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Intrinsic Acceptor Site Selectivity in the Proton Transfer from Alkane Radical Cations to Alkane Molecules. Evidence in γ-Irradiated CCl_3F/Undecane

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A study is made of intrinsic acceptor site selectivity in the proton transfer from alkane radical cations to alkane molecules. The research is conducted by studying the relative degree of protonation at the various C−H bonds in undecane in irradiated CCl_3F/undecane systems at cryogenic temperatures. It is observed that protonation occurs preferentially at the penultimate position, the difference between the other secondary C−H bonds being marginal; very little primary C−H protonation is observed under the experimental conditions.

Introduction

The occurrence of proton transfer from alkane radical cations to alkane molecules in condensed systems

$$RH^{\bullet+} + RH \rightarrow R^{\bullet} + RH_2^{+} \qquad (1)$$

has clearly been established in recent years. Strong indication for this process came from pulse radiolytic detection of fast alkane radical cation decay in the radiolysis of liquid and glassy alkanes, indicating that $RH^{\bullet+}$ partly reacts with something other than solvated (in the near-infrared observable) electrons.[1] The occurrence of *a reaction* between saturated hydrocarbon radical cations and molecules is clearly indicated by the observed dependence on solute concentration of the signal intensity of fluorescence-detected magnetic resonance (FDMR) spectra of different hydrocarbon radical cations in liquid systems.[2] Conclusive evidence for the actual occurrence of hydrogen/proton transfer between higher alkanes and their cations has been obtained by X-irradiation of alkanes adsorbed on synthetic zeolites at 4 K[3] and in particular by γ-irradiation of alkanes in CCl_3F matrices at 77 K,[4,5] using ESR spectroscopy. Such experiments also clearly indicate that for the higher alkanes the reaction occurs essentially by proton transfer to and not by hydrogen abstraction from the neutral alkane molecules.

Intrinsic donor site selectivity in the proton transfer from alkane radical cations to alkane molecules and its relation to the electronic structure of the radical cations involved have already been studied in considerable detail. Evidence has been derived first and foremost from ESR experiments on the nature of the alkyl radicals formed by proton transfer from alkane radical cations to alkane molecules in various irradiated systems (*viz.*, hexane and octane in synthetic zeolites,[3] heptane and octane in CCl_3F,[5] and octane in pentane-d_{12}[6]), which clearly show that the radical site in such radicals is related very strictly to the structure of the semioccupied molecular orbital of the parent cations. It is indeed observed that a high unpaired-electron density in a particular carbon−hydrogen bond leads to proton transfer from that site, giving rise to a particular alkyl radical. Additional evidence on intrinsic donor site selectivity has been obtained by ESR spectroscopic and gas chromatographic investigation of γ-irradiated n-C_7H_{16}/n-C_8D_{18} and n-C_7H_{16}/n-C_8H_{18}/1-$C_6H_{13}Cl$ mixed crystals.[7]

In the present research, the possibility of intrinsic acceptor site selectivity in the proton transfer from alkane radical cations to alkane molecules is investigated. To that effect, the relative degree of protonation at the various C−H bonds in undecane by proton transfer from undecane radical cations is determined in small γ-irradiated undecane clusters dispersed in a CCl_3F matrix. The evidence is derived from chromatographic analyses of the isomeric chloroundecanes formed after melting and supplemented with ESR investigations on the paramagnetic species present at 77 K, to assist in the assessment of the degree of alkane aggregation and proton transfer and in the elucidation of the reaction processes involved.

Experimental Section

Products used in this study, *viz.*, CCl_3F from Fluka and undecane from Janssen Chimica, were of the highest purity commercially available and were used as received. Solutions, prepared by conventional techniques, 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). Deoxygenation was performed by bubbling with argon for 10 min, while maintaining the sample at 0 °C. After oxygen removal, samples 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}.

The procedure for ESR measurements was largely as described before.[8] Irradiated samples were transferred quickly into a Dewar vessel filled with liquid nitrogen, which was inserted in the cavity of a Bruker ER 200tt ESR spectrometer. ESR absorptions were recorded in the X band of the spectrum at a microwave power of 0.6 mW. The spectra were accumulated 100 times with a BNC-12 minicomputer. Samples for chromatographic analysis were warmed slowly to room temperature and were preconcentrated very considerably by controlled blowing of argon over the surface. The analyses were performed on a Sigma 3 gas chromatograph (Perkin-Elmer), which was equipped with an inlet-splitting capillary injector and a flame ionization detector. Adequate separations were obtained on a SCOT column (52 m × 0.5-mm-i.d.) made of glass and coated with OV-101 with helium as carrier gas, at a temperature of 90 °C.

