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ESR, Structure, and Reactions of Specifically Deuterium-Labeled Pentane Cations in X-Irradiated Freon Matrices

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Solutions of 1-2 mol % of pentane, pentane-3- d_2 , pentane-2,4- d_4 , and pentane-1,5- d_6 in CFCl₃, CF₃CCl₃, and CF₂ClCFCl₂ have been X irradiated at 77 K. ESR spectra of the molecular ions were recorded at temperatures between 77 K and either the glass transition temperature for CF₃CCl₃ (140 K) and CF₂ClCFCl₂ (about 110 K) or the melting point for CFCl₃ (162 K). It was found that the pentane molecular ions in these matrices have not only the structure of an extended chain, but also that of several gauche conformers. Their identity and proportions depend on the matrix and on the labeling. INDO calculations were made to elucidate the detailed structure of the conformers of the pentane molecular ions in these matrices. Tilting both methyl groups toward the central -CH₂- leads to a significant decrease in the energy of the ion with a minimum at about 90° and to significant changes in hyperfine coupling constants, giving a much better agreement with experimental data. Isotope effects were discovered for the deprotonation reaction in CF₂ClCFCl₂ and especially for the photofragmentation in CF₃CCl₃.

Introduction

Molecular ions of alkanes can be generated and stabilized by γ or X irradiation of dilute solutions of the parent alkanes in various halogenated matrices.¹⁻⁸ They are produced by charge transfer from the host matrix cations and are thus considered as isolated and thermal species. Practically no fragmentation products are formed by this process.⁹ The ESR spectra of nalkanes molecular ions are characterized by large hyperfine splittings attributed to a high spin density on the two in-plane end H atoms, assuming an extended chain configuration. In certain cases, it is possible to observe a detailed substructure due to the out-of-plane hydrogens. The radical ions are thus described as σ delocalized radicals. The magnitude of the hyperfine coupling constant is inversely proportional to the length of the extended chain.² Only very recently³ it was reported, on the basis of INDO calculations, that *n*-alkane molecular ions, in some cases, can also have the structure of a gauche conformer, obtained by 120° rotation of an ethyl group around the bond C_2 - C_3 . The molecular ions of butane and pentane in CF3CCl3 are known to have another yet undetermined structure than the extended one.⁷ The use of specifically D-labeled pentanes, together with INDO calculations, allows us to probe the detailed nature of these conformers.

Alkane molecular ions can undergo a variety of reactions, depending upon the host matrix: deprotonation was reported for *n*-propane⁴ and *n*-butane² in CF₂ClCFCl₂, dissociation to olefin cations for *n*-propane in CFCl₃,⁴ and photofragmentation of pentane⁺, hexane⁺, and heptane⁺ to 2-C₄H₈⁺ was discovered in CF₃CCl₃.⁷ To investigate the mechanism of this latter reaction we wanted to use specific labeled pentanes, a well-known approach widely used in mass spectrometry¹⁰ to study the fragmentation of ions.

Experimental Section

CF₃CCl₃ (Aldrich, 98%), CF₂ClCFCl₂ (Fluka >99% or Merck >99.7%), and CFCl₃ (Alfax) were degassed and then "distilled" to a reservoir attached to a vacuum line. The quantity used to make the samples was determined by allowing the solvent to expand to a known pressure in a calibrated volume. *n*-Pentane (Kebo p.a) was used as received. The specifically labeled pentanes were synthesized according to the following procedures. Pentane-1,5-d₆ was prepared by the reaction of LiAlD₄ with pentane-1,5-dioic acid. The resulting pentane-1,5-diol was then converted to the corresponding tosylate which was subsequently reduced by LiD/LiAlD₄.

For pentane-2,4- d_4 the starting compound was acetic acid, which gave ethanol-1- d_2 upon reaction with LiAlD₄ in dibutyl ether. The ethanol was converted into a bromide by reaction with PBr₃, which by reaction with Mg/CO₂ gave propanoic-2- d_2 acid. By reduction with LiAlD₄ propanol-2- d_2 was obtained, and then converted into 1-bromopropane-2- d_2 . This compound gave the desired product by reaction with the tosylate of ethanol-2- d_2 , in presence of Li₂CuCl₄ as a catalyst.

