chlorodecane isomers. As far as the secondary chlorodecanes are concerned, the yield decreases markedly towards the center of the C–C chain; the yield of 1-chlorodecane is also quite low. Relative yield values obtained by dividing the different $G_{heptane}$ values by that of 3-chlorodecane are given in Table 1 under the heading $G_{r,heptane}$. As will be indicated in the Discussion section, the C5 position is virtually inaccessible in relation to the proton transfer studied so the (spuriously low) formation of 5-chlorodecane must be (largely) due to other reaction processes specified below; these reaction processes may reasonably be expected to yield the other inner chlorodecanes to similar (low) yields. To compensate for this corrected G values are calculated, denoted by $G_{c,heptane}$, by subtracting the yield of 5-chlorodecane from the G value of the respective chlorodecanes. Site-selectivity data (SSD) for the formation of the different chlorodecane isomers *via* the proton transfer studied are subsequently obtained by dividing the different $G_{c,heptane}$ values by that of 3-chlorodecane; these are indicated in Table 1 as $SSD_{heptane}$.

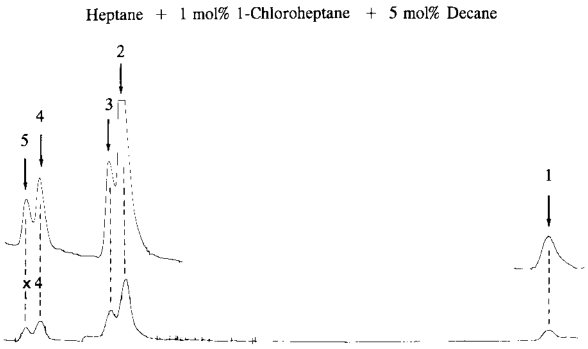

Fig. 1 Relevant part of the chromatogram showing the analysis of the chlorodecanes formed upon γ-irradiation at 77 K and subsequent warming of heptane containing 1 mol% 1-chloroheptane and 5 mol% decane. The numbers indicate the position of the chlorine atom in the chlorodecane isomers. The number preceded by a multiple sign is indicative for the combined effect of increased detector sensitivity and higher amount of sample injected relative to the base chromatogram.

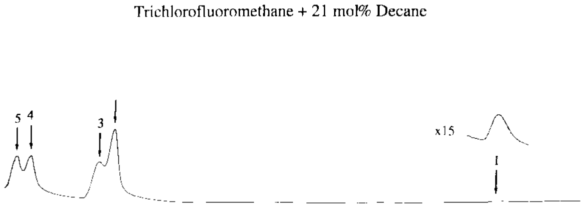

Fig. 2 Relevant part of the chromatogram showing the analysis of the chlorodecanes formed upon γ-irradiation at 77 K and subsequent warming of CCl_3F containing 21 mol% decane. The numbers indicate the position of the chlorine atom in the chlorodecane isomers. The number preceded by a multiple sign is indicative for the combined effect of increased detector sensitivity and higher amount of sample injected relative to the base chromatogram.

The relevant part of the chromatogram showing the analysis of the chlorodecanes, formed upon γ-irradiation at 77 K and subsequent warming of CCl_3F containing 21 mol% decane, is shown in Fig. 2. Site-selectivity data for the formation of the different chlorodecane isomers *via* proton transfer from decane radical cations to decane molecules in γ-irradiated CCl_3F/decane are obtained from this analysis by calculating the yields relative to that of 3-chlorodecane; they are given in Table 1 under the heading SSD_{TCFM}. Comparison of these site-selectivity data with those in the heptane/1-chloroheptane/decane system reveals some obvious similarities and dissimilarities; similarities in that the penultimate isomer is by far the most prominent and that the formation of the chain-end isomer is quite restricted, dissimilarities in that the interior isomers are all formed to about the same extent in the CCl_3F/decane system. Also, the selectivity towards the penultimate isomer appears to be somewhat higher in the heptane/1-chloroheptane/decane system than in CCl_3F/decane.

Discussion

Mechanism of the selective formation of 2-chlorodecane

Irradiation of heptane/decane/1-chloroheptane crystals results in preferential formation of 2-chlorodecane. By analogy with the selective formation of 2-chlorooctane in irradiated heptane/octane/1-chlorohexane crystals,[6] the preferential formation of 2-chlorodecane in the present system may be attributed to proton transfer from matrix (heptane) radical cations to decane solute molecules, followed by neutralization of the so-formed protonated decanes by chloride ions, and is therefore the result of the sequence of reactions outlined below.