Results

The chromatogram showing the analysis of the chloroundecanes formed by γ-irradiation at 77 K and subsequent melting of 3.5 mol % undecane in CCl_3F is shown in Figure 1. This

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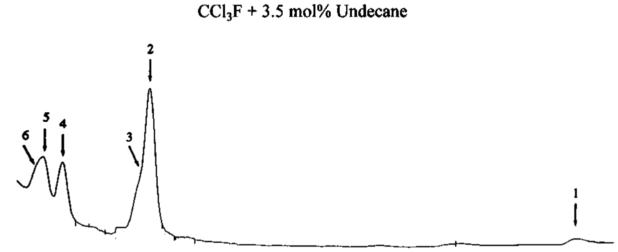

Figure 1. Relevant part of the chromatogram showing the analysis of the chloroundecanes formed by γ-irradiation at 77 K and subsequent melting of 3.5 mol % undecane in CCl_3F. The number indicates the position of the chlorine atom in the chloroundecane isomers.

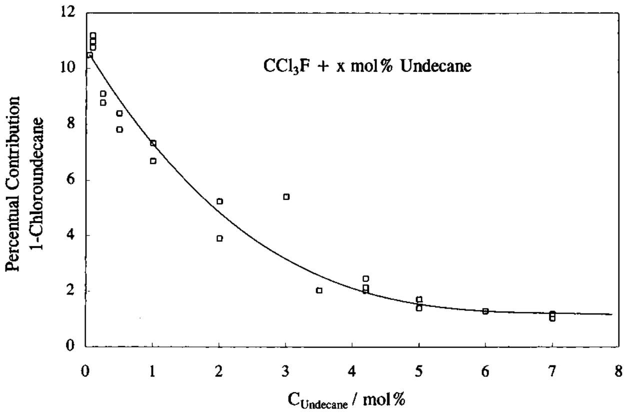

Figure 2. Effect of undecane concentration on the contribution of the chain-end isomer to chloroundecane formation resulting from γ-irradiation at 77 K and subsequent melting of CCl_3F/undecane.

analysis can be considered typical for the results obtained at high (>3 mol %) undecane concentration in CCl_3F. The chromatographic peak due to 1-chloroundecane is quite weak in such "high concentration" experiments. As a matter of fact, the relative importance of this product decreases drastically with increasing undecane concentration, as is clearly evident from Figure 2. As will be demonstrated below, this observation is a clear indication of increasing proton transfer from undecane radical cations to undecane molecules with increasing undecane concentration, resulting in near-complete transformation of undecane radical cations into protonated undecanes at "high concentration". As far as the secondary chloroundecane isomers are concerned, 2-chloroundecane is by far the most prominent in the "high-concentration" experiments. The other (interior) secondary chloroundecanes are formed to mutually comparable extents, with the exception of 6-chloroundecane, whose formation is less pronounced, as is statistically expected. No branched chloroundecanes are observed under the experimental conditions, neither at low nor at high undecane concentration. Chloroalkanes with lower carbon number were not fully systematically investigated in the present study, but indications are that they are not present after irradiation.

ESR spectra obtained after irradiation of undecane at 1.0 and 3.5 mol % in CCl_3F at 77 K are shown in Figure 3. The left part of these spectra is considerably distorted as a result of underlying matrix absorption.[9] The main feature of the spectra, especially at high undecane concentration, is the spectral absorption of primary and secondary undecyl radicals, which extends over the entire spectral region recorded. Superimposed on this is a central absorption, whose exact shape cannot be determined from the present experiments because of the underlying absorptions. From previous experiments in different chlorofluorocarbon, perfluorocarbon, and SF_6 matrices, the central absorption can be attributed to undecane radical cations.[10] Obviously, with increasing undecane concentration the importance of the central absorption due to undecane radical cations decreases relative to that of the more lateral absorptions due to undecyl radicals. This again constitutes evidence for the proton transfer from undecane radical cations to undecane molecules. The paramagnetic absorption due to undecane radical cations is quite weak, especially at high undecane concentration, which corresponds with the weak electronic absorption of these cations in CCl_3F reported previously.[10b] The most prominent features in the undecyl radical spectrum, most notably the relatively sharp intense ESR lines, are quite characteristic for *chain-end* alkyl radicals, as is clearly indicated by theoretical treatments of the hyperfine interactions in such radicals.[11] The prominence of these features stands in sharp contrast to the near absence of the chain-end isomer in the chloroundecane analyses at high (>3 mol %) undecane concentration.