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solute	structure	<i>T</i> , K	hf coupling const, ^b G	conformer ^a	proportions, %
pentane-d _o	1/2 3/2 5	77	57 (2 H; H ₁ , H ₅), 8 (6 H)	extended	50
			100 (H ₂), 45 (H ₅), 8 (5 H)	$120^{\circ} C_{2} - C_{3}$	50
		135	85 (2 H; H ₂ , H ₄), 17 (6 H; H ₅)	90° C ₂ -C ₃ /90° C ₃ -C ₄	100
pentane-3-d ₂	\sim	77	57 (2 H; H_1 , H_5), 8 (4 H; H_2 , H_4)	extended	50
	D D		100 (H ₂), 45 (H ₅), 8 (4 H)	$120^{\circ} C_{2} - C_{3}$	50
		135	85 (2 H; H ₂ , H ₄), 17 (6 H; H ₁ , H ₅)	90° C ₂ -C ₃ /90° C ₃ -C	100
pentane-2,4-d ₄	0 <u>00</u> 0	77	45 (H ₅)	$120^{\circ} C_{2} - C_{3}$	100
	\times	135	14 (2 $D; D_2, D_4$), 17 (6 $H; H_1, H_5$)	$90^{\circ} C_{2} - C_{3} / 90^{\circ} C_{3} - C_{4}$	100
pentane-1,5-d		77a ^c	100 (H ₂)	120° Č ₂ -Č,	70
	0,0 00,		$40 (H_2)$	$30^{\circ} C_2 - C_3 / 60^{\circ} C_3 - C_4$	30
		77b ^c	74 (H_2) , 26 (H_4)	$60^{\circ} C_{2} - C_{3} / 90^{\circ} C_{3} - C_{4}$	100
		135^{d}			90
			85 (2 H; H ₂ , H ₄)	$90^{\circ} C_2 - C_3, 90^{\circ} C_3 - C_4$	10

^a The conformers are designated by the value of the angle of rotation around a specific C-C bond. ^b The H atoms have a number designating the C atom to which they are bonded. ^c a and b are two possible interpretations of the ESR spectrum. ^d a or b as at 77 K.

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solute	hf coupling const, G	conformer ^a	proportions, %
pentane-d ₀	57 (2H; H ₁ , H ₅)	extended	50
	96 (H ₂), 58 (H ₅)	$120^{\circ} C_2 - C_3$	50
pentane- $3-d_2$	57 (2 H; H ₁ , H ₅)	extended	50
	96 (H ₂), 58 (H ₅)	$120^{\circ} C_2 - C_3$	50
pentane-2,4-d ₄	57 (2 H; H ₁ , H ₅)	extended	80
	58 (H ₅)	$120^{\circ} C_2 - C_3$	20
pentane-1,5-d ₆	8 (D ₁ , D ₅ , 3 H)	<i>b</i>	10
	96 (H ₂)	120° C ₂ -C ₃	90

TABLE II: Conformer Ions in CF₂ClCFCl₂ at 77 K

^a The conformers are designated by the angle of rotation around a specific C-C bond, starting at 0° for the extended conformer. The H atoms are numbered by the C atom to which they are bonded. ^b Slightly distorted extended chain (see text).

Pentane-2- d_2 was synthesized in three steps: the reaction of propanoic acid with LiAlD₄ gave propanol- $1-d_2$ which was then converted into its bromide by PBr₃. The bromide was added to CH₃CH₂I in presence of Mg/Li₂CuCl₄ as a catalyst. They were then purified by preparative gas chromatography. Their chemical purity was better than 99.9%. The isotopic composition was determined by GC/MS. Isotopically, pentane- $3-d_2$ was pure, whereas pentane- $2,4-d_4$ contained 3% of pentane- d_3 and pentane- $1,5-d_6$ 6% of pentane- d_5 .

The quantity of pentane used to make the sample was injected with a microsyringe through a septum directly into the evacuated ESR Suprasil quartz tube cooled to 77 K. The pentane condensed instantaneously in the tip of the tube. The concentration of the solute could thus be varied very easily and be adjusted with good reproducibility. X irradiations (70 kV, 20 mA) were made with an X-ray tube with an Au anode.

ESR spectra were recorded on a Varian E-9 spectrometer with 100-kHz field modulation, fitted with a double cavity and a temperature control device. First- and second-derivative spectra were recorded with modulation amplitudes of 2 G. The temperature was measured with a Chromel-Alumel thermocouple. Bleaching experiments were done at 77 K with the 150-W lamp of a slide projector fitted with Oriel glass color filters. INDO calculations were performed with a program due to Oloff.¹¹

ESR Spectra: Results and Interpretation

All the interpretations, particularly the relative proportions of conformers, were assessed after computer simulations of the experimental data were made. The geometric structures of the ions were deduced by combining experimental and theoretical data, the latter obtained by INDO. A summary is given in Tables I and II.

The INDO program we used has two options; the "open" one uses the ordinary UHF approach and the "closed" one uses the RHF-CI treatment with the 1/2 electron procedure of Dewar et



Figure 1. (a) First-derivative ESR spectrum at 157 K of pure CFCl₃ irradiated at 77 K. (b) Second-derivative ESR spectrum at 123 K of pure CF₂ClCFCl₂, irradiated at 77 K.

al.¹² For pentane, the two methods in general gave hyperfine coupling constants in good agreement with each other. We have found that the closed version generally correctly predicts the ground state obtained experimentally, but tends to give too small couplings for the equatorial H atoms.