Interaction of the ionizing radiation in the heptane/decane/1-chloroheptane system under study occurs mainly with heptane molecules, resulting in ionization and excitation, as shown in eqns. (1a) and (1b). The electrons formed have a definite

$$\text{n-C}_7\text{H}_{16} \rightsquigarrow \text{n-C}_7\text{H}_{16}{}^{\bullet+} + \text{e}^- \qquad (1a)$$

$$\text{n-C}_7\text{H}_{16} \rightsquigarrow \text{n-C}_7\text{H}_{16}{}^* \qquad (1b)$$

probability of escaping from the coulomb attraction of the corresponding radical cations and in doing so will have a high probability of reacting with the chloroalkane solute in the system by dissociative electron attachment[11] yielding chloride ions, as shown in eqn. (2).

$$\text{1-C}_7\text{H}_{15}\text{Cl} + \text{e}^- \longrightarrow \text{1-C}_7\text{H}_{15}{}^{\bullet} + \text{Cl}^- \qquad (2)$$

The heptane radical cations formed in the ionization process are usually substantially excited and may be transformed into other cationic species (carbenium or carbonium ions) by dissociation and proton-transfer reactions. Heptane radical cations, for which such a transformation does not take place before substantial relaxation, will transfer their hole to adjacent heptane molecules, resulting in positive-hole migration,[12] as shown in eqn. (3). The driving force for the hole-migration

$$\text{n-C}_7\text{H}_{16}{}^{\bullet+} + \text{n-C}_7\text{H}_{16} \longrightarrow \text{n-C}_7\text{H}_{16} + \text{n-C}_7\text{H}_{16}{}^{\bullet+} \qquad (3)$$

process is the inhomogeneous coulombic field in the sample, resulting from the presence of various trapped ions (carbenium ions, carbonium ions and chloride ions). When, as a result of this process, a matrix (heptane) radical cation becomes adjacent to a solute (decane) molecule, proton transfer to the solute molecule may take place, as shown in eqn. (4). The occurrence

$$\text{n-C}_7\text{H}_{16}{}^{\bullet+} + \text{n-C}_{10}\text{H}_{22} \longrightarrow \text{1-C}_7\text{H}_{15}{}^{\bullet} + \text{n-C}_{10}\text{H}_{23}{}^+ \qquad (4)$$

of this process despite the presence of heptane molecules, which are altogether much more abundant, results from the fact that (i) planar chain-end C–H bonds in heptane radical cations, from which proton donation takes place, can come into contact with secondary C–H bonds in decane molecules, in contrast to the situation for heptane molecules in pure heptane crystals in which case only contact with primary C–H bonds is possible[5,13] and that (ii) the proton affinity for secondary C–H protonation is considerably larger than for primary C–H protonation.[6–8,14] The dislocation of heptane molecules by decane can make secondary C–H bonds in heptane accessible, but such dislocations do not extend far beyond the place of origin.

Upon warming the sample, the protonated decanes are neutralized by chloride ions. In C–H protonated alkanes, bonding is provided by a three-center two-electron bond which essentially results from the overlap of the σ-orbital of a hydrogen molecule with an empty sp^3 orbital on the appropriate carbon atom.[15–17] The withdrawal of electrons from H_2 appears to be rather small. Consequently, the attack of chloride ions on the C–H protonated group will be directed towards the carbon atom. Neutralization of C–H protonated decanes by chloride ions will therefore result in the formation of chlorodecanes and molecular hydrogen, as shown in eqn. (5), with the isomeric

$$\text{n-C}_{10}\text{H}_{23}{}^+ + \text{Cl}^- \longrightarrow \text{n-C}_{10}\text{H}_{21}\text{Cl} + \text{H}_2 \qquad (5)$$

composition of the chlorodecanes being indicative of the site of C–H protonation. Formation of C–C protonated decanes must be considered a very unlikely process under the conditions of the experiment;[7,8] also, neutralization of C–C protonated decanes would not be expected to result in the formation of chlorodecanes, but rather in the formation of shorter-chain alkanes and 1-chloroalkanes.

