Carbon−Hydrogen vs Carbon−Carbon Protonation in the Proton Transfer from Alkane Radical Cations to Alkane Molecules. A Study in γ-Irradiated CCl_3F/Decane at 77 K

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A study is made of the formation of the isomeric chlorodecanes, and a search is made for shorter-chain 1-chloroalkanes ($5 \leq n_C \leq 9$) formed in CCl_3F/decane by γ-irradiation at 77 K and subsequent melting at various concentrations of decane. In such systems, proton transfer from decane radical cations to decane molecules resulting in the formation of pentacoordinated decane carbonium ions (protonated decanes) is quite extensive at high decane concentration, as is evidenced by the fact that under such conditions (i) the ESR spectrum of the irradiated system at 77 K largely consists of decyl radicals and (ii) the contribution of 1-chlorodecane to chlorodecane formation after melting the sample is quite small. The contribution of decyl radicals to the paramagnetic absorption sharply increases and the contribution of 1-chlorodecane to chlorodecane formation strongly decreases with increasing concentration of decane. It is observed that at high decane concentration formation of secondary chlorodecanes is extensive, with 2-chlorodecane being by far the most prominent, but that shorter-chain 1-chloroalkanes are essentially absent. From the results obtained it is concluded that proton transfer from decane radical cations to decane molecules in γ-irradiated CCl_3F/decane results in the selective formation of secondary C−H protonated decanes with a clear preference for the penultimate position and that formation of C−C and primary C−H protonated decanes by this process is negligible.

Introduction

Investigations on the intrinsic properties of ionic species derived from alkanes and on the reactions of such species are of fundamental importance for a proper understanding of ionic processes in general. Pentacoordinated alkane carbonium ions (or protonated alkanes) and the proton-transfer reaction from alkane radical cations to alkane molecules, which generates these species, are quite interesting in this regard and certainly deserve a detailed investigation. Whether or not proton transfer from higher alkane radical cations to alkane molecules actually takes place has long been an important unsolved problem, which has only recently been solved unambiguously. A strong indication for the occurrence of the reaction has been obtained by thermal conversion studies of alkane radical cations in SF_6 and CCl_2FCF_2Cl,[1] by the pulse-radiolytic detection of fast alkane radical cation decay in the radiolysis of liquid and glassy alkanes[2] and by the observation that the signal intensity of fluorescence detected magnetic resonance (FDMR) spectra of saturated hydrocarbon radical cations in liquid systems decreases with increasing hydrocarbon solute concentration.[3] Conclusive evidence for the occurrence of the reaction in the case of higher alkanes has been obtained by X irradiation of C_4−C_8 *n*-alkanes adsorbed on synthetic zeolites at 4 K[4] and by γ-irradiation of different *n*-alkanes at various concentrations in CCl_3F matrixes at 77 K.[5,6] The occurrence of proton transfer from alkane radical cations to alkane molecules is now well established and (especially from excited cations) is considered to play a major role in the formation of neutral alkyl radicals in the radiolysis of *n*-alkanes.[7] Unlike alkenes whereby both radical cation dimerization and proton transfer can occur,[8] ionic condensation reactions do not take place in the case of *n*-alkanes[9] and hydrogen abstraction/proton transfer appears to be the sole reaction between the radical cations and the parent neutral molecules. For the higher members of the series and (near) ground-state cations, the process is essentially restricted to proton transfer.[6,10]

In the study of the proton-transfer reaction from alkane radical cations to alkane molecules by ESR spectroscopy in irradiated zeolite/alkane[4] and CCl_3F/alkane[6] systems at cryogenic temperatures, a clear relation has been established between the electronic structure of the alkane radical cation and the site of proton donation that gives rise to very pronounced *intrinsic donor site selectivity*. Confirmation of this could be obtained by the study of octyl radicals in γ-irradiated pentane-d_{12}/octane systems by ESR spectroscopy[10] and by observation of *structurally determined proton-acceptor site selectivity* (i.e., acceptor site selectivity resulting from donor site selectivity in combination with structural factors) in γ-irradiated heptane/octane/1-chlorohexane mixed crystals by analysis of stable radiolysis products using gas chromatography.[11] The present paper deals with *intrinsic acceptor site selectivity* in the proton transfer from alkane radical cations to alkane molecules.

