Acc. Chem. Res. **2002,** *35,* 523−531

Proton Transfer from Alkane Radical Cations to Alkane Molecules: Selectivity with Respect to the Site of Proton Donation and Proton Acceptance

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Received November 16, 2001

ABSTRACT

Information on the donor and acceptor site selectivity in the proton transfer from *n*-alkane radical cations to *n*-alkane molecules is gathered from γ-irradiated frozen CCl_3F/*n*-alkane solutions (symmetric transfer) and mixed *n*-alkane crystals (asymmetric transfer) by EPR spectroscopy at 77 K and gas chromatographic analysis after melting. The proton-donor site is related very strictly to the structure of the semi-occupied molecular orbital of the parent radical cation, with proton transfer taking place from those C−H bonds that carry appreciable unpaired-electron and positive-charge density. Proton acceptance is 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 equal (but considerably lower) transfer to the interior sites. In mixed *n*-alkane crystals, additional selectivity with respect to the site of proton acceptance results from structural factors in combination with the donor site selectivity (structurally determined acceptor site selectivity).

Introduction

Proton transfer from alkane radical cations to alkane molecules results in the transformation of alkane radical cations to alkyl carbonium ions with concomitant formation of neutral alkyl radicals.

$$RH^{\bullet+} + RH \rightarrow R^{\bullet} + RH_2^{+} \tag{1}$$

Alkane radical cations are the species that result from the ionization of neutral alkane molecules and have both radical and ionic properties. In the alkane radical cations, the unpaired-electron and positive-charge density is distributed over a large part of the molecular frame in a manner that depends on the carbon chain conformation. Alkyl carbonium ions (i.e., protonated alkanes) are the species resulting from the protonation of alkane molecules. In contrast to typical organic bases that contain heteroatoms (e.g., amines), in which the protonation takes place at the heteroatom involving the lone-pair electrons, protonation in alkanes does not take place at a particular atom but at a particular bond. Both C−H and C−C bonds may be protonated, resulting in the formation of a so-called three-center two-electron bond. In C−H protonated *n*-alkanes, the bonding is provided by a three-center two-electron bond resulting from the overlap of the σ-orbital of an hydrogen molecule with an empty sp^3 orbital of the appropriate carbon atom. In C−C protonated alkanes, the bonding is due to an overlap of two sp^3 orbitals belonging to adjacent carbon atoms and the 1s orbital of atomic hydrogen; this group also contains only two electrons.

Three questions are posed in this Account. (i) Is the proton transfer selective with respect to the site of proton donation and, if so, does this site selectivity correlate with the electronic structure of the reacting radical cation and/or with the energetics of the neutral radical formed? (ii) Are specific C−C and/or C−H bonds preferentially protonated or does the protonation occur randomly? (iii) If there is site selectivity with respect to the site of proton acceptance, how does this relate to the energetics of alkyl carbonium ions?

The research that constitutes the framework of this Account comprises studies on γ-irradiated frozen CCl_3F/*n*-alkane solutions and mixed *n*-alkane crystals, using EPR spectroscopy at 77 K and gas chromatographic analysis after melting. CCl_3F/alkane systems allow the study of "symmetric" proton transfer, i.e., with the alkane radical cation and the neutral alkane having the same number of carbon atoms. Mixed *n*-alkane crystals, on the other hand, have proven useful for the study of "asymmetric" proton transfer.

Methodology: Comparison with Conventional Scavenger Studies in Radiation Chemistry

Substances that have a specific effect on a particular process in radiolysis, i.e., "scavengers" in the conventional radiation-chemical terminology (e.g., neutral-radical 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 these scavengers have on the reactive intermediates and the stable radiolysis products. In this regard the research presented in this Account is rather special as it invokes the study of reactive intermediates and stable radiolysis products derived *from the scavenger*. This tends to make the experiments more difficult to perform. In EPR spectroscopy, information on the nature of the alkyl radicals has often to be derived from quite small features in the lateral parts of the spectra, necessitating extensive use of spectral averaging and enlargement by computer techniques. In gas-chromatographic analyses, substantial preconcentration is generally required to increase the concentration of the relevant radiolytic products to a detectable level. A very important *advantage* of the approach adopted, compared to conventional scavenger studies, is that the

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10.1021/ar0100430 CCC: $22.00

information can be derived *directly* from specific features in the EPR spectra or gas chromatographic analyses of specific compounds (e.g., isomeric distributions of chloroalkanes) instead of from *changes* in the EPR spectra or *variations* in the radiolytic yields as a function of the scavenger concentration.

Symmetric Proton Transfer: Studies in γ-Irradiated CCl_3F/Alkanes

The following reaction scheme is pertinent to alkane radical cation formation and stabilization in CCl_3F. At low and moderate alkane concentrations, absorption of ionizing radiation, which is nonselective, mainly occurs by CCl_3F resulting in its excitation and ionization.

$$CCl_3F \rightsquigarrow CCl_3F^* \qquad (2a)$$

$$CCl_3F \rightsquigarrow CCl_3F^{\bullet+} + e^- \qquad (2b)$$

As a result of long-range electron tunneling the positive hole is transferred efficiently from trichlorofluoromethane radical cations to the alkane solute,

$$CCl_3F^{\bullet+} + RH \rightarrow CCl_3F + RH^{\bullet+} \qquad (3)$$

resulting in the formation of alkane radical cations. These radical cations are stable at cryogenic temperatures when fully isolated in the CCl_3F matrix. No neutralization occurs because the electrons formed in the ionization process react with the trichlorofluoromethane matrix by dissociative electron attachment.