In the γ-irradiated CCl_3F/decane system, decane radical cations are formed by positive-hole transfer from matrix cations[18] and by direct interaction of the ionizing radiation with decane. As decane forms small aggregates in CCl_3F at higher concentrations,[2,3] proton transfer from decane radical cations to decane molecules takes place resulting in the formation of decane carbonium ions. The neutralization (upon warming) of these ions by chloride ions, formed by reaction of electrons with CCl_3F, results in the formation of the chlorodecanes observed.

Origin of the selectivity in the formation of 2-chlorodecane

Results obtained in heptane/octane/1-chlorohexane[6] firmly indicate that in the proton transfer from alkane radical cations to alkane molecules in γ-irradiated binary *n*-alkane crystals, proton transfer takes place selectively from planar chain-end C–H bonds in the radical cations to directly accessible secondary C–H bonds in adjacent alkane molecules (*viz.*, only penultimate C–H bonds in octane in the case of the heptane/octane/1-chlorohexane system). In the present heptane/decane/1-chloroheptane system 2-chlorodecane is preferentially formed, with considerably smaller yields for the other chlorodecane isomers. The radiolytic formation of the chlorodecanes decreases gradually on shifting the chlorine substitution from penultimate to more interior positions; the formation of the chain-end isomer, on the other hand, is also quite low. The strong preference for the formation of 2-chlorodecane cannot be fully explained by structural considerations, however, but requires the introduction of a thermodynamic dimension (*intrinsic* acceptor site selectivity) as will be shown below by careful analysis of appropriate structural diagrams.

Ample information is available on the crystalline structure of pure *n*-alkanes and *n*-alkane mixtures, which is relevant to the system under study. X-Ray diffraction studies clearly indicate that in the crystalline state pure *n*-alkanes are packed in the extended all-*trans* conformation within layers.[19] For long chain *n*-alkanes $10 \leq n_C \leq 25$ the crystalline structure alternates between triclinic and orthorhombic, the long molecular axis being perpendicular to the stacking planes in odd-numbered-carbon and tilted in even-numbered-carbon compounds. No regular alternation is observed for the lower alkanes and heptane (odd-numbered) crystals have been shown to have a triclinic structure.[19c] Investigations on binary mixtures of *n*-alkanes have demonstrated that for many composition ranges and temperatures these mixtures make a mixed crystal and that such binary solid solutions of *n*-alkanes also have a lamellar structure when either the short-chain or the long-chain component is predominant.[20] The mismatch in length of the two components in such systems will naturally produce crystal imperfections, which in principle might be located in the interior of the layers in the form of 'kinks' as proposed by Blasenbrey and Pechhold[21] or in the border regions between the layers as suggested by Lauritzen *et al.*[22] Apparently, the second model is preferred;[20] it appears that the interiors of chain layers are not significantly affected by mixing but that it is the chain packing at or near the layer surface that is most affected by chain-length mismatch. Two structure models for the crystal imperfections in the border regions between the layers have been introduced and are suggested to be valid within different composition ranges.[20c,23] They are respectively characterized by the creation of voids (longer component predominant) and by the presence of end-*gauche* conformers of the longer component (shorter component predominant). A third packing structure formed by interleaving of chains at the layer surface has been suggested by Maroncelli *et al.* for intermediate compositions.[20e] Experimental support for these packing models has been obtained; most important to the present work, an infrared study on mixed crystals of nonadecane–henicosane has clearly established the presence of C21 end-*gauche* conformers in the low and intermediate composition ranges of the longer alkane.[20e]

On the basis of this information, structural diagrams showing the packing in heptane crystals containing decane molecules in the *gauche*-at-C2 conformation, with the excess alkyl group protruding respectively at the left and right hand side into the intermolecular boundary region and adjacent molecular layer, can be depicted as shown in Figs. 3 and 4. In the system under study, proton transfer from (electronically relaxed) heptane radical cations will take place from the in-plane chain-end C–H bonds, because these are the only C–H bonds that carry appreciable unpaired-electron and positive-hole density, as can be derived from structural information and information on the electronic structure of alkane radical cations. As already indicated, X-ray diffraction studies clearly demonstrate that in the crystalline state pure *n*-alkanes are packed in the extended all-*trans* conformation.[19] Studies by fluorescence-detected magnetic resonance indicate that matrix *n*-alkane radical cations retain this conformation in crystalline systems.[24] EPR studies, on the other hand, have clearly shown that in *n*-alkane radical cations in the extended conformation the unpaired electron is delocalized over the carbon–carbon σ bonds as well as the two *in-plane chain-end* carbon–hydrogen bonds.[25] Possibilities for proton transfer from planar chain-end C–H bonds in heptane radical cations to secondary C–H bonds in decane are indicated with arrows. Transfer between layers along the *b*-axis in general and transfer options indicated by dashed arrows in particular must be considered less likely because of the greater distances involved. Transfer options to primary C–H bonds in decane are not taken into account because of thermodynamic considerations (see below).