Pentacoordinated alkane carbonium ions or protonated alkanes may be of two major types, depending on whether protonation occurs on a carbon−hydrogen or a carbon−carbon bond.[12] Ion-equilibrium measurements indicate that both C−H and C−C protonated alkanes may be observed in the gas phase in experiments that are specifically designed to produce one or the other of these species;[13] i.e., C−H protonated alkanes are produced by reaction of alkyl carbenium ions with molecular hydrogen and C−C protonated alkanes result from reaction of alkyl carbenium ions with neutral alkanes. Little or no information is available at present, however, on the relative importance of C−H vs C−C protonation in the proton transfer from alkane radical cations to alkane molecules and the relative propensity

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of C−H vs C−C bonds in general to act as proton acceptor. The present paper intends to remedy this by reporting a study of the relative importance of carbon−hydrogen vs carbon−carbon protonation in the proton transfer from decane radical cations to decane molecules in γ-irradiated CCl_3F/decane at 77 K. The study is performed by chromatographic analysis of the isomeric chlorodecanes and of shorter-chain 1-chloroalkanes ($5 \leq n_C \leq 9$), which are the logical outcome of neutralization with chloride ions of respectively C−H and C−C protonated decanes upon melting. Information on the occurrence of proton transfer in the system is available from ESR analysis at 77 K,[14] and quantitative information on the extent of proton transfer is obtained in the present work from the decreasing contribution of 1-chlorodecane to chlorodecane formation with increasing concentration of decane.

Experimental Section

Products used in this study were trichlorofluoromethane from Fluka and decane from Janssen Chimica. These products were of the highest purity commercially available. Decane was purified by passing through a column containing silica gel, which had been activated immediately prior to use by heating at 250 °C for 24 h. Solutions were prepared by conventional techniques and were contained in large (11 mm i.d.) cylindrical tubes with a narrow orifice made of borosilicate glass (chromatographic measurements) or in small (3 mm i.d.) cylindrical tubes made of quartz of Suprasil grade (ESR measurements). Samples were deoxygenated by bubbling with argon for 30 min at 0 °C, after which they were carefully sealed and rapidly cooled to 77 K by immersing in liquid nitrogen. Irradiations were performed with ^{60}Co γ-rays to a dose of 7.5×10^{19} eV g^{-1}.

For ESR analysis, samples were transferred quickly into a Dewar vessel filled with liquid nitrogen, which was inserted in the cavity of a Bruker ER 200 tt ESR spectrometer. ESR absorptions were recorded in the X band of the spectrum and spectra were accumulated 100 times with a BNC-12 minicomputer to improve the signal-to-noise ratio. The procedures in general for ESR analysis were largely as described before.[5b,15] Samples for chromatographic analysis were warmed slowly to room temperature; subsequently, they were preconcentrated very considerably by controlled blowing of argon over the surface while maintaining the temperature at 80 °C. 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 SCOT column (52 m × 0.5 mm i.d.) made of glass and coated with OV-101 was employed, and helium was used as carrier gas. The chromatographic separations were carried out either isothermally at a column temperature of 75 °C or with linear temperature programming at a rate of 0.4 °C min^{-1} starting at 60 °C.

Results

Chromatograms obtained (by temperature programming) after irradiation of decane at various concentrations in trichlorofluoromethane at 77 K and subsequent warming to room temperature are shown in Figure 1. Also shown in this figure are (i) the chromatogram obtained after irradiation of decane at 16.0 mol % in trichlorofluoromethane, to which 1-chloroalkanes ($n_C = 8-10$) were added after irradiation and melting of the sample, and (ii) a chromatogram obtained by elution of 1-chloroalkanes ($n_C = 5-8$) in pentane; these two chromatograms greatly assist in determining the chromatographic position of the respective 1-chloroalkanes. The chromatographic region between the elution of trichlorofluoromethane and decane (i.e., between the two major peaks) was plagued by rather large detector instability in most cases and is therefore omitted in the figure, except for one typical high-concentration study, viz. CCl_3F containing 10.0 mol % decane, in which case special care was exercised to obtain it properly.