$$CCl_3F + e^- \rightarrow CCl_2F^{\bullet} + Cl^- \qquad (4)$$

In CCl_3F at 77 K, *n*-alkane molecules form small aggregates to which positive-hole transfer from the matrix cations occurs efficiently.[1,2] The degree of *n*-alkane aggregation increases with increasing alkane concentration and increasing chain length of the alkane solute.[3] As a result, the reaction of *n*-alkane radical cations with *n*-alkane molecules can be studied in γ-irradiated frozen CCl_3F/*n*-alkane solutions. The reaction manifests itself through the appearance and gradual increase in intensity of the resonance signal from neutral alkyl radicals with increasing alkane concentration.[1-3] EPR spectra of γ-irradiated frozen CCl_3F/octane solutions, shown in Figure 1, may serve to illustrate this trend. In this figure, the EPR spectrum obtained for low concentration of octane (i.e., 0.5 mol %) is fully due to octane radical cations. With increasing octane concentration, the resonance signal from neutral octyl radicals also appears and gradually increases in magnitude; this signal is most clearly detectable in the right lateral part of the spectra. Such observations indicate the occurrence of hydrogen and/or proton transfer between *n*-alkane radical cations and their parent molecules.

1. Nature of the Transfer Process and Site of Proton Donation. Information on the nature of the alkyl radicals formed in reaction 1 can be derived from the EPR spectra of γ-irradiated frozen CCl_3F/*n*-alkane solutions but only at relatively low alkane concentration, viz., at the very onset of alkane aggregation and alkyl radical formation.[4,5] Working at the onset of alkyl radical formation is essential because otherwise all radicals are transformed into the thermodynamically most stable ones by intermolecular radical-site transfer. The most notable example, the EPR spectrum obtained after γ-irradiation of CCl_3F containing 1.75 mol % heptane, is shown in Figure 2. The spectrum mainly consists of a (distorted) triplet due to heptane radical cations in the extended all-trans conformation. In addition to the triplet spectrum, a weak resonance signal that can be attributed to 1-heptyl radicals is observed,

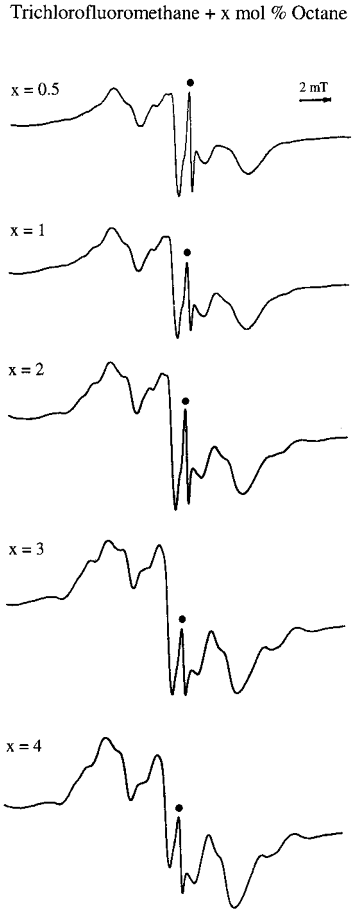


FIGURE 1. First-derivative EPR spectra obtained after γ-irradiation at 77 K of octane at various concentrations in CCl_3F; ● indicates a background signal.

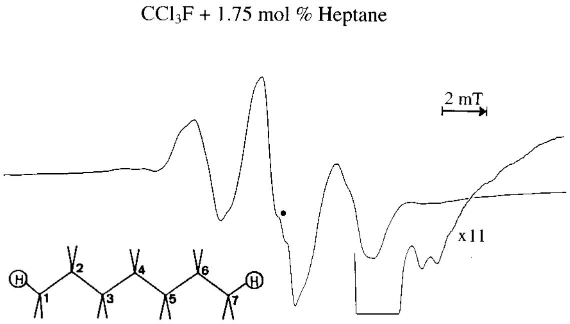


FIGURE 2. First-derivative EPR spectrum obtained after γ-irradiation at 77 K of 1.75 mol % heptane in CCl_3F; ● indicates a background signal.

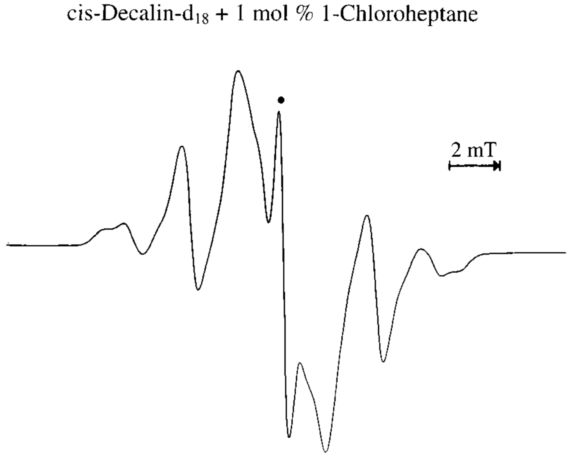


FIGURE 3. First-derivative EPR spectrum obtained after γ-irradiation at 77 K of *cis*-decalin-d_{18} containing 1 mol % 1-chloroheptane; ● indicates a background signal.

indicating that the proton transfer takes place from a chain-end position.[4] The exclusiveness of the 1-heptyl formation can be appreciated by comparison with the powder spectrum of 1-heptyl radicals formed by γ-irradiation of 1-chloroheptane in *cis*-decalin-d_{18} shown in Figure 3, in which the central part is largely due to deuterated decalyl radicals, whereas the singlet line and "double-humped" structure on both sides of the EPR spectrum originate from the 1-heptyl. Secondary heptyl radicals absorb in a considerably broader spectral region (outside the double-humped structure) and would thus be easily observable in Figure 2.