From the structural diagrams it can easily be seen that C–H bonds at the C4 position in decane are directly accessible to planar chain-end C–H bonds in heptane radical cations, but to a much lesser extent than C–H bonds at the C3 position; C–H bonds at the C5 position in decane are virtually inaccessible. It is to be remarked in this regard that C–H bonds at the C3 position in decane are readily accessible from heptane radical cations above *and* below the decane molecule, but efficient transfer to C–H bonds at the C4 position only occurs from heptane radical cations above *or* below the decane molecule as a result of steric hindrance by the *gauche* methyl group. (In the structural diagrams shown this transfer is from below, as the methyl group points upward.) In addition to this, competition between C–H bonds at C2 and C4 in decane for transfer from the same planar chain-end C–H bond in heptane radical cations must also be taken into account. Such structural considerations easily explain the selectivity in the formation of 4- over 5-chlorodecane, as well as the observation that site selectivity for 4-chlorodecane is considerably lower than that for 3-chlorodecane. *The higher selectivity for 2- over 3-chlorodecane cannot be explained, however, on the basis of structural considerations.* From the structural diagrams shown in Figs. 3 and 4, it follows that C–H bonds at the C2 and C3 position in decane are both easily accessible to planar chain-end C–H bonds in heptane radical cations, but with a clear positive bias towards the C3 position. As with the C4 position, efficient transfer to C–H bonds at the C2 position only occurs from heptane radical cations above *or* below the decane molecule as a result of steric hindrance by the *gauche* methyl group and competition between C2 and C4 for transfer from the same site further diminishes the transfer options from a structural point of view. Examination of structural diagrams showing the packing in heptane crystals containing decane molecules in the extended all-*trans* conformation, with the excess alkyl group protruding respectively at the left and right hand side into the intermolecular boundary region and adjacent molecular layer, leads to a similar conclusion though with a less pronounced positive bias towards C3. In stark contrast to the accessibility for proton transfer of the C2 and C3 position in decane in heptane crystals, the site selectivity for transfer to the penultimate position is quite considerably higher than for transfer to the C3 position. The results obtained therefore indicate that when both penultimate and more interior C–H bonds are directly accessible, proton transfer takes place preferentially to the penultimate position. This, in turn, indicates that the proton affinity for C–H protonation at the penultimate position in *n*-alkanes is

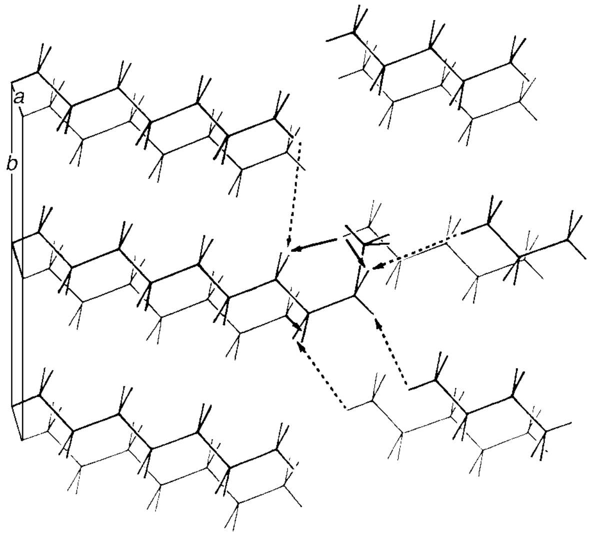

Fig. 3 Structural diagram showing the packing in heptane crystals containing decane molecules in the *gauche*-at-C2 conformation, with the excess alkyl group protruding at the right hand side into the intermolecular boundary region and adjacent molecular layer. Major transfer sites are indicated by solid arrows; dashed arrows indicate minor transfer options.