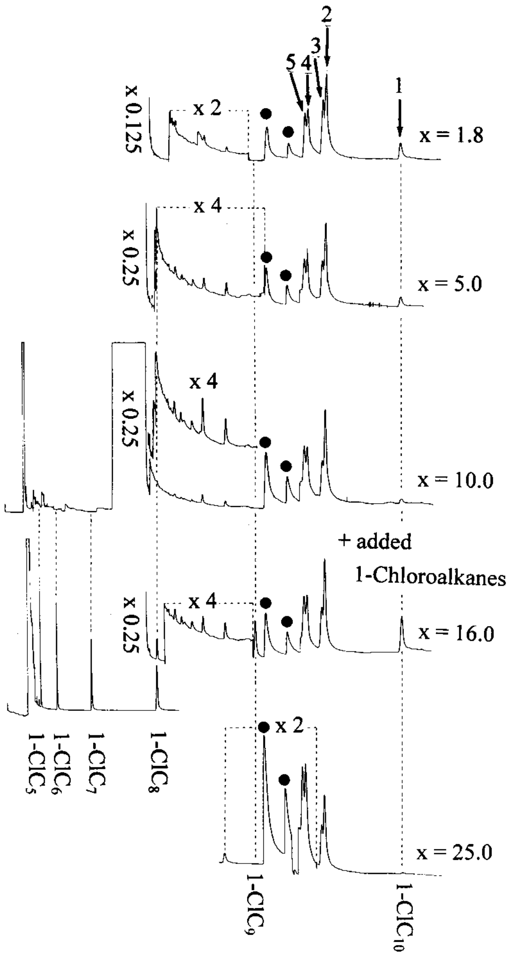

Figure 1. Chromatograms obtained after irradiation at 77 K and subsequent melting of CCl_3F containing various concentrations (x, mol %) of decane. The chromatogram at 16.0 mol % is with added 1-chlorooctane (1-ClC$_8$), 1-chlorononane (1-ClC$_9$), and 1-chlorodecane (1-ClC$_{10}$) to clearly reveal the elution position of these products; the chromatogram obtained by elution of 1-chloropentane (1-ClC$_5$), 1-chlorohexane (1-ClC$_6$), 1-chloroheptane (1-ClC$_7$), and 1-chlorooctane (1-ClC$_8$) in pentane is also shown. The numbers above the arrows indicate the position of the chlorine atom in the chlorodecane isomers; ● indicates spurious peaks due to detector instability. Numbers preceded by a multiple sign are indicative for detector sensitivity (binary scale), relative to detector sensitivity during elution of the chlorodecane isomers. The chromatograms were recorded with linear temperature programming at a rate of 0.4 °C min^{-1}, starting at 60 °C.

The relevant part with respect to the analysis of the chlorodecanes of some typical chromatograms obtained (by isothermal analysis) after irradiation of decane at various concentrations in trichlorofluoromethane at 77 K and subsequent warming to room temperature are shown in Figure 2. A similar chromatogram for trichlorofluoromethane containing 16 mol % decane and clearly showing the isomeric distribution of the chlorodecanes formed by γ-irradiation (at high decane concentration) is shown in Figure 3.

The first point on which attention must be focused with respect to these chromatograms is the gradual reduction in the contribution of 1-chlorodecane to chlorodecane formation with increasing concentration of decane. This decrease is clearly

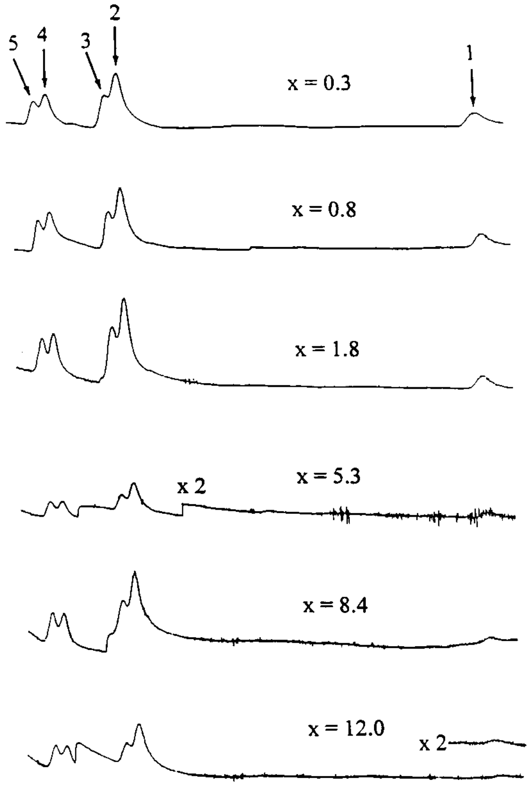

Figure 2. Relevant part of some chromatograms obtained after irradiation at 77 K and subsequent melting of CCl_3F containing various concentrations (*x*, mol %) of decane, showing the analysis of the chlorodecanes. The numbers above the arrows indicate the position of the chlorine atom in the chlorodecane isomers. The chromatograms were recorded isothermally at 75 °C.