The EPR result on γ-irradiated CCl_3F/heptane characterizes the process as proton transfer (hydrogen abstraction would lead to preferential formation of secondary heptyl radicals) and shows that the site of proton donation is related very strictly to the structure of the semi-occupied molecular orbital in the cation. In *n*-alkane radical cations in the extended all-trans conformation, the unpaired electron is delocalized over the C−C σ-bonds as well as the two in-plane chain-end C−H bonds.[6] EPR experiments on partially deuterated *n*-alkane radical cations established that the major proton hyperfine coupling is for the chain end rather than for interior hydrogens.[7−9] The attribution of the triplet spectrum to the extended all-trans conformation has been supported by fluorescence-detected magnetic resonance (FDMR) spectroscopy of irradiated crystalline *n*-alkanes[10] in conjunction with previous X-ray diffraction studies.[11] The high unpaired-electron and positive-hole density in the *in-plane chain-end C−H bonds* leads to proton transfer from those sites, giving rise to the selective formation of 1-heptyl radicals. Experiments with *n*-alkane radical cations in different conformations confirm the relation between electronic structure and site of proton donation. Octane radical cations in CCl_3F, for instance, are largely in a gauche-at-C_2 conformation obtained by one 120° rotation around C_2–C_3 in the extended conformer (see Figure 4). In this conformation there is large unpaired-electron and positive-hole density in the planar C−C skeleton as well as in one chain-end and one penultimate C−H bond at opposite sides.[7,9] Proton-transfer results in the formation of secondary *as well as* primary octyl radicals, as both are present from the very first appearance of octyl radicals with increasing octane concentration in such systems.[5]

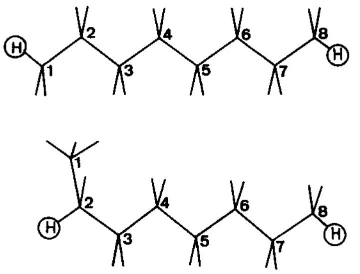
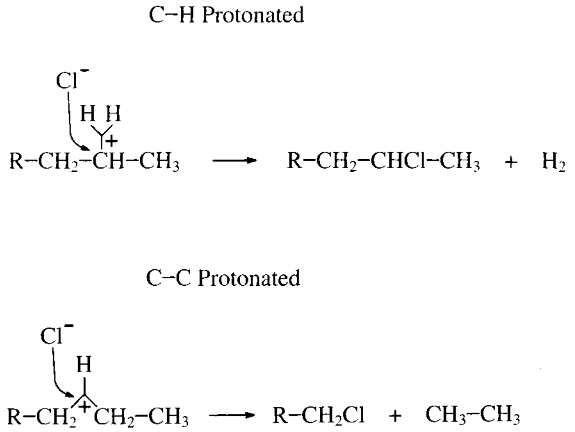


FIGURE 4. Extended all-trans and gauche-at-C_2 conformers of octane.

Information on the site of proton donation in symmetric proton transfer from alkane radical cations to alkane molecules has been derived from systems other than γ-irradiated CCl_3F/alkanes. Two approaches have basically been taken to bring alkane radical cations into contact with alkane molecules in solid systems in order to study their reaction: (i) increasing the concentration of the alkane solute to a point where it is not fully isolated and the appearance of neutral alkyl radicals is observed experimentally and (ii) increasing the temperature of the irradiated system and bringing it to a point where as a result of diffusion and migration alkane radical cations disappear and neutral alkyl radicals are formed. Concentration studies have been conducted in the synthetic zeolites ZSM-5 and Linde-5A.[12] Radical cations of C_6 and C_8 *n*-alkanes prepared by irradiation at 4 K in ZSM-5 at low alkane concentration are in the extended all-trans conformation. At high alkane concentration, alkyl radicals were observed with dominant (but not exclusive) formation of the chain-end isomer; the minor formation of secondary alkyl radicals has been attributed to intermolecular radical site transfer. In Linde-5A only 1-octyl radicals were observed, but no spectrum of octane radical cations has been reported in this zeolite. Thermal conversion of alkane radical cations into neutral alkyl radicals, a process that phenomenologically can be termed "deprotonation", has been conducted in SF_6 and CCl_2FCF_2Cl and conflicting results have been obtained in these matrixes.[6−9,13,14] *n*-Alkane radical cations (C_4−C_7) radiolytically produced in SF_6 at 77 K exhibit the planar extended structure with no detectable gauche conformers; upon warming above 100 K transformation into 1-alkyl radicals is observed exclusively as is expected from the unpaired-electron and positive-hole distribution.[14] In sharp contrast, 2-alkyl radicals are selectively formed by thermal conversion in CCl_2FCF_2Cl regardless of the conformation of the alkane radical cations.[6−9,13] This has been ascribed to thermal conversion of extended conformers into gauche-at-C_2 conformers followed by "deprotonation" via these gauche conformers,[14] but an alternative explanation based on charge neutralization in CCl_2FCF_2Cl is far from inconceivable.

2. Site of Proton Acceptance. The discussion on proton-acceptor site selectivity in symmetric proton trans-

Scheme 1. Neutralization of C–H and C–C Protonated Alkanes by Chloride Ions



fer from *n*-alkane radical cations to *n*-alkane molecules is based on research of the present author only; no other data appear to be available in the literature. The relative importance of C–H vs C–C protonation and the preferential protonation sites at specific C–H and/or C–C bonds in symmetric proton transfer may be examined by analysis of the isomeric chloroalkanes and of shorter chain 1-chloroalkanes by γ-irradiation of CCl_3F/alkanes at 77 K and subsequent melting. Melting will result in the reaction of protonated alkanes with chloride ions, both species being trapped in the solid system at 77 K, which will lead to the formation of isomeric chloroalkanes and shorter chain 1-chloroalkanes for C–H and C–C protonation, respectively (see Scheme 1). For charge-distribution reasons, the attack of chloride ions on the C–H protonated group will be directed toward the carbon atom, and neutralization of C–H protonated alkanes by chloride ions will result in the formation of chloroalkanes and molecular hydrogen, with the position of the chlorine atom being indicative of the site of C–H protonation. Pentacoordinated alkane carbonium ions that have the C–C protonated structure can be formed from and dissociate into alkyl carbenium ions and neutral alkanes[15] and it is quite logical to expect that neutralization with chloride ions will take place accordingly, i.e., with formation of shorter chain 1-chloroalkanes and alkanes. For short-chain *n*-alkanes ($n_C \leq 6$), hydride affinities of 1-alkyl carbenium ions are known to decrease with increasing chain length.[16] In view of this, attack of chloride ions on C–C protonated alkanes when occurring at an asymmetric position is likely to be directed preferentially toward the carbon attached to the longer chain.