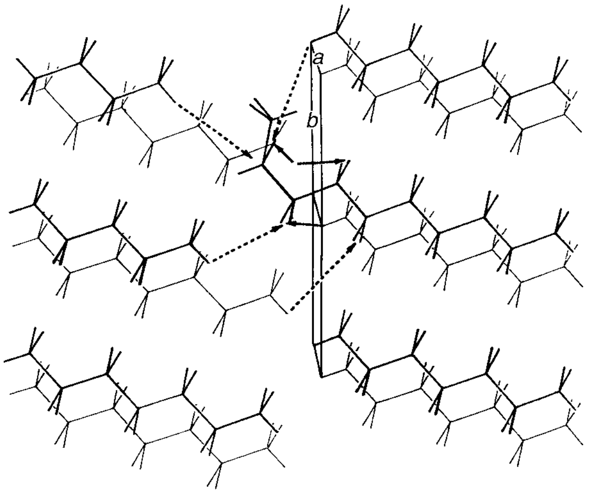

Fig. 4 Structural diagram showing the packing in heptane crystals containing decane molecules in the *gauche*-at-C2 conformation, with the excess alkyl group protruding at the left hand side into the intermolecular boundary region and adjacent molecular layer. Major transfer sites are indicated by solid arrows; dashed arrows indicate minor transfer options.

larger than for C–H protonation at a more interior position. These observations and conclusions are in line with those obtained recently in a study of γ-irradiated CCl_3F/decane and CCl_3F/undecane.[7,8] The fact that analogous results have been obtained in two completely different systems lends considerable credence to the conclusions drawn.

From the structural diagrams shown in Figs. 3 and 4, it can easily be seen that fully interior (C5) C–H bonds in decane molecules are virtually inaccessible to planar chain-end C–H bonds in heptane radical cations, from which proton donation takes place. The formation of 5-chlorodecane in the present system can therefore hardly be the result of proton transfer from (electronically relaxed) heptane radical cations to decane molecules, which is the reaction process studied in this paper. Other more random processes that may explain the formation of 5-chlorodecane include (i) dissociation of electronically excited decane radical cations,[26] as shown in eqn. (6a), formed

$$\text{n-}C_{10}H_{22}{}^{\bullet+*} \longrightarrow C_{10}H_{21}{}^{+} + H^{\bullet} \qquad (6a)$$

by direct interaction of the ionizing radiation with the decane solute, followed by neutralization by chloride ions upon warming, as shown in eqn. (6b), and (ii) proton transfer to

$$C_{10}H_{21}{}^{+} + Cl^{-} \longrightarrow C_{10}H_{21}Cl \qquad (6b)$$

decane molecules from *electronically excited* heptane radical cations, formed by interaction of the ionizing radiation with heptane molecules packed adjacent to decane molecules. No site selectivity with respect to the inner C–H bonds is expected for these processes,[27] so they may be assumed to contribute about equally to the different inner chlorodecane isomers; to compensate for these processes the associated yield, *i.e.*, the yield of 5-chlorodecane, is therefore subtracted from the overall yield to obtain the site-selectivity data (SSD). It should be noted that formation of 5-chlorodecane in the heptane/1-chloroheptane/decane system can be the result of proton transfer from (electronically relaxed) heptane radical cations to decane molecules when these molecules are dislocated in the crystal. At the solute concentrations utilized, such dislocations can be expected to be of minor importance, however. Any contribution from this process or from the transfer option to the C5 position indicated by the dashed arrow in Fig. 4 would result in a lowering of the site-selectivity data, the absolute limit of this being indicated by the $G_{\mathrm{r,heptane}}$ values in Table 1; the prominence of the penultimate isomer remains however undisputed.

The selectivity towards the penultimate isomer appears to be somewhat higher in the heptane/1-chloroheptane/decane system than in CCl_3F/decane. This can be attributed to excess energy present in the radical cation at the instant of proton transfer in the CCl_3F/decane system, excess energy resulting from positive-hole transfer from matrix cations or from direct interaction of the ionizing radiation with the decane solute. In the heptane/1-chloroheptane/decane system, heptane radical cations are intercepted in their migration (by positive-hole migration) towards chloride ions by decane molecules and consequently have lost most of their excess energy in the migration process. 'Soft' proton transfer, *i.e.*, with little or no excess energy, can reasonably be expected to result in higher site selectivity.

A final remark at this point concerns the possibility of proton migration within protonated decane before neutralization. Clearly, this process cannot be excluded by the experiments conducted. However, such proton exchange would not alter the fundamental conclusion that protonation occurs preferentially at the penultimate position in the case of mild protonation under cryogenic conditions, as proton exchange would merely result in transfer to the thermodynamically preferred site, quite irrespective of structural considerations.