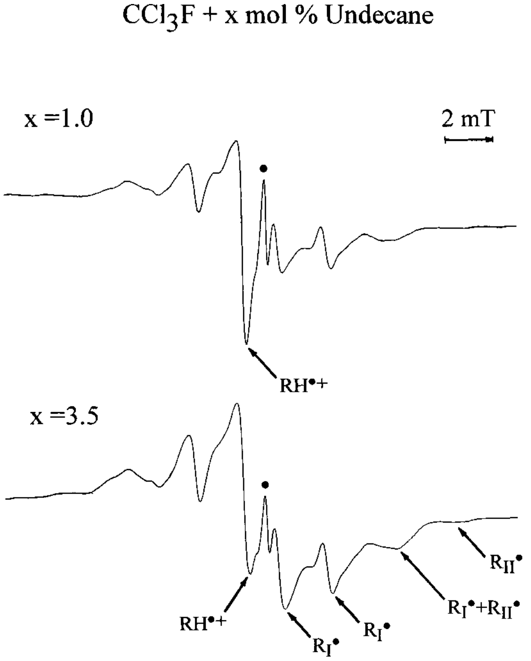

Figure 3. First-derivative ESR spectra obtained after γ-irradiation of undecane at 1.0 and 3.5 mol % in CCl_3F at 77 K. Spectral features due to alkane radical cations and to primary and secondary alkyl radicals are respectively designated by $RH^{\bullet+}$, $R_I^\bullet$, and $R_{II}^\bullet$; ● indicates a background absorption.

Discussion

Chromatographic analyses of the isomeric chloroundecanes formed in cryogenically irradiated CCl_3F/undecane during warming and melting yield detailed information on the relative extent of protonation at the various C−H bonds in undecane by proton transfer from undecane radical cations, as is outlined below. With trichlorofluoromethane dominant in the binary CCl_3F/alkane system, absorption of ionizing radiation mainly occurs by this compound, resulting in excitation and ionization,

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

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

leaving the solute alkane largely unaffected as far as direct interaction with the ionizing radiation is concerned. As a result of long-range electron tunneling, the positive hole is transferred efficiently from trichlorofluoromethane radical cations to the alkane solute, however, resulting in the neat and selective formation of alkane radical cations.

$$CCl_3F^{\bullet+} + RH \rightarrow CCl_3F + RH^{\bullet+} \quad (4)$$

At cryogenic temperatures, these alkane radical cations are stable when fully isolated in the CCl_3F matrix, because electrons formed in the ionization process react with trichlorofluoromethane by dissociative electron attachment.

$$CCl_3F + e^- \rightarrow CCl_2F^{\bullet} + Cl^- \quad (5)$$

The study of proton transfer from alkane radical cations to alkane molecules (reaction 1) is possible in irradiated CCl_3F/alkane systems, because alkanes form small aggregates in this matrix, aggregates to which positive-hole transfer still occurs efficiently.[4] The degree of aggregation increases with increasing alkane concentration and at a specific concentration increases quite strongly with increasing chain length of the alkane solute.[12] As a result of this aggregation, a gradual transformation (with respect to the cationic species) takes place of alkane radical cations into protonated alkanes by proton transfer to neutral alkane molecules. The occurrence of such proton transfer in irradiated CCl_3F/alkane systems at cryogenic temperatures has clearly been established by ESR spectroscopy.[4,5]

It is well established that 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.[13] The withdrawal of electrons from H_2 appears to be rather small. As a consequence, 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,

$$RH_2^{\ +} + Cl^- \rightarrow RCl + H_2 \quad (6)$$

with the isomeric composition of the chloroalkanes formed by this process being determined by the relative degree of protonation at the different C−H bonds.

The results show that the contribution of 1-undecyl radicals to undecyl ESR absorptions is quite extensive in the systems under study, which contrasts sharply with the chromatographic observation that the contribution of the chain-end isomer to chloroundecane formation is quite low, especially at high (*e.g.* 3.5 mol %) undecane concentration. From these combined observations, it may be concluded that trapped undecyl radicals do not contribute significantly to the formation of chloroundecanes. Instead, the formation of these products can be attributed confidently to neutralization of undecane radical cations by chloride ions (at low undecane concentration) and to proton transfer from undecane radical cations to undecane molecules followed by neutralization of the so-formed protonated undecanes by chloride ions (at high undecane concentration). The isomeric composition of the chloroundecanes at high undecane concentration therefore yields detailed information on the relative extent of protonation at the various C−H bonds in undecane by proton transfer from undecane radical cations. The shift in neutralization from undecane radical cations to protonated undecanes with increasing undecane concentration is clearly reflected in the results by the drastic decrease of the contribution of the chain-end isomer to chloroundecane formation (see Figure 2), indicating that protonation of primary C−H bonds is minimal.