Pure Matrices. The central parts of the spectra contain two sharp lines at g = 2.007 and 2.0012 due to the irradiated quartz tubes. Only the first line can be bleached by red light ($\lambda > 630$ nm). The 77 K spectra of the three matrices are strongly asymmetrical and consist of broad bands due probably to matrix anions. The spectrum of CF₂ClCFCl₂ is reduced by a factor of 10 either by a 3-5-min illumination with red light ($\lambda > 630$ nm) or by annealing at 120 K. Bleaching with red light was then routinely done after irradiation. At or near the transition temperature, i.e., 100 K for CF₂ClCFCl₂, 140 K for both CFCl₃ and CF₃CCl₃, strong signals arise which are usually attributed to the neutral radicals generated by the detachment of Cl⁻ from the matrix anions, giving CF₃CCl₂ in CF₃CCl₃ and CFCl₂ in CFCl₃.^{5.6} The spectrum we observe in CFCl₃ (Figure 1a) can be assigned to a

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Figure 2. First-derivative ESR spectrum of pentane⁺- $1,5-d_6$ in CFCl₃, taken at 77 K, after annealing at 135 K; \bullet , background signal.

TABLE III: Hyperfine Coupling Constants of Equatorial (on C_2-C_4) and Axial (in-Plane on C_1 and C_5) H and Total Energy of the Extended Pentane Cation as a Function of the $C_1-C_2-C_3$ Angle Calculated by the INDO Method (Open Version)

$C_1 - C_2 - C_3$ angle, deg	a _{eq} , G	a _{axial} , G	energy, au
112.47			-43.0797
109	-8.7	48.3	-43.1290
106	-7.1	49.9	-43.1390
103	-5.6	51.4	-43.1478
100	-4.3	52.7	-43.1558
97	-2.9	54.1	-43.1626
94	-1.5	55.5	-43.1681
91	-0.1	56.9	-43.1720
88	+1.4	58.4	-43.1741ª
85	+1.9	59.9	-43.1736

^aE min.

species with couplings to an F atom with $a_{\rm F} = 130$ G and to two Cl atoms with $a_{\rm Cl} = 18$ G. These couplings do not agree at all with the isotropic couplings reported for CFCl₂, perhaps because of hyperfine coupling anisotropy in the frozen matrix. The signal shown in Figure 1b for CF₂ClCFCl₂ is very similar, though much weaker, to the ESR spectrum of irradiated CF₃CCl₃ at 140 K. Apparently there is some CF₃CCl₃ impurity acting as an efficient trap in CF₂ClCFCl₂.

Pentane Solutions in Freon Matrices. In CFCl₃. The yields of pentane- d_0 , $-d_2$, and $-d_4$ cations are low in this matrix. The spectra consist of a triplet of broad lines (a = 50 G, line width lw = 20 G for $-d_0$ and $-d_2$, and of a triplet (a = 56 G) of triplets (a = 5 G, lw = 4 G) for $-d_4$. These signals disappear irreversibly at temperatures higher than 100 K. The 77 K spectra are assigned to the extended form of the pentane cation. The presence of other conformers could not be detected. The 77 K spectrum of the pentane- d_6 cation is shown in Figure 2. Its integrated intensity is 2-3 times higher than for the other deuterated pentanes. It consists of six broad lines. The two outer lines have lw = 20 G and are 4 times less intense than the four inner lines of lw = 15G. When the temperature was raised to 104 K, a reversible change occurred. The intensity of the outer lines was doubled, the other lines being unchanged. The ESR signal disappeared when the temperature was further increased. The interpretation is discussed together with the data with CF₃CCl₃ solutions as the results are similar in both matrices.

In $CF_2ClCFCl_2$. The spectrum of pentane- d_0 at 77 K was remeasured and perfect agreement with that from the literature^{2,3} was found. The analysis of Iwasaki et al.³ fits well our data with equal proportions of ions in an extended and in a gauche configuration. The spectrum of the pentane- d_2 (Figure 3a) molecular ion is a superposition of a triplet (a = 57 G, lw = 13 G) and a quartet ($a_1 = 58$ G, $a_2 = 96$ G, lw = 25 G). It can be attributed, as for pentane- d_0 , to two species in equal proportions: the extended conformer is responsible for the sharper triplet and the conformer obtained by 120° rotation around C_2 - C_3 gives the four broader lines. The resolution is better because of the specific D-labeling (lw = 13 G vs. 16 G for pentane- d_0). This allows a determination