The state of affairs with respect to the energetics of pentacoordinated decane carbonium ions, protonated respectively at interior and terminal C–C and primary and secondary C–H bonds, which is relevant to the present discussion, is depicted in Figure 5. The figure relates to the interior C–C protonation at the central C–C bond, but essentially identical energy schemes are obtained regardless of the site of the inner C–C protonation; the energetics for the terminal C–C protonation is different, as indicated. The data indicate that the proton affinities of *n*-alkanes are in the following order: secondary C–H > C–C > primary C–H.

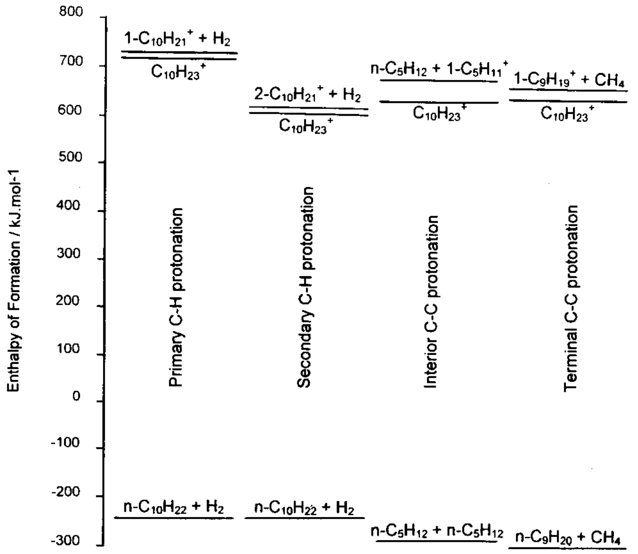


FIGURE 5. Scheme establishing the energetics of pentacoordinated decane carbonium ions, protonated respectively at interior and terminal C–C and primary and secondary C–H bonds. For details on the calculation, see ref 18.

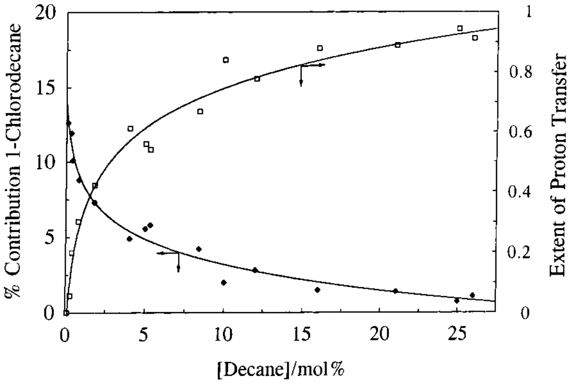


FIGURE 6. Contribution percentage of 1-chlorodecane to chlorodecane formation and extent of proton transfer from decane radical cations to decane molecules as a function of decane concentration in γ-irradiated CCl_3F/decane.

A manifest effect observed upon analysis of chloroalkanes with the same carbon number as the parent alkane in CCl_3F/alkanes after γ-irradiation at 77 K and subsequent melting is the gradual reduction in the contribution of the chain-end isomer with increasing alkane concentration;[17,18] data for CCl_3F/decane are shown in Figure 6. The effect is related to the fact that the proton affinity for primary C–H protonation is substantially lower than that for C–C protonation and secondary C–H protonation and provides further evidence for a gradual transformation of alkane radical cations into protonated alkanes with increasing alkane concentration in γ-irradiated CCl_3F/alkanes. The extent of proton transfer as a function of decane concentration in CCl_3F/decane calculated from these data is shown in Figure 6. A search for 1-chloroalkanes with smaller carbon number than the parent alkane revealed the absence of such products in CCl_3F/decane after γ-irradiation at 77 K and subsequent

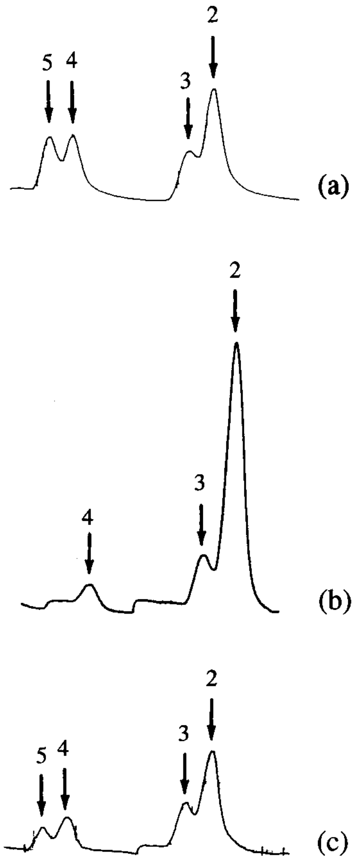


FIGURE 7. Relevant part of some chromatograms obtained after γ-irradiation at 77 K and subsequent melting showing the analysis of the secondary chlorodecanes in CCl_3F/decane (a), the secondary chlorooctanes in heptane/octane/1-chlorohexane (b), and the secondary chlorodecanes in heptane/decane/1-chloroheptane (c). The concentration of the alkane solute is respectively 16 mol % (a), 3 mol % (b), and 5 mol % (c). The numbers above the arrows indicate the position of the chlorine atom in the chloroalkane isomers.

melting, providing strong evidence for the nonoccurrence of C−C protonation of *n*-alkanes by proton transfer from alkane radical cations.[18] The analysis of chloroalkanes with the same carbon number as the parent alkane, on the other hand, showed protonation to take place preferentially at the penultimate C−H bonds in *n*-alkanes, an observation that is supported by thermochemical data.[17,18] Protonation at the inner (nonpenultimate) C−H bonds in *n*-alkanes apparently all occurs to about the same extent. A relevant chromatogram for CCl_3F/decane is shown in Figure 7a (Figures 7b and 7c are discussed in the section on asymmetric proton transfer in mixed alkane crystals).