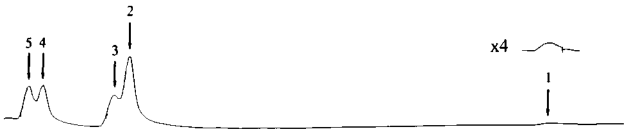

Figure 3. Relevant part of the chromatogram obtained after irradiation at 77 K and subsequent melting of CCl_3F containing 16 mol % decane and showing the analysis of the chlorodecanes. The numbers above the arrows indicate the position of the chlorine atom in the chlorodecane isomers. The chromatogram was recorded isothermally at 75 °C.

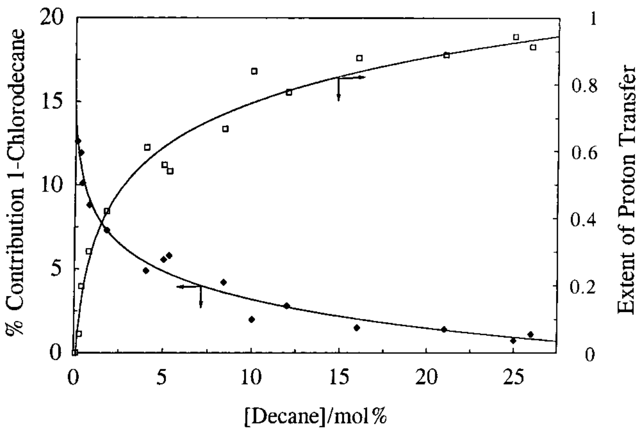

Figure 4. Contribution percentage of 1-chlorodecane to chlorodecane formation and extent of proton transfer from decane radical cations to decane molecules as a function of decane concentration.

evident from Figure 4, in which the contribution percentage of 1-chlorodecane to chlorodecane formation is shown as a function of decane concentration. As will be shown in the Discussion, the decrease in the contribution of 1-chlorodecane constitutes evidence for a gradual increase in proton transfer from decane radical cations to decane molecules with increasing concentration of decane. The contribution percentage of 1-chlorodecane to chlorodecane formation amounts to 12.6 at very low concentration (0.1 mol % decane), at which ESR studies indicate that proton transfer from decane radical cations to decane molecules is essentially absent. Indeed, ESR spectra at 0.2 mol % and below only contain an absorption in the central region of the spectrum, which can be attributed to decane radical cations, superimposed upon an asymmetric matrix absorption (i.e., an absorption due to the irradiated matrix) that is clearly discernible in the left lateral part of the spectrum;[16] no paramagnetic absorption is present, however, in the right lateral part of the spectrum (see Figure 5). In contrast, paramagnetic absorption in this region is quite extensive in spectra at high decane concentration (e.g., 5.0 mol %) and this additional absorption can be attributed unambiguously to decyl radicals, largely formed by proton transfer from decane radical cations to decane molecules.[17] On the basis of the contribution percentage of 1-chlorodecane to chlorodecane formation of 12.6 at 0.1 mol % decane and assuming that the proton transfer never leads to formation of 1-chlorodecane, the extent of the transformation of decane radical cations into protonated decanes by proton transfer from decane radical cations to decane molecules can be calculated. The extent of proton transfer as a function of decane concentration is shown in Figure 4. In case some of the assumptions in the calculation are not fully valid, i.e., if proton transfer to some (minor) extent leads to formation of 1-chlorodecane or if this product is formed (slightly) by some other process, slightly higher protonation extents would be obtained. This, and most probably the latter, may well be the case, as 1-chlorodecane contributes even at very high decane concentration to some minor extent to the formation of chlorodecanes.