Energetics of alkyl carbonium ions (protonated alkanes)

Direct experimental determinations of proton affinities of alkanes are very scarce, but point to a consistent order: tertiary > secondary > primary. The main observations in this regard are that, while proton affinities of methane and ethane differ only slightly, the corresponding values for secondary C–H protonation in propane and *n*-butane are considerably higher, while still higher values are reported for tertiary C–H protonation in isobutane.[14] This rather scant information obtained directly by ion-equilibrium studies can be supplemented nicely with data on ionization energies of alkyl radicals and hydride affinities of alkyl carbenium ions. This is warranted by the fact that the ion-equilibrium studies[14] indicate that C–H protonated alkanes quite readily dissociate into alkyl carbenium ions and hydrogen, as shown in eqn. (7), and that the reaction enthalpy

$$RH_2{}^{+} \longrightarrow R^{+} + H_2 \qquad (7)$$

of this process is very low, having an order of magnitude of only 10 kJ mol^{-1}. This is the case for all C–H protonated alkanes investigated so far, with the exception of protonated methane, indicating that the energetics of C–H protonated alkanes largely parallels that of alkyl carbenium ions. Information on the energetics of alkyl carbenium ions, as derived from experimental studies of the ionization energy of neutral alkyl radicals, may therefore be used to supplement the quite scarce data on proton affinities of alkanes. In particular, heterolytic bond strengths, $D(R^{+}–H^{-})$, *i.e.*, hydride ion affinities of alkyl carbenium ions, may be quite useful in this regard. Generally, hydride ion affinities of alkyl carbenium ions are in the order primary > secondary > tertiary,[28a,b] the greater thermodynamic stability of tertiary > secondary > primary alkyl carbenium ions can be rationalized in terms of both electrostatic induction and hyperconjugation. Thermochemical data for long-chain ($n_{\mathrm{C}} \geq 5$) 1- and 2-alkyl carbenium ions show that there is no appreciable change with chain length of hydride ion affinities,[29] indicating that the proton affinity for C–H protonation at a particular position in *n*-alkanes is not affected by chain length from $n_{\mathrm{C}} \approx 5$. The hydride affinities of the higher 2-alkyl carbenium ions are some 100 kJ mol^{-1} lower than those of the corresponding 1-alkyl carbenium ions and similar (but reversed) differences can be anticipated between proton affinities for primary and secondary C–H protonation of the higher *n*-alkanes. An energy diagram presenting the calculated enthalpy of formation of decane carbonium ions protonated at either primary or secondary C–H bonds and the corresponding proton affinities (PA) for primary and secondary C–H protonation is shown in Fig. 5. The much higher proton affinity for secondary than for primary C–H protonation explains the observation that little (probably no) primary C–H protonation takes place as a result of the proton transfer from (electronically relaxed) heptane radical cations to decane molecules in γ-irradiated heptane containing 1 mol% 1-chloroheptane and 5 mol% decane, despite the fact that primary C–H bonds in decane are quite readily accessible to the planar chain-end C–H bonds in heptane radical cations from where the proton transfer takes place. A similar conclusion applies to γ-irradiated CCl_3F/decane as noted before.[8]

Information on the energetics of penultimate *vs.* interior C–H protonated alkanes may also be derived from that of the corresponding alkyl carbenium ions. Unfortunately, although experimental data on ionization energies of 1- and 2-alkyl radicals are plentiful,[30,31] corresponding data for more interior alkyl radicals are quite scarce. As a matter of fact there appears to be only one study, reported by Taubert and Lossing,[32] in which the ionization energy of 2- and 3-pentyl radicals was determined by electron impact on radicals generated by thermal decomposition of the appropriate hexyl nitrites. The fact that the determinations were made in one consistent study