Asymmetric Proton Transfer: Studies in γ-Irradiated Mixed Alkanes

Radical cations of higher alkanes ($R_{II}H$) may be formed by γ-irradiation and trapped in lower alkane (R_IH) matrixes at cryogenic temperatures in the presence of a suitable electron acceptor, e.g., CO_2 or a chloroalkane (RCl). When a higher alkane solute is present at low concentration in a lower alkane matrix, γ-irradiation mainly results in excitation and ionization of the lower alkane.

$$R_IH \rightsquigarrow R_IH^* \qquad (5a)$$

$$R_IH \rightsquigarrow R_IH^{\bullet +} + e^- \qquad (5b)$$

Considerable geminate neutralization of the so-formed ions will take place, but part of the electrons will become trapped by reaction with the electron acceptor.

$$CO_2 + e^- \rightarrow CO_2^{\bullet -} \qquad (6)$$

$$RCl + e^- \rightarrow R^\bullet + Cl^- \qquad (7)$$

Radical cations of the lower alkane formed in the ionization process are usually substantially excited and may be transformed into other cationic species (carbenium and carbonium ions) by dissociation and proton-transfer reactions. For some R_IH radical cations such transformation does *not* take place before substantial relaxation, and they can participate in a process of positive-hole migration.

$$R_IH^{\bullet +} + R_IH \rightarrow R_IH + R_IH^{\bullet +} \qquad (8)$$

The driving force for the hole-migration process is the inhomogeneous Coulombic field in the sample, resulting from the presence of various trapped ions. When, as a result of this process, a matrix (R_IH) radical cation becomes adjacent to a solute ($R_{II}H$) molecule, positive-hole transfer to the solute may occur.

$$R_IH^{\bullet +} + R_{II}H \rightarrow R_IH + R_{II}H^{\bullet +} \qquad (9)$$

The reaction scheme thus far is fully satisfactory to explain electronic absorption studies of alkane radical cation trapping in lower alkane matrixes. Attempts to link such studies to investigations on stable radiolysis products formed upon melting showed, however, that it only reflects part of reality and that additional processes have to be taken into account. As in irradiated mixed alkanes the higher alkane radical cations are trapped next to matrix molecules, proton transfer from alkane solute radical cations to matrix molecules can certainly be envisaged.

$$R_{II}H^{\bullet +} + R_IH \rightarrow R_{II}^\bullet + R_IH_2^+ \qquad (10)$$

On the other hand, it appears conceivable that the positive-hole transfer from matrix radical cations to solute molecules (reaction 9) could be in competition with proton transfer in the same direction.

$$R_IH^{\bullet +} + R_{II}H \rightarrow R_I^\bullet + R_{II}H_2^+ \qquad (11)$$

Actually, both reactions take place as could be demonstrated with experiments on systems that are specifically designed to reveal either one of these reactions *separately*.

1. Proton Transfer from Solute Radical Cations to Matrix Molecules. a. Site of Proton Donation. The site of proton donation in the proton transfer from solute radical cations to matrix molecules has been investigated

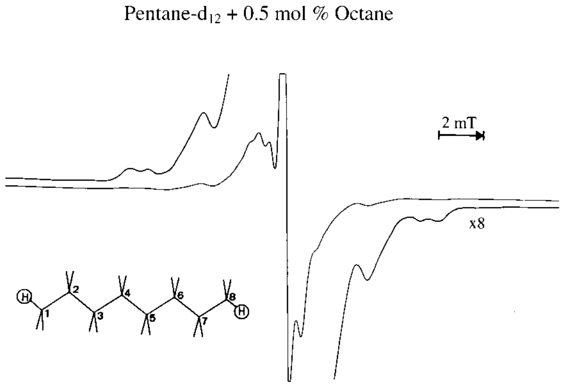


FIGURE 8. First-derivative EPR spectrum obtained after γ-irradiation at 77 K of 0.5 mol % octane in perdeuterated pentane, containing CO_2 as electron acceptor.

by using γ-irradiated pentane-d_{12} containing 0.5 mol % octane as well as trapped CO_2,[19] the reaction studied being

$$n\text{-}C_8H_{18}^{\bullet+} + n\text{-}C_5D_{12} \rightarrow 1\text{-}C_8H_{17}^{\bullet} + n\text{-}C_5D_{12}H^+ \quad (12)$$

The first-derivative EPR spectrum is shown in Figure 8. The EPR spectrum is largely due to deuterated pentyl radicals (this spectrum is narrowed by the deuteration); the very intense and relatively sharp asymmetric feature near the center of the spectrum, with a pseudodoublet structure at the high-field side, is due to $CO_2^{\bullet-}$. The (weak) lateral features can be attributed with certainty to 1-octyl radicals; no secondary octyl radicals are observable in the system. In association with the results of Ichikawa et al., which show that octane radical cations in pentane matrixes are in the extended all-trans conformation,[20] these data thus confirm the relation between the electronic structure of alkane radical cations and the site of proton donation.

b. Site of Proton Acceptance. This type of experiment has not been conducted. This would have been a conventional scavenger experiment, in which the presence of a higher alkane would have induced some (probably complex and rather small) changes in the yield of stable radiolysis products derived from the main alkane.