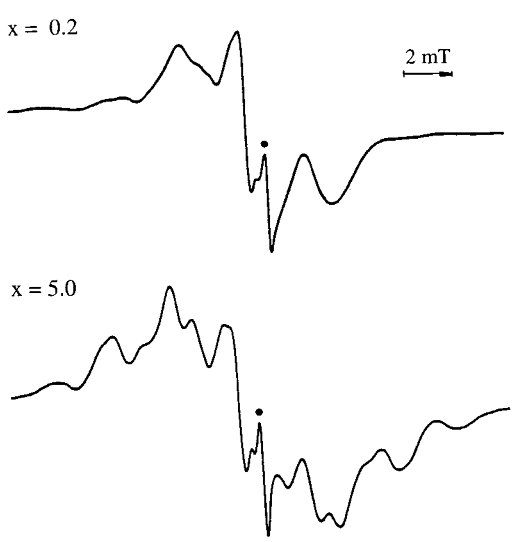

Figure 5. First-derivative ESR spectra obtained after irradiation of CCl_3F containing 0.2 and 5.0 mol % decane, respectively. ● indicates a background absorption. Temperature of irradiation and spectral analysis: 77 K.

The second point on which attention must be focused when examining the chromatograms is the essential absence of 1-chloroalkanes with $5 \leq n_C \leq 9$ (see Figure 1 in this regard). This is of very special importance at conditions under which proton transfer from decane radical cations to decane molecules takes place extensively, e.g., at 10.0 mol % decane in CCl_3F. The chromatogram obtained after irradiation of CCl_3F containing 10.0 mol % decane clearly reveals the absence of the formation of 1-chloropentane, 1-chlorohexane, 1-chloroheptane, and 1-chlorononane. It may be important at this point to stress that the detector sensitivity in the chromatographic region between the elution of trichlorofluoromethane and decane is the same as that during the elution of the chlorodecanes and that an even increased detector sensitivity was utilized in the chromatographic region between the elution of decane and the chlorodecanes. A minor peak appears to be present, whose position more or less matches that of 1-chlorooctane and which may or may not be due to this product, but its size clearly is quite small when compared to that of the chlorodecanes. (Chromatograms at increased detector sensitivity, i.e., ×4, do not yield information on the possible formation of 1-chlorooctane, because the frequent detector sensitivity changes obscure the elution of this product under such conditions.) Results at both lower (5.0 mol %) and higher (25.0 mol %) concentration are more fragmented but are clearly consistent with the stated observation that no appreciable 1-chloroalkanes with $5 \leq n_C \leq 9$ are formed by γ-irradiation of decane in CCl_3F at 77 K and subsequent melting.

The third point on which attention must be focused when examining the chromatograms is the isomeric composition of the chlorodecanes at high decane concentration (see Figure 3 in this regard). As already stated, the contribution of 1-chlorodecane to chlorodecane formation is quite small at such concentrations. The secondary chlorodecanes are formed to mutually comparable extents, with the exception of 2-chlorodecane whose formation is much more pronounced. A similar predominance of the penultimate isomer has previously been observed with respect to the formation of chloroundecanes in γ-irradiated CCl_3F/undecane systems at high undecane concentration.[18]

Discussion

Isomeric Chlorodecanes and Shorter-Chain 1-Chloroalkanes as a Measure for C−H and C−C Protonation, Respectively. Information on the relative importance of carbon−hydrogen vs carbon−carbon protonation in the proton transfer from decane radical cations to decane molecules may be obtained by analysis of the isomeric chlorodecanes and shorter-chain 1-chloroalkanes in CCl_3F/decane at high decane concentration, after γ-irradiation at 77 K and subsequent melting. The rationale for this is (i) that under such conditions proton transfer from decane radical cations to decane molecules is quite extensive, resulting in near-complete transformation of decane radical cations into protonated decanes and (ii) that neutralization of C−H and C−C protonated decanes by chloride ions leads to the formation of chlorodecanes and shorter-chain 1-chloroalkanes, respectively. These points are elaborated first below.

Radical cations of saturated hydrocarbons (and of many other compounds as well) may be generated by exposure of these compounds to ionizing radiation in a trichlorofluoromethane matrix at cryogenic temperatures.[19] As trichlorofluoromethane is the dominant component in the binary CCl_3F/decane systems at moderate decane concentrations, absorption of ionizing radiation that is nonselective mainly occurs by that compound, resulting in its excitation and ionization.

$$CCl_3F \rightsquigarrow CCl_3F^* \tag{1a}$$

$$\rightsquigarrow CCl_3F^{\bullet+} + e^- \tag{1b}$$

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

$$CCl_3F^{\bullet+} + n\text{-}C_{10}H_{22} \rightarrow CCl_3F + n\text{-}C_{10}H_{22}^{\bullet+} \tag{2}$$