The main chromatographic observations made in this work are (i) that the contribution of the chain-end isomer to chloroundecane formation decreases drastically with increasing undecane concentration and that it effectively is quite low at high concentration, (ii) that the penultimate isomer is by far the most prominent in the "high concentration" experiments, and (iii) that in such experiments the other secondary isomers are formed to mutually comparable extents with the exception of the innermost isomer, whose formation is less pronounced, as is statistically expected. As the isomeric composition of the chloroundecanes at high undecane concentration can be considered a measure of the relative extent of protonation at the various C−H bonds in undecane by proton transfer from undecane radical cations (see above), the results obtained thus differentiate between primary and secondary C−H bonds in *n*-alkanes, clearly indicating that secondary C−H bonds are strongly favored over primary C−H bonds in acting as proton acceptor. Most importantly, they further indicate that when both penultimate and more interior C−H bonds are equally accessible, proton transfer (proton acceptance) from alkane radical cations to alkane molecules takes place preferentially at the penultimate position. This is a quite novel observation. In view of the complete similarity in the reaction processes involved, the differences in reactivity can be related to differences in proton affinity for C−H protonation at the respective positions and thus to differences in thermodynamic stability of the various C−H protonated alkanes. Together with information on the (much wider) divergence in proton affinity for protonation at respectively primary, secondary, and tertiary C−H bonds in alkanes, which can be derived from mass spectrometric data, the present differentiation between secondary C−H bonds in *n*-alkanes provides a comprehensive picture of the relative thermodynamic stability of C−H protonated alkanes.

Determinations of proton affinities by ion-equilibrium measurements, though sketchy, 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, whereas still higher values are reported for tertiary C−H protonation in isobutane.[14] This (rather scant) information is supplemented nicely with data on ionization energies of alkyl radicals and hydride affinities of alkyl carbenium ions. As C−H protonated alkanes can be considered as weak complexes between alkyl carbenium ions and molecular hydrogen,[14] the order of magnitude of the dissociation energy being only some 10 $kJ \cdot mol^{-1}$, quite reliable information on proton affinities for protonation at various C−H bonds in alkanes may be derived from hydride affinities of alkyl carbenium ions and, taking into account (or neglecting small) differences in C−H bond dissociation energies, from ionization energies of neutral alkyl radicals. Mass spectrometric studies consistently reveal that ionization energies of alkyl radicals are in the order tertiary < secondary < primary.[15,16] Hydride affinities of long-chain ($n_C \geq 5$) secondary alkyl carbenium ions are some 100 $kJ \cdot mol^{-1}$ lower than those of the corresponding primary alkyl carbenium ions,[17] and this trend continues with similar but somewhat lower differences between hydride affinities of secondary and tertiary alkyl carbenium ions.[18] Obviously, the effect of alkyl substitution on the stabilization energy of alkyl carbenium ions as expressed in terms of the decrease in the heterolytic bond dissociation energy or hydride ion affinity, $D(R^+{-}H^-)$, is much larger than the decrease in the homolytic bond dissociation energy, $D(R{-}H)$, which expresses the stabilization energy of the corresponding neutral alkyl radicals. The information on the dissociation energy of C−H protonated alkanes combined with that on heterolytic bond dissociation energies of alkanes thus clearly (but indirectly) also points to a consistent order: tertiary > secondary > primary, with respect to the proton