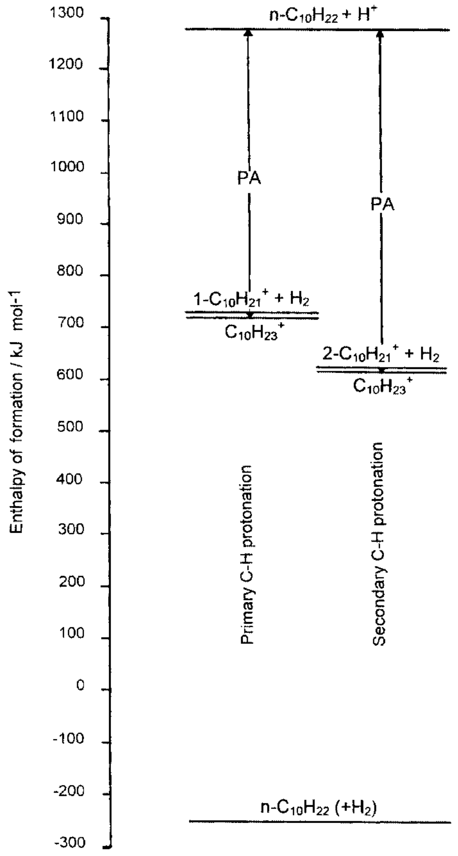

Fig. 5 Scheme establishing the energetics of pentacoordinated decane carbonium ions protonated at either primary or secondary C–H bonds. The enthalpy of formation of the neutral alkane was obtained from ref. 33. Heterolytic bond strengths were taken from ref. 29, assuming complete leveling off at $n_C = 7$. 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 decanes were assumed equal to those for the lower members of the alkane series and were taken from ref. 14.

lends confidence to the relative order of the determined ionization energies. The study shows that the ionization energy of 2-pentyl radicals (7.73 eV) is lower than that of 3-pentyl radicals (7.86 eV), indicating that the trend for increasing ionization energy as a result of the decrease in inductive effect in going from interior to penultimate alkyl radicals is more than offset by the trend for decreasing ionization energy as a result of increased hyperconjugation. In alkyl carbenium ions, the p_z orbital is unoccupied and hyperconjugation can result in partial transfer of electrons of both α- and β-spin without inducing electrostatic polarization, (the transfer simply results in charge delocalization), making the process particularly effective. The difference in ionization energy puts the enthalpy of formation of penultimate carbenium ions at least 12 kJ mol^{-1} below that of interior carbenium ions. (The homolytic C–H bond strength will add somewhat to this value, as penultimate neutral alkyl radicals are also energetically favored over interior alkyl radicals as a result of (more extensive) hyperconjugation.) Because of the parallel between the energetics of C–H protonated alkanes and that of alkyl carbenium ions, a similar difference may be anticipated between enthalpies of formation of alkyl carbonium ions protonated at penultimate *vs.* at interior C–H bonds in *n*-alkanes. Such an outcome is certainly supported by the results presented, which clearly indicate selective protonation at the penultimate position as evidenced by the selective formation of 2-chlorodecane in the systems studied.

Intrinsic *vs.* structurally determined proton-acceptor site selectivity

The results obtained provide evidence on intrinsic acceptor site selectivity as well as on structurally determined acceptor site selectivity (*i.e.*, acceptor site selectivity resulting from donor site selectivity in combination with structural factors) and allow extension of the rule on acceptor site selectivity in the proton transfer from alkane radical cations to alkane molecules in irradiated binary alkane crystals. From the selective formation of 2-chlorooctane in irradiated heptane/octane/1-chlorohexane crystals,[6] it was concluded that in the proton transfer from alkane radical cations to alkane molecules in γ-irradiated binary *n*-alkane crystals, proton transfer takes place selectively from planar chain-end C–H bonds in the radical cations to those secondary C–H bonds in adjacent alkane molecules that are in direct contact with the proton-donating planar C–H bonds (structurally determined acceptor site selectivity). On the basis of the present results and of recently reported data on γ-irradiated CCl_3F/alkanes[7,8] it may be concluded that, when different secondary C–H bonds in the accepting alkane molecule are equally accessible to the planar chain-end C–H bonds in the radical cation from which proton donation takes place, then transfer occurs preferentially to the penultimate position (intrinsic acceptor site selectivity).

The disparity between the site-selectivity data for protonation of the inner (C3 to C5) positions of decane in heptane *vs.* in CCl_3F can unambiguously be attributed to structurally-determined acceptor site selectivity *with respect to these positions* in heptane. In CCl_3F the inner chlorodecane isomers are formed to comparable extents, which is indicative of the fact that decane aggregates in CCl_3F (at such concentrations) are essentially unstructured. In contrast, the yield of the inner chlorodecanes in heptane decreases markedly towards the center of the carbon chain, which can unambiguously be attributed to the crystalline structure of the system resulting in strongly diminished accessibility to the C4 position and even virtual inaccessibility for the C5 position in decane to the planar chain-end C–H bonds in heptane radical cations from where proton donation takes place.

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