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

$$CCl_3F + e^- \rightarrow CCl_2F^\bullet + Cl^- \tag{3}$$

When decane radical cations are not fully isolated in the CCl_3F matrix, however, but are in contact with neutral decane molecules, proton transfer from the radical cations takes place, resulting in the formation of decyl radicals and protonated decanes.

$$n\text{-}C_{10}H_{22}^{\bullet+} + n\text{-}C_{10}H_{22} \rightarrow C_{10}H_{21}^\bullet + C_{10}H_{23}^+ \tag{4}$$

Such a state of affairs prevails in CCl_3F/decane systems at high decane concentration. It has indeed been discovered that alkanes form small aggregates in CCl_3F, aggregates to which positive-hole transfer still occurs efficiently.[5,14,20] The degree of aggregation increases with increasing alkane concentration and at a specific concentration increases markedly with increasing chain length of the alkane solute. The occurrence of proton transfer from alkane radical cations to alkane molecules in irradiated CCl_3F/alkane systems as a result of such aggregation has been evidenced by ESR observations of neutral alkyl radicals, which become increasingly prominent with increasing alkane concentration. Alternative mechanisms for the formation of these alkyl radicals (at moderately high alkane concentration) have been excluded on various grounds.[5,6,14] As is clearly evident from Figure 5, decyl radicals are very prominent in the ESR absorption of irradiated CCl_3F/decane at (moderately) high (e.g., 5.0 mol %) decane concentration, indicating that proton transfer takes place extensively. The marked decrease in the contribution percentage of 1-chlorodecane to chlorodecane formation also constitutes evidence for the occurrence of extensive proton transfer from decane radical cations to decane molecules at high decane concentration;= (see below). At the upper concentrations of decane (e.g., 16 mol %) direct interaction of the ionizing radiation with the decane solute becomes significant. Such interaction also leads to the formation of decane radical cations and, if the electrons formed can escape the alkane cluster, to the formation of chloride ions. Decyl radicals are under such conditions formed both by proton transfer from decane radical cations to decane molecules and by dissociation (C−H scission) of excited decane molecules.

The relative importance of C−H vs C−C protonation in the proton transfer from decane radical cations to decane molecules in irradiated CCl_3F/decane at 77 K may be examined by analysis of the isomeric chlorodecanes and of shorter-chain 1-chloroalkanes after melting the sample. Melting will result in the reaction of protonated decanes with chloride ions, both species being trapped in the solid system at 77 K, which will lead to the formation of isomeric chlorodecanes and shorter-chain 1-chloroalkanes for C−H and C−C protonation, respectively. Indeed, it is well established[12] that in C−H protonated alkanes bonding is provided by a three-center two-electron bond that essentially results from the overlap of the σ-orbital of a hydrogen molecule with an empty sp^3 orbital on the appropriate carbon atom. As the withdrawal of electrons from H_2 appears to be rather small, the attack of chloride ions on the C−H protonated group will be directed toward the carbon atom. Neutralization of C−H protonated decanes by chloride ions will therefore result in the formation of chlorodecanes and molecular hydrogen,

$$C_{10}H_{23}^{+} + Cl^{-} \rightarrow C_{10}H_{21}Cl + H_2 \qquad (5)$$

with the position of the chlorine atom being indicative for the site of C−H protonation. In C−C protonated alkanes bonding is by overlap of two sp^3 orbitals of adjacent carbon atoms and one 1s orbital of atomic hydrogen, the group containing two electrons (three-center two-electron bond). Pentacoordinated alkane carbonium ions that have the C−C protonated structure are formed from and dissociate into alkyl carbenium ions and neutral alkanes,[12,13] 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

$$C_{10}H_{23}^{+} + Cl^{-} \rightarrow 1\text{-}C_nH_{2n+1}Cl + C_mH_{2m+2} \qquad (6)$$

with $n + m = 10$. For short-chain *n*-alkanes ($n_C < 5$), hydride affinities of 1-alkyl carbenium ions are known to decrease with increasing chain length.[21] As a result of this, the dissociation of C−C protonated alkanes, when occurring asymmetrically, preferentially leads to a long-chain 1-alkyl carbenium ion and a short-chain alkane. Similarly, it is therefore to be expected that attack of chloride ions on C−C protonated alkanes, when occurring at an asymmetric position, will preferentially be directed toward the carbon attached to the longer chain. An investigation of the occurrence in irradiated CCl_3F/decane of C−C protonation by proton transfer from decane radical cations to decane molecules may therefore be conducted by searching for the formation of 1-chloroalkanes with $5 \le n_C \le 9$ after melting the sample.