2. Proton Transfer from Matrix Radical Cations to Solute Molecules. Much of the data below are related to proton transfer to octane; the relevant thermochemical data on octane carbonium ions are therefore given in an energy scheme in Figure 9.

a. Site of Proton Donation. This type of experiment is similar to a conventional scavenger experiment and involves studying the effect of the higher (solute) alkane on the radical distribution for the irradiated matrix alkane.[21,22] The information is derived from EPR spectral analysis of γ-irradiated heptane containing perdeuterated octane (see Figure 10), and the reaction studied is

$$n\text{-}C_7H_{16}^{\bullet+} + n\text{-}C_8D_{18} \rightarrow 1\text{-}C_7H_{15}^{\bullet} + 2\text{-}C_8D_{18}H^+ \quad (13)$$

In Figure 10, clearly observable differences resulting from the addition of octane-d_{18} to heptane are indicated by arrows and the symbols A (inner spectral feature increases considerably in importance with respect to the feature just next to it) and B (a narrower spectral line becomes superimposed on the broad EPR line already present after irradiation of neat heptane). These changes are attributed to a greater abundance of 1-heptyl radicals in the systems containing octane-d_{18}, due to proton transfer to this solute from the planar chain-end C−H bonds in the heptane radical cations; these cations are in the extended all-trans conformation in heptane crystals.[10,11] The increased occurrence of proton transfer from the (electronically relaxed) heptane radical cations results from a combination of thermodynamical and structural factors. Thermodynamically, proton transfer to secondary C−H (or C−D) bonds is favored over the transfer to primary C−H bonds (see Figure 9). Structurally, in heptane crystals containing octane-d_{18} there is a close contact between the planar chain-end C−H bonds of heptane and secondary C−D

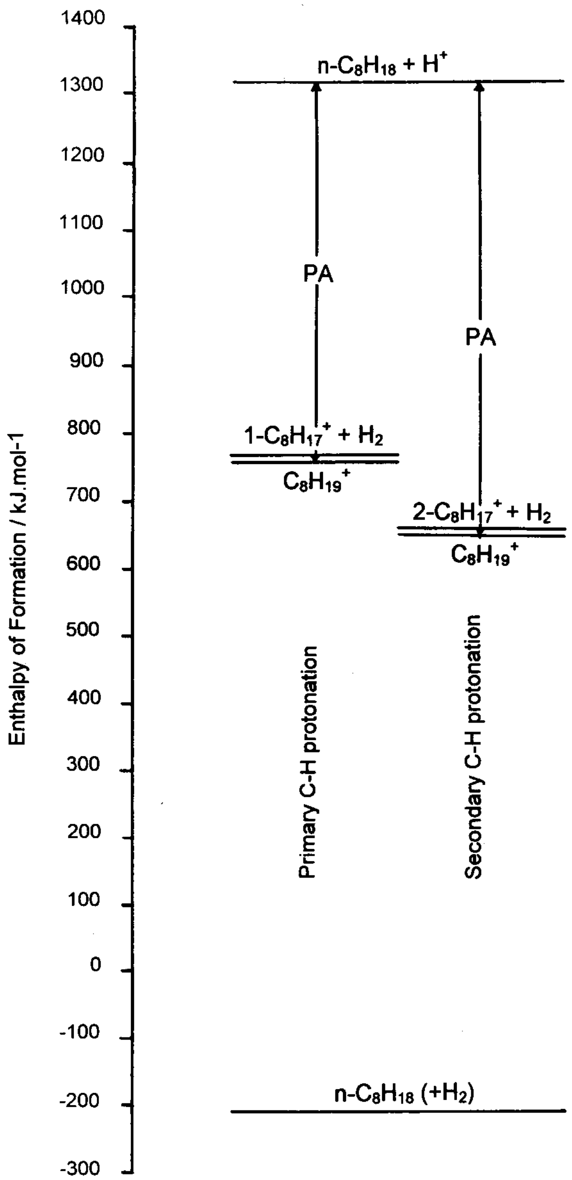


FIGURE 9. Energy diagram showing the calculated enthalpy of formation of octane carbonium ions protonated at either primary or secondary C−H bonds. For details on the calculation, see ref 17.

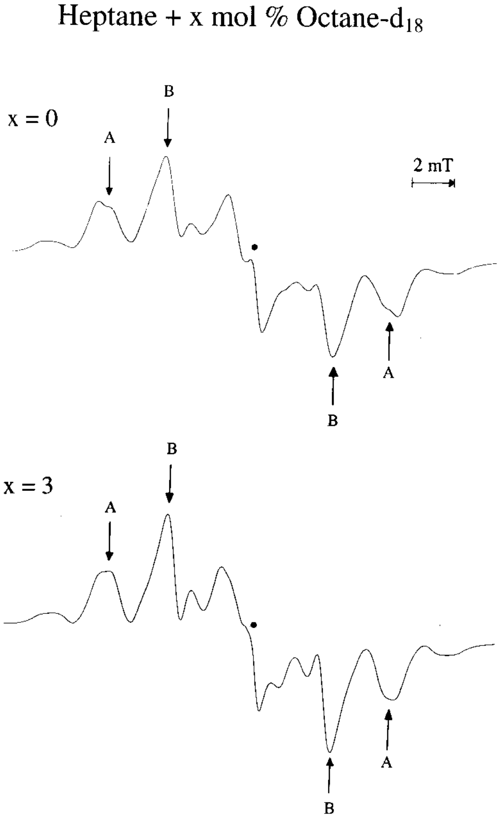


FIGURE 10. First-derivative EPR spectra obtained after γ-irradiation at 77 K of heptane, both neat and with 3 mol % octane-d_{18} added before irradiation; ● indicates a background signal.