Figure 3. (a) First-derivative ESR spectrum of pentane- $3-d_2^+$ in CF₂-ClCFCl₂, recorded at 77 K. (b) First-derivative ESR spectrum of 2pentyl radicals obtained by warm-up to 99 K of a solution of pentane- $3-d_2$ in CF₂ClCFCl₂. (c) Second derivative ESR spectrum of 2-pentyl radicals obtained by warm-up to 104 K of a solution of pentane- $3-d_2$ in CF₂Cl-CFCl₂. The line marked by \bullet is due to some background.

of the coupling constants of the conformer which is in even better agreement with our INDO calculations $(a(H_2) = 98 \text{ G}, a(H_3) = 54 \text{ G})$. Here and in all other cases the subscript refers to the carbon atom to which the hydrogen is attached. In the previous INDO calculations^{2,3} the spin densities on the in-plane end H, for both the extended and the gauche conformer, are always too low, with the only exception of butane. In the case of pentane we have determined, with the closed and open versions, the total energy of the extended ion and the in-plane H coupling constants as the CH₃ groups are tilted toward the next CH₂ group. The results for both versions of the program are in excellent agreement, and we will report only the open version results in Table III. These data clearly show that the best agreement with the experimental data of 57 G is obtained when the C₁-C₂-C₃ angle is about 90° and that there is also an energy minimum of the ion at this angle.



Figure 4. First-derivative ESR spectrum of pentane⁺--2,4- d_4 in CF₂Cl-CFCl₂ at 77 K.

These two results *together* strongly suggest that the extended form of the ion is slightly distorted in the C skeleton plane in comparison with the neutral molecule.

The spectrum of the pentane- d_4 molecular ion (Figure 4) consists mainly of a triplet (a = 57 G, lw = 16 G). The sharp features are attributed to the extended conformer. The 120° conformer proportion can be estimated as being about 20%. For the latter species we found $a(H_5) = 58$ G and $a(D_2) = 15$ G. According to the INDO calculation we expect $a(H_5) = 58$ G and $a(D_2) = 15$ G.

The spectrum of the pentane- $1,5-d_6$ molecular ion (Figure 5a) consists of two broad lines (lw = 20 G) with a coupling constant of 93 G and of several narrow lines (lw = 4 G) with a = 8 G in the center. In Figure 5b is shown a second-derivative spectrum with eight central lines. We interpret these data as evidence for a major (90%) proportion of the 120° conformer, with $a(H_2) = 96$ G, the $a(D_5) = 8$ G being unresolved. The central part can be fitted very well by taking a = 8 G (2 D, 3 H) (Figure 5c). This conformer is present as only 10% of the total pentane- d_6 molecular ion. It is tentatively interpreted as being due to a conformer ion derived from the extended chain by two clockwise rotations of 10° and 30°, respectively, about the C_2 - C_3 and C_3 - C_4 bonds. It was the only structure which, according to INDO calculations, gave three equivalent H coupling constants of about 5 G and unresolvable coupling constants to the other H atoms.

When solutions of pentane in $CF_2ClCFCl_2$ were heated to 100 K, an irreversible change took place. The spectra of the molecular cations disappeared, and new paramagnetic species were detected. The integrated intensities of these spectra are low, and a clear interpretation is possible only for the cases of pentane- d_0 and $-d_2$. These signals are attributed to neutral alkyl radicals. The spectrum shown in Figure 6 contains 13 lines and can be interpreted in two ways:

(a) Two species are present. One species, the 2-pentyl radical, gives a septet, the other, 3-pentyl, a sextet due to hyperfine couplings with 6 and 5 H atoms, respectively, having the same coupling constant of a = 24.5 G.

(b) One main species is present, the 2-pentyl radical, with inequivalent couplings of $a_{CH_3} = 24.5$ G (3 H), $a_{\beta 1} = 34.5$ G (1 H), $a_{\alpha} = 21.0$ G (1 H), and $a_{\beta 2} = 9.0$ G (1 H). The latter interpretation is deduced from spectra recorded at 112 K. The resolution is better at that temperature (lw = 3 G), but the high-temperature spectrum of the matrix interferes so that the intensity distribution of the solute radical spectrum could not be correctly measured.

This latter interpretation is coherent with the data reported in Figure 3b for pentane- d_2 . The 100 K spectrum consists of five





Figure 5. ESR spectra of pentane^{+.-1,5-d6} in CF₂ClCFCl₂ taken at 77 K: (a) first derivative; (b) second derivative; (c) simulation of central part of b by taking a = 8 G (2 D, 3 H), lw = 5 G.