It is to be noted that in the system under study chloroalkanes are not formed to an appreciable extent by combination of alkyl radicals with chlorine atoms, for the simple reason that trapped chlorine atoms are essentially absent after the irradiation under cryogenic conditions. Chlorine atoms are formed during irradiation by C−Cl scission of excited CCl_3F molecules, but they either abstract from an adjacent molecule or, as a result of the cage effect, recombine with the corresponding $CCl_2F^{\bullet}$ radical (geminate radical recombination). Evidence for this has been obtained in irradiated CCl_3F/undecane systems,[18] by the observation that there is a sharp contrast between the prominence of primary undecyl features in the ESR spectra and the near absence of the chain-end isomer in the chloroundecane analyses at high (>3 mol %) undecane concentration, clearly indicating that trapped undecyl radicals do not contribute significantly to the formation of chloroundecanes in such systems. The same information cannot be derived from irradiated CCl_3F/decane systems, because secondary decyl radicals are much more prominent in such systems as a result of the gauche-at-C_2 conformation of the trapped decane radical cations yielding decyl radicals by proton transfer, but the fate of chlorine atoms in such systems is undoubtedly the same as that in CCl_3F/undecane.

Relative Propensity of Different C−H and C−C Bonds in Decane To Act as Proton Acceptor. Relation to Thermochemical Data of Protonated Decanes. Experimentally, it is observed that at high decane concentration the formation of secondary chlorodecanes is quite extensive, with 2-chlorodecane being the major component, but that formation of 1-chlorodecane becomes of minor importance. Shorter-chain 1-chloroalkanes remain essentially undetected under the conditions of the experiments. These findings indicate that proton transfer from decane radical cations to decane molecules results in protonation of secondary carbon−hydrogen bonds only, with clear preference for the penultimate position; carbon−carbon and primary carbon−hydrogen bonds appear essentially unaffected by the protonation process. This selectivity in the protonation process can be correlated nicely with data on the energetics of C−H and C−C protonated alkanes as (i) obtained experimentally from ion-equilibrium measurements[13] and (ii) estimated from heterolytic bond dissociation energies, $D(R^+{-}H^-)$, of alkanes, dissociation energies of protonated alkanes, and additional thermochemical data. Determinations of proton affinities by ion-equilibrium measurements indicate 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. These results thus indicate that the proton affinity for secondary C−H protonation is higher than for primary C−H protonation. As far as C−C vs C−H protonation is concerned, the same studies indicate that while the enthalpy of formation of the C−C protonated structure is lower than that of the C−H protonated structure in the case of ethane (primary C−H protonation), the opposite appears to be true for secondary C−H protonation in higher *n*-alkanes. As a matter of fact, the proton affinity for secondary C−H protonation in both propane and butane is higher than that for C−C protonation. This points to a consistent order with respect to proton affinities in *n*-alkanes: secondary C−H > C−C > primary C−H. The data as such are rather sketchy, but they are supplemented nicely by mass spectrometric results on the energetics of alkyl carbenium ions. The key data that allow the use of information on the energetics of alkyl carbenium ions in this regard are the dissociation energies of alkyl carbonium ions as determined by ion-equilibrium measurements.[13] As far as C−H protonation is concerned, such studies indicate that C−H protonated alkanes quite readily dissociate into alkyl carbenium ions and molecular hydrogen and that the dissociation energy of this process is very low, amounting only to some 10 kJ mol^{-1}, allowing us to conclude that the energetics of C−H protonated alkanes largely parallels that of alkyl carbenium ions. As a consequence, heterolytic bond dissociation energies of alkanes, $D(R^+{-}H^-)$, i.e., hydride ion affinities of alkyl carbenium ions, may be quite useful to supplement the quite scarce data on proton affinities of alkanes. Experimentally, it is observed that hydride affinities of long-chain ($n_C \ge 5$) 2-alkyl carbenium ions are some 100 kJ mol^{-1} lower than those of the corresponding 1-alkyl carbenium ions,[22] which strongly indicates that proton affinities for primary and secondary C−H protonation of the corresponding alkanes differ by about the same amount. The situation for C−C protonated alkanes is more complex as (i) the dissociation energy of C−C protonated alkanes into alkyl carbenium ions and neutral alkanes is substantial[13] and (ii) the thermochemistry of the neutral alkanes, i.e., original alkane vs products resulting from the C−C dissociation, must be taken into account. The effect of these factors can easily be assessed from Figure 6, in which 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 is depicted. The figure relates to interior C−C protonation at the central carbon−carbon bond, but essentially identical energy schemes are obtained irrespective of the site of inner C−C protonation; the energetics for terminal C−C protonation though is somewhat different. The calculations confirm the conclusion reached from analysis of the ion-equilibrium data; i.e., it is again concluded that the proton affinities of *n*-alkanes are in the order secondary C−H > C−C > primary C−H.