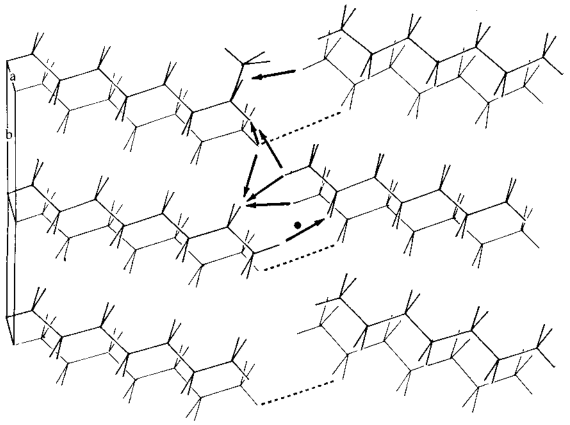


FIGURE 11. Structural diagram depicting the packing in heptane crystals containing octane molecules in the extended all-trans and gauche-at-C$_2$ conformation. The arrows indicate potential sites for proton transfer from planar chain-end C–H bonds in heptane radical cations to penultimate C–H bonds in octane molecules (and *vice versa* heptane vs octane, indicated by ●). The nearest approach of planar chain-end C–H bonds in heptane radical cations to penultimate C–H bonds in heptane molecules is indicated by dashed lines.

bonds of octane-d_{18} at the penultimate position. This is the case regardless of the fact that octane is in the extended (all-trans) or gauche-at-C$_2$ conformation, as is evident from Figure 11. Secondary C–H bonds of heptane in neat heptane crystals are much less accessible to the planar chain-end C–H bonds from which the proton donation takes place.

The results of this experiment illustrate the complexity of interpretation in conventional scavenger experiments, as compared to studies in which the reactive entities that are derived from the scavenger are studied. Though recognizable to the "trained eye" and confirmed by computer simulations, the results of Figure 10 lack the obviousness of most of the other data presented in this Account.

b. Site of Proton Acceptance. Two systems have been investigated in this regard, viz., γ-irradiated heptane/octane/1-chlorohexane[22] and heptane/decane/1-chloroheptane.[23] The first study is the direct chromatographic counterpart of the above EPR investigation and the reaction studied is

$$n\text{-C}_7\text{H}_{16}^{\bullet+} + n\text{-C}_8\text{H}_{18} \rightarrow 1\text{-C}_7\text{H}_{15}^{\bullet} + 2\text{-C}_8\text{H}_{19}^{+} \quad (14)$$

followed by neutralization of the octyl carbonium ions by chloride ions upon melting.

$$2\text{-C}_8\text{H}_{19}^{+} + \text{Cl}^{-} \rightarrow 2\text{-C}_8\text{H}_{17}\text{Cl} + \text{H}_2 \quad (15)$$

From Figure 11 it is evident that penultimate C–H bonds in octane, which for reasons of energetics have the greatest propensity to act as proton acceptor, are also structurally favored over the interior C–H bonds as proton acceptor from planar chain-end C–H bonds in the heptane radical cations. Both structural and thermodynamic factors thus favor the penultimate position and this translates into a high selectivity with respect to this site (see Figure 7b). As a matter of fact, the minor formation of 3- and 4-chlorooctane is (largely) attributed to other (random) processes.

In the heptane/decane/1-chloroheptane system[23] protonation of decane by heptane radical cations is studied.

$$n\text{-C}_7\text{H}_{16}^{\bullet+} + n\text{-C}_{10}\text{H}_{22} \rightarrow 1\text{-C}_7\text{H}_{15}^{\bullet} + s\text{-C}_{10}\text{H}_{23}^{+} \quad (16)$$

Information on the accessibility of the different C–H bonds in decane for planar chain-end C–H bonds in heptane radical cations may be derived from the structural diagrams shown in Figures 12 and 13. Some of the proton transfers indicated therein may take place from the heptane radical cations *above and below* the decane molecule, whereas other transfers proceed via single transfer sites either due to steric hindrance by the gauche methyl group or due to the transfer occurring in the b-plane of the crystal. Competition between different sites for the same planar chain-end C–H bond in heptane radical cations should also be taken into account. From the structural diagrams it can be seen that the C–H bonds at the C$_4$ 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 C$_3$ position; C–H bonds at the C$_5$ position in decane are only to a very minor extent accessible. C–H bonds at the C$_2$ and C$_3$ position in decane are both easily accessible with a clear positive bias toward C$_3$ for the gauche-at-C$_2$ conformer. In stark contrast, the selectivity for the proton

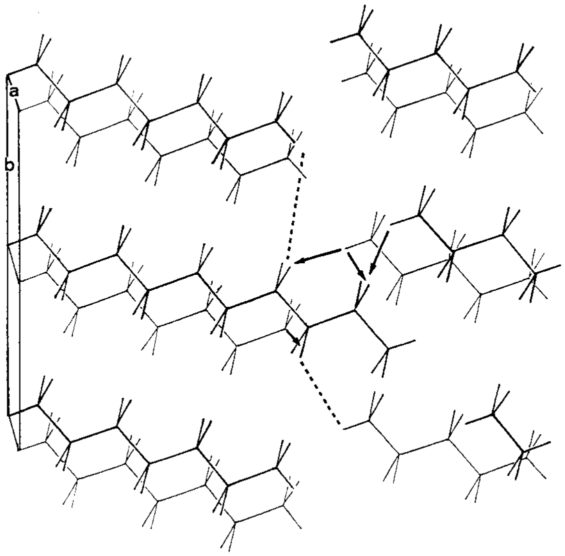


FIGURE 12. Structural diagram depicting the packing in heptane crystals containing decane molecules in the extended all-trans conformation. The arrows indicate potential sites for proton transfer from planar chain-end C−H bonds in heptane radical cations to C_2, C_3, and C_4 carbon−hydrogen bonds in decane molecules; points of approach that are deemed irrelevant or of minor importance to the proton-transfer process for structural reasons are indicated by dashed lines.