Figure 6. Second-derivative ESR spectrum of pentyl radicals taken at 104 K, after warm-up of a solution of *n*-pentane in CF₂ClCFCl₂. The line marked with \bullet is due to some background. The stick plot is a reconstruction of the 2-pentyl radical with $a_{\alpha} = 21.0$ G, $a_{CH_3} = 24.5$ G, $a_{\beta_1} = 34.5$ G, and $a_{\beta_2} = 9.0$ G.

broad lines (lw = 15 G) separated by 25 G. In the second-derivative spectrum obtained at 104 K the lines are narrower (lw = 4 G). Each component is split to yield a triplet with an intensity ratio of 1:1:1 (Figure 3c). The spectrum can be interpreted as due to mainly one species with $a_{CH_3} = 24.5$ G (3 H), $a_{\beta 1} = 5.0$ G (1 D), and $a_{\alpha} = 21.0$ G (1 H). We expect $a_{\beta 1} = 34.5/6.5 =$ 5.3 G for the deuteron splitting in good agreement with the measured value. The coupling due to the other methylene deuteron $a_{\beta 2} = 9.0/6.5 = 1.4$ G is not resolved in this case. The alternative assignment to two species with couplings of 24-25 G would lead to a deuteron splitting of 3.8 G which is not consistent with the experimental spectrum in Figure 3c. Upon further heating, the high-temperature spectrum of the matrix appears progressively, superposed on the spectrum of the solute. At 122 K, the spectrum is identical with the one observed in the pure matrix. For pentane- d_4 and $-d_6$, results are less clear.

In CF_3CCl_3 . In a previous work⁷ no interpretation could be made of the spectrum of the pentane cation at 77 K. The first-derivative spectra of pentane- d_0 (Figure 4 in ref 7) and pentane- d_2 (Figure 7a) ions are very similar, though the outer lines are better resolved in the $-d_2$ spectrum. A comparison of the corresponding second-derivative spectra (not shown) suggests that the substructure of the outer lines has changed from a sextet in the pentane- d_0 to a quintet in the $-d_2$ compound. We conclude that two species in about equal proportions are present. One species which gives four lines with a substructure is ascribed to the gauche conformer mentioned earlier. The coupling constants in the CF₃CCl₃ matrix are $a(H_2) = 100$ G and $a(H_5) = 45$ G. The other species is thought to be the molecular cation with an extended chain. The central part is seen in Figure 7, but the outer lines of the triplet overlap with the four-line spectrum and with lines due to the matrix. The substructure of a = 8 G present in the spectra of the gauche conformer and the extended ion is caused by out-of-plane H atoms, but their positions cannot be uniquely determined from the data.

When the temperature is raised to 109 K (Figure 7b), the outer lines begin to change and new outer lines appear. The inner lines and the central part of the spectrum are not affected. All these features are exactly as for pentane- d_0 . When the temperature is raised further up to 138 K, the spectrum shown in Figure 7c appears. It is exactly like the one reported for the pentane- d_0 ion (see Figure 4b of ref 7), i.e., a triplet (a = 85 G) of septets (a = 17 G). The inner lines of the low-temperature spectrum have disappeared. All these changes are reversible, the original spectrum being restored exactly upon cooling to 77 K.

In order to interpret the ESR spectra of the pentane molecular ions in CF₃CCl₃, we have calculated the coupling constants of all the conformers obtained by one rotation around C₂-C₃ starting at 0° for the extended chain up to 180° and by two rotations around C₂-C₃ and C₃-C₄ up to 180° for the case with both being clockwise and for the case of one being clockwise and the other counterclockwise. The open and closed versions of the INDO



Figure 7. ESR spectra of pentane⁺-3- d_2 in CF₃CCl₃: (a) first derivative at 77 K; (b) first derivative at 109 K; (c) second derivative at 138 K. In all spectra the intense center line is due to the matrix.

program gave similar results, except for some distorted structures, where the closed version gave sounder results; in particular the closed version never gives a sudden and large change in the coupling constants of the equatorial H when the conformation is gradually changed.

On the basis of the INDO calculations (Table IV), we attribute the high-temperature form of pentane- d_0 and $-d_2$ in CF₃CCl₃ (cf. Figure 4b of ref 7) to the conformer obtained by two clockwise rotations of ethyl groups of 90° around bonds C₂-C₃ and C₃-C₄ (Figure 8). This conformer lies at a clear minimum in energy compared with other symmetric conformers with angles of rotation of 80°, 100°, or 120° around both C₂-C₃ and C₃-C₄ bonds. To

TABLE IV: Experimental and Theoretical Couplings of the Pentane Ion in CF_3CCl_3 Observed at 138 K^a

	coupling constants, G		
atom	INDO	exptl	
H _{1.1} H _{5.1}	29.6	17.0	
$H_{1,2}H_{5,2}$	27.5	17.0	
$H_{1,3}H_{5,3}$	0.2	17.0	
$H_{2,1}H_{4,1}$	12.2		
$H_{2,2}H_{4,2}$	78.6	85.0	
H _{3.1}	-4.7		
H _{3,2}	-6.0		

^aThe numbering and the proposed geometry are shown in Figure 8.