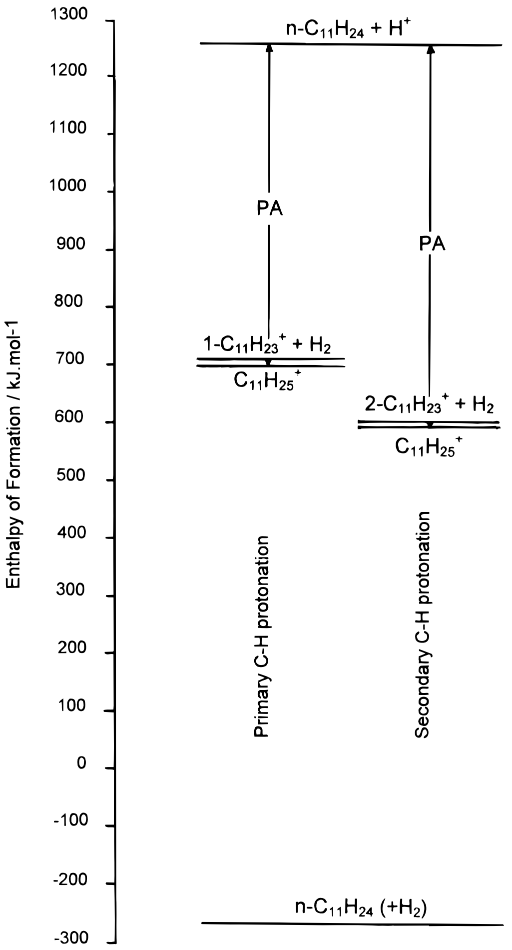

Figure 4. Energy diagram showing the calculated enthalpy of formation of undecane carbonium ions protonated at either primary or secondary C−H bonds. The enthalpy of formation of the neutral alkane was obtained from ref 21, whereas hydride affinities of [C_7] alkyl carbenium ions were taken from ref 17. The enthalpy of formation of hydride ions was calculated from the commonly available dissociation energy of H_2 and electron affinity of hydrogen atoms. The dissociation energy for primary [C_2] and secondary [C_3] C−H protonated alkanes was obtained from ref 14.

affinity for protonation at various C−H bonds in alkanes and the thermodynamic stability of C−H protonated alkanes.

On condition (i) that the dissociation of higher C−H protonated alkanes into alkyl carbenium ions and molecular hydrogen is characterized by the same low dissociation energy as that of the lower ($n_C = 2-4$) members of this series and (ii) that hydride affinities of higher ($n_C > 5$) alkyl carbenium ions are essentially independent of chain length, which, in view of the localized nature of the positive charge in the cationic species in question and with due consideration of experimental data available, can both be considered quite realistic assumptions, the enthalpy of formation of primary and secondary C−H protonated undecanes may be calculated from existing thermodynamic data. Such calculations are presented in the energy diagram shown in Figure 4; they lead to a proton affinity (PA) of 571 kJ·mol^{-1} for primary C−H protonation of undecane and to a much higher value of 667 kJ·mol^{-1} for secondary C−H protonation. In the present study, the corresponding much higher propensity of secondary than of primary C−H bonds to act as proton acceptor in the proton transfer from undecane radical cations to undecane molecules is *proven unambiguously* by the drastic decrease with increasing undecane concentration of the contribution of the chain-end isomer to chloroundecane formation and the near absence of this isomer at high concentration. Clear differentiation between primary and tertiary C−H bonds in acting as proton acceptor has been obtained by protolytic attack with deuterated superacids like DSO_3F-SbF_5 and $DF-SbF_5$ on isobutane.[19] A higher proton affinity for tertiary than for primary and secondary C−H protonation is indicated by studies on the acid-catalyzed isomerization of saturated hydrocarbons by conventional and superacids.[20]

A final remark concerns the possibility of reactions of protonated undecanes between incipience and neutralization, most notably isomerization and dehydrogenation reactions, and the possible occurrence of C−C protonation. With respect to "simple" isomerization by proton exchange, both intermolecular and intramolecular exchange must be taken into consideration. Proton transfer from protonated alkanes to neutral alkane molecules resulting in the formation of thermodynamically more stable species must be quite restricted in the course of the radiolytic process at concentrations ≤ 3.5 mol %, as a result of the limited size of the undecane aggregates. This can be deduced from the fact that primary undecyl radicals are still very prominent under such conditions (see ESR spectra in Figure 3). Efficient neutral radical isomerization by intermolecular radical site transfer is known to take place in irradiated CCl_3F/alkane systems, but only when allowed by the size of the alkane aggregates, and quite the same size limitations must apply to proton exchange between alkanes. In any event, 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. The same remark applies to intramolecular (intraionic) proton exchange between C−H bonds, since this would merely result in transfer to the "preferred site", which may not always be accessible directly in the small undecane clusters for structural reasons. Occurrence (to some extent) of dehydrogenation into alkyl carbenium ions and molecular hydrogen cannot be excluded by the present results. However, such dehydrogenation would not affect the results obtained, as the carbenium site would be located at the site of C−H protonation and neutralization of undecyl carbenium ions also results in the formation of chloroundecanes, with the position of the chlorine atom being determined by that of the carbenium site. Further isomerization of the C_{11} carbocations into branched species does not appear to take place under the experimental conditions, since the chromatographic analyses clearly show branched chloroundecanes to be absent after irradiation. Obviously, the reactivity of the carbocations is considerably reduced by the cryogenic conditions of the experiments. The results further indicate that no C−C protonation occurs in the system investigated, as no chloroalkanes with lower carbon number were detected. A detailed study of (the absence of) C−C protonation in the case of mild protonation under cryogenic conditions is currently in progress.

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