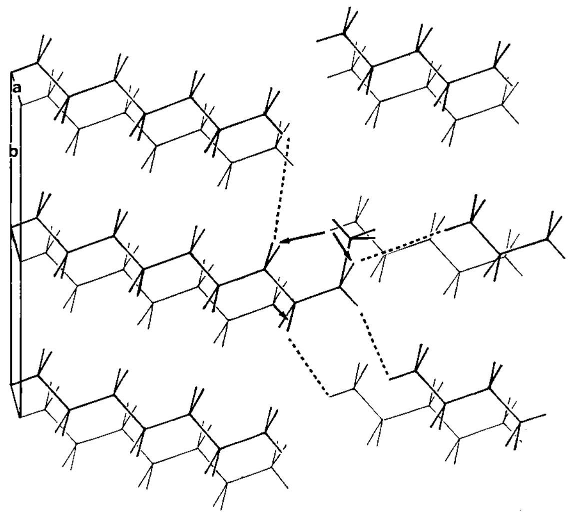


FIGURE 13. Same as Figure 12 with decane in the gauche-at-C_2 conformation.

transfer to the penultimate position is higher than for the transfer to the C_3 position, as can be derived from the isomeric composition of the chlorodecanes (see Figure 7c). The site selectivity factor (relative to C_3) obtained after correction for a yield due to random processes (as defined by the yield of 5-chlorodecane) amounts to 3.29, *confirming that the proton transfer in n-alkanes preferentially occurs to the penultimate C−H bonds*. The disparity between the site selectivity for the protonation of the inner (C_3 to C_5) positions of decane in heptane vs in CCl_3F, as illustrated by the site selectivity factors (heptane/CCl_3F; C_3, 1/1; C_4, 0.49/1.02; C_5, 0/0.96), can be attributed to *structurally determined acceptor site selectivity* in heptane crystals, i.e., acceptor site selectivity resulting from the donor site selectivity in combination with the accessibility differences due to the structural factors.

A Look Back and a Look Forward

The question whether hydrogen and/or proton transfer between higher alkanes and their cations takes place in condensed phases had long been an important unsolved problem. A number of experiments indicated the occurrence of such processes but failed to provide conclusive evidence. The results for γ-irradiated frozen CCl_3F/alkane solutions presented in this Account give clear evidence for the formation of neutral alkyl radicals and protonated alkanes and link their formation and increasing prominence to increases in the alkane solute concentration. By doing so, these results point to the occurrence of reaction 1. The nature of the neutral alkyl radicals formed characterizes the reaction as proton transfer and excludes hydrogen abstraction from alkane molecules by the alkane radical cations as a contributing process. The results for γ-irradiated mixed alkane crystals confirm this view and provide evidence for asymmetric proton transfer between the solute alkane radical cations and the matrix molecules and *vice versa*, processes that have not been studied previously.

The remarkable site selectivity observed in solid-state proton transfer, as outlined in this Account, contrasts strongly with the results of more conventional radiation-chemical studies of *n*-alkanes that generally give an impression of more or less random energy deposition, bond breakage, and reaction. Two factors contribute to this difference. (i) Radiolytic processes in general are complex and various reactions contribute to the radiation chemistry of *n*-alkanes, whereas in the present study one reaction (viz., the proton-transfer process) is singled out by careful planning of the irradiated system and of the intermediates and products studied. The exclusion of alternative reaction pathways for the observations requires much insight and reflection and is often assisted with specially designed experiments; the reader is referred to the original publications and in particular ref 22 for details. (ii) The emphasis on studying reactive intermediates and radiolysis products that are derived *from the scavenger* has the great advantage that the initial ionization event and the actual reaction studied (viz., the proton-transfer process) are separated in both space and time. As a result, most excitation energy is lost before the proton transfer occurs, which greatly contributes to the selectivity.

This brings us to the point of future studies. I believe that focusing on the effect of excess energy on the (donor and acceptor) site selectivities, in conjunction with theoretical calculations on the electronic structure of electronically excited alkane radical cations, is worthy of detailed studies. Also, dissociation reactions of alkane radical cations are poorly understood; e.g., the role of the matrix and the energetic pathways in selecting a particular dissociation channel deserve to be clarified.[24] From a radiation-chemical point of view, the study of the relative importance of positive-hole transfer vs asymmetric proton transfer with respect to “energy transfer” in irradiated mixed alkanes appears quite interesting.

I thank my co-workers who participated in this research. Geert Luyckx was involved in the early stages of (then still) “hydrogen/proton” transfer in γ-irradiated CCl_3F/alkanes. Dominique Stienlet participated in research on proton-donor site selectivity in γ-irradiated CCl_3F/alkanes and mixed alkane crystals. Adelheid Demeyer was involved in the studies on intrinsic and structurally determined proton-acceptor site selectivity in such systems. In this regard, the contribution of Lutgart Slabbinck also has to be mentioned. Special mention should be made to Ann Kinnaes who suffered most of the frustration resulting from the presence of asymmetric proton transfer in irradiated binary alkanes, which greatly hampered the studies she intended. Though not contributing directly to any of the results presented in this Account, her work opened new horizons for the study of proton transfer with the use of mixed alkane crystals. I finally wish to thank the Belgian institutions for funding of fundamental research, the (former) NFWO as well as FWO-Vlaanderen, for financial support.

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AR0100430