Figure 9. First-derivative ESR spectrum of pentane⁺ $\cdot -2,4-d_4$ in CF₃CCl₃ at 77 K. The sharp lines in the middle are due to some background.

explain the six equivalent H with a = 17 G, we need to consider a rotation of CH₃ groups fast enough (≥ 80 MHz) to average the coupling constants. The average calculated value of 19.0 G is in very good agreement with the experimental value.

The spectrum of pentane- d_4 (Figure 9) consists of a doublet with a = 52 G and a lw of 28 G. A second-derivative spectrum shows some substructure with $a_2 = 4$ G, but the multiplicity is difficult to determine (about 9–11) due to the poor resolution. When heated successively to 100, 110, 124, and 138 K, the broad doublet decreases progressively by about 30% and acquires a substructure (a = 15-17 G, multiplicity undetermined). Upon cooling back to 77 K, the original spectrum is restored with a slight decrease in intensity.

The 77 K spectrum can be ascribed entirely to the 120° conformer having $a(H_5) = 45$ G and $a(D_2) = 15$ G, again in fair



Figure 10. (a) First-derivative ESR spectra of pentane⁺ $-1,5-d_6$ in CF₃CCl₃: (a) at 77 K; (b) at 100 K; (c) at 133 K.

agreement with the INDO calculations. As the temperature is raised above 100 K, the spectrum could be reasonably well fitted with 10–20% of the low-temperature form and 80–90% of a species with $a_1 = 14$ G (2 D on C₂,C₄) and $a_2 = 17$ G (6 H on end C); according to our INDO calculations this species is the 90°–90° conformer observed for pentanes- d_0 and $-d_2$.

For pentane- d_6 , at 77 K the first-derivative spectrum (Figure 10a) consists of four strong and two weak outer lines. A second-derivative spectrum reveals an incompletely resolved substructure of the main lines with a spacing of 6-6.5 G. When heated to 100 K (Figure 10b) and then to 133 K (Figure 10c) the outer lines grow significantly (by a factor of about 10 at 133 K) while the inner lines are not affected up to 113K. At 136 K, a strong signal from the matrix interferes and the form of the inner lines is affected.

As mentioned above the spectrum of the molecular ion of pentane- d_6 is similar in CFCl₃ and CF₃CCl₃ matrices at all the temperatures studied. It is therefore likely that the same conformers are present in both matrices. The outermost bands are more intense at 77 K and at 105 K in the CFCl₃ matrix. On the basis of computer fitting and of INDO calculations, it was not possible to determine unambiguously the identity of the conformer. Both first- and second-derivative spectra at 77 K could be fitted with structures having some sense. We have considered conformers obtained by rotation around the C_2 - C_3 and C_3 - C_4 bonds. They are denoted by one and two angles below.

(a) 70% of 120° conformer with $a(H_2) = 100$ G and $a(D_5) =$ 8 G and 30% of a 30°--60° conformer (both rotations clockwise). For the latter structure the INDO program gave a coupling of 40 G, for one of the H atoms on C_2 , all other couplings being smaller than 14 G. Traces of the 90°-90° conformer with a =90 G (2 H) and unresolved structure due to 6 D on the end C atoms could be present.

(b) 100% of a species with $a_1 = 74$ G (1 H), $a_2 = 26$ G (1 H), and $a_3 = 6.7$ G (7 H) which could correspond to a 60°-90° conformer (both clockwise). According to our INDO calculations one H on C₂ has a coupling constant of 84 G, the 2 H on C₄ being 35 and 16 G. The other couplings are about 6-8 G for 3 H in the central part of the molecule and smaller than 6 G for the D at C_1 and C_5 .