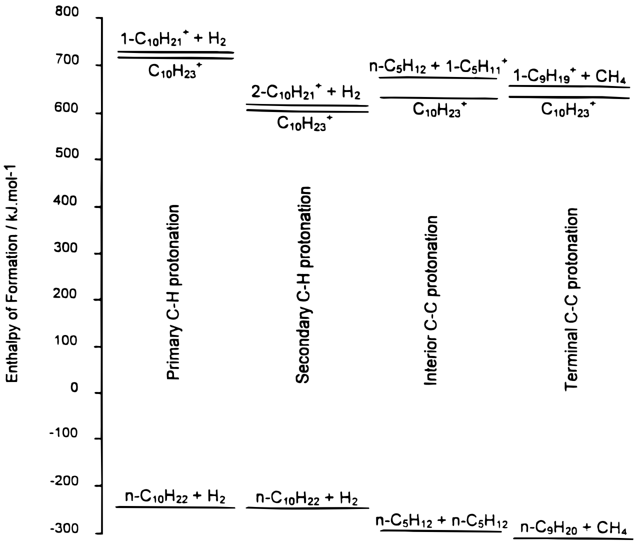

Figure 6. Scheme establishing the energetics of pentacoordinated decane carbonium ions, protonated respectively at interior and terminal C−C and primary and secondary C−H bonds. The enthalpy of formation of the neutral alkanes was obtained from ref 27. Heterolytic bond dissociation energies were taken from ref 22, assuming complete leveling off at $n_C = 7$. The enthalpy of formation of hydride ions was calculated from the commonly available dissociation energy of H_2 and electron affinity of hydrogen atoms. Dissociation energies of C−C and C−H protonated decane were assumed equal to those for the lower members of the alkane series ($2 \leq n_C \leq 4$; see ref 13).

Information on the thermodynamics of penultimate vs interior C−H protonated alkanes may also be derived from that of the corresponding alkyl carbenium ions. Unfortunately, though data on ionization energies of 1- and 2-alkyl radicals are plentiful,[23,24] information on ionization energies of interior secondary alkyl radicals is quite scant. As a matter of fact, there appears to be only one set of data present in the literature, obtained in one consistent study and concerning the ionization energy of pentyl radicals generated by thermal decomposition of the appropriate hexyl nitrites.[25] The results obtained in that study are in line with our expectation that the thermodynamic stability of penultimate C−H protonated alkanes is larger than for alkyl carbonium ions protonated at an interior C−H position, as it is observed that the ionization energy of 2-pentyl radicals (7.73 eV) is lower than that of 3-pentyl radicals (7.86 eV), putting the enthalpy of formation of penultimate carbenium ions at least some 12 kJ mol^{-1} below that of interior carbenium ions. (The homolytic C−H bond dissociation energy will somewhat add to this value, as penultimate alkyl radicals are energetically favored over interior alkyl radicals as a result of more extensive hyperconjugation.[26]) This enthalpy difference can be anticipated to translate itself into a similar difference between enthalpies of formation of alkyl carbonium ions protonated at penultimate vs at interior C−H bonds in *n*-alkanes. It appears quite reasonable to accept that it is this difference in thermodynamic stability that is at the origin of the greater propensity of penultimate vs interior C−H bonds in *n*-alkanes to act as proton acceptor.

Conclusion

In conclusion, it can be stated that secondary C−H protonation is energetically favored over protonation of C−C and primary C−H bonds in *n*-alkanes. This order in the energetics of secondary C−H vs C−C and primary C−H protonated alkanes is nicely reflected in the observation in the present work that the proton transfer from decane radical cations to decane molecules in irradiated CCl_3F/decane at 77 K results in the quite selective formation of secondary C−H protonated decane. This protonation takes place preferentially at the penultimate position, an observation that is also supported by thermochemical data.

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