Discussion

Structural Aspects. From our data it appears that not only the identity of the host matrix, but also the extent of D-labeling has a large effect on the structure of the molecular ions, especially in CF₃CCl₃. In this matrix pentane- d_0 and $-d_2$ ions have the same structures (50% extended, 50% 120° conformer), but pentane- d_4 ion is present only as the 120° gauche conformer, and the extended conformer pentane- d_6 ion is not present. In CFCl₃ the situation is similar though results are less clear due to the poor yield of molecular ions. In $CF_2ClCFCl_2$ pentane- d_0 , $-d_2$, and maybe $-d_4$ ions are present in about equal proportions as the extended and as the 120° conformer, but the pentane- d_6 is present to 90% as the 120° conformer. It is thus quite clear that D-labeling has a strong stabilizing effect on the gauche conformers. According to INDO theory this conformer has a higher energy (E = -43.1160au) than the extended form or even the $90^{\circ}/90^{\circ}$ conformer (E = -43.1196 au). Thus it does not lie at an energy minimum and the matrix is apparently forcing the solute to take a distorted structure. Generally speaking CF₃CCl₃ and CFCl₃ seem to induce larger distortions than CF₂ClCFCl₂. It seems likely that this phenomenon is related to differences in solvation, the details of which are not understood. One important result obtained in this work is the chemical confirmation that, at least in $CF_2ClCFCl_2$, the 120° conformer is indeed present in quite high concentration. Its existence was previously deduced from INDO calculations.³ But, both our own INDO calculations and our results with labeled pentanes (especially $-d_4$ and $-d_6$) indicate quite clearly that the headings in the columns 2 and 3 as well as 5 and 6 of Table III in ref 3 are to be reversed: the larger coupling constant is not to be assigned to the terminal in-plane H, but to the in-plane H on C_2 . The structure of the pentane ion observed in CF_3CCl_3 at increased temperature above 110 K is now better understood, and the assignment (Figure 7c) to a 90°/90° conformer is supported by the data using pentane- d_2 , $-d_4$, and $-d_6$. The conformer could not be observed at 77 K, indicating that the conformation changes with temperature. Also in this case we must assume that the distorted 90°/90° structure is induced by the matrix.

Finally our finding, by INDO calculations, that the tilting of end CH₃ groups toward the -CH₂- chain lowers the total energy of the molecular ion is in agreement with ab initio calculations on propane molecular ion.¹³ The INDO calculations on the extended form of the pentane cation in fact gave an excellent fit to the observed couplings at the equilibrium angle of 90°.

Deprotonation in $CF_2ClCFCl_2$. As mentioned above we have found that the 2-pentyl radical is the major component formed after thermal decomposition of the molecular ion. According to the literature¹⁴ the 2-pentyl radical gives a 12-line spectrum (a_1) = 21.9 G (1 H), $a_2 = 24.8$ G (5 H)). In one of the two interpretations suggested here the couplings are different, indicating a distorted geometry. The values of the couplings $a_{\beta 1} = 34.5$ G, $a_{\beta 2} = 9.0$ G due to the methylene hydrogens indicate that the angle θ viewed along the C_a-C_b bond between the C_b-H bonds and the orbital axis of the unpaired electron is different for the two methylene hydrogens. From the usual relation $a_{\beta} = 4 + 47 \cos^2$ θ we estimate that $\theta_1 = 35^\circ$ and $\theta_2 = 71^\circ$. A distorted geometry of the neutral radical is not surprising in view of the distorted geometry of the cationic precursor.

It was shown quite conclusively by Iwasaki and co-workers^{3,4} that the site of deprotonation depends on the nature of the SOMO, which is itself related to the geometry of the molecular ion. They pointed out that the butane molecular ion should give the 1-butyl radical instead of the 2-butyl radical observed experimentally,² and proposed three hypotheses to explain this unexpected result: deprotonation from a π -radical structure, isomerization of 1-butyl to 2-butyl, and finally H abstraction by matrix radicals from undamaged neutral butane. We have shown, with our INDO calculations, that the ground state is not a π radical for the butane⁺.; the second hypothesis can be examined in light of our results on labeled pentanes.

If one admits that the probability of a proton to leave the molecular cation is proportional to the spin density, the extended conformer of pentane will yield only the 1-pentyl radical. The gauche conformer will give a 1:2 mixture of 1 and 2-pentyl radicals. As the two parent ion structures are present in equal amounts, one should detect a 2:1 mixture of 1- and 2-pentyl radicals. This is in sharp disagreement with our data according to which the 2-pentyl radical is exclusively stabilized; this is an indication that the 1-pentyl radical isomerizes to the more stable 2-pentyl radical. This scheme is further supported by data on pentane-3- d_2 , indicating that 2-pentyl-3- d_2 radical is formed. Results from pentane-2,4- d_4 and -1,5- d_6 are less clear because of the low yield of radicals. Similarly the butane molecular ion, in its extended conformer, will yield 1-butyl radicals isomerizing into more stable 2-butyl radicals. As for the third hypothesis of ref 2, it is known¹⁵ that there is a preferential H abstraction from CH_3 rather than from $-CH_2$, at least for abstraction by methyl radicals. Thus the radical found would be the 1-pentyl. Furthermore, matrix radicals would rather abstract Cl from neutral solvent molecules.9

Finally it is worthwhile mentioning that the yield of pentyl radicals is lowered by the D-labeling, in agreement with published results on deprotonation of propane.^{3,4}

Photofragmentation in CF3CCl3. The ESR spectrum obtained after bleaching of partially labeled pentanes is the same for all pentanes and contains some lines which are already present before bleaching; it is the same spectrum which is measured after bleaching of partially labeled hexanes.⁸ It thus appears that either specifically labeled *n*-pentanes have other channels of decomposition than protiated n-pentane, or that the photofragmentation mechanism is not a simple cleavage. It looks highly unlikely that partially labeled butene cations are not stable in CF₃CCl₃. But if smaller ionic fragments than C4 are produced, it is quite possible that they are not stabilized in CF_3CCl_3 , as no molecular ions of

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propane or ethane could be generated in this matrix at 77 K^{7} Comparison with gas-phase photofragmentation is not straightforward. Dunbar¹⁶ and van der Hart¹⁷ have reported on photofragmentation of pentane molecular ions studied by ICR. According to ref 17, *n*-pentane⁺ decomposes to $C_3H_7^+$, whatever the wavelength used between 300 and 700 nm. No photofragmentation product is given in ref 16, but the photodissociation spectrum is in good agreement with ref 17.

Conclusion

By using specifically labeled n-pentanes and INDO calculations, we were able to determine the structures of the various n-pentane molecular ions in CF_3CCl_3 , to show that these structures are influenced by the labeling, to obtain the correct assignment of the large splittings due to in-plane H in the 120° conformer, and to shed some light on the isomerization of the deprotonation

products of these molecular ions in $CF_2ClCFCl_2$. We have also shown that the identity and proportion of various conformers are dependent on the matrix and on the D-labeling of the solutes. The experimental data have been compared with INDO calculations. This shows that the $C_1-C_2-C_3$ angle of about 90° corresponds to a minimum in total energy and an excellent agreement between experimental and theoretical hyperfine coupling constant is obtained for the in-plane H atoms. A strong isotope effect of unknown nature was discovered in the photoinduced fragmentation of the pentane molecular ion in CF_3CCl_3 .

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Registry No. Pentane radical cation, 34479-74-8; pentane-3,3-d₂ radical cation, 97390-82-4; pentane-2,2,4,4-d₄ radical cation, 97374-41-9; pentane-1,1,1,5,5,5-d₆ radical cation, 97374-42-0.

Monte Carlo Studies of Counterion–DNA Interactions. Comparison of the Radial Distribution of Counterions with Predictions of Other Polyelectrolyte Theories

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The canonical Monte Carlo (MC) method is used to compute small-ion radial distributions around a model polyion representing native B-DNA in aqueous solution. In the absence of added salt, radial distributions are computed for counterions modeled as hard spheres with diameters from 0.1 to 0.7 nm. For solutions containing added uni-univalent salt at concentrations ranging from a 20% excess to a ninefold excess over DNA phosphate, radial distributions are computed for counterions and co-ions, modeled as hard spheres of equal diameter (0.6 nm). Various features of the MC ion distributions are compared with corresponding results predicted either by the conventional cylindrical Poisson-Boltzmann (PB) equation or by the counterion condensation (CC) theory for highly charged cylindrical polyions. The PB prediction for the number of counterions within a small volume around the model polyion is lower than that predicted by the MC simulations. This discrepancy diminishes with increasing counterion size, because in the MC calculations short-range repulsions partially compensate the effect of electrostatic correlations, which are completely neglected in the PB approximation. The salt dependences of the MC and PB counterion distributions near DNA are qualitatively similar and larger than that characteristic of condensed counterions according to CC theory. However, the CC prediction for the number of (point) counterions within the condensation layer falls within the range of values calculated from the MC simulations for counterions of finite diameter (0.6 nm). From the general cell model for a cylindrical polyion in salt-free solution a relationship is derived between local counterion concentrations at the polyion surface and at the outer cell boundary. This expression generalizes an earlier result derived from the PB cell model and establishes a link between properties of the counterion radial distribution near a cylindrical polyion and a bulk thermodynamic property, the osmotic pressure. The discrepancy between PB and MC predictions for the osmotic pressure can be viewed as a manifestation of counterion correlations primarily in the near vicinity of the polyion.

I. Introduction

The conformational stability, thermodynamic and transport properties, and ligand binding equilibria of helical DNA in aqueous solution are in important respects determined by the interactions of this highly charged polyanion with its counterions and with the ions of the supporting electrolyte (if present).¹⁻⁴ Polyelectrolyte theories concur that near a highly charged polyion the local counterion concentration is in the molar range, which is at least an order of magnitude higher than the bulk salt concentration under typical conditions of interest. There are differences in the predictions of the Poisson-Boltzmann (PB) and counterion condensation (CC) theories for the number of counterions within a small volume surrounding a highly charged cylindrical polyion and, especially, for the dependence of this complement of counterions on the concentration of added salt. Because the PB and CC theories proceed from essentially equivalent models of a polyelectrolyte solution, the quantitative discrepancies between predictions made by the two theories must result from some difference(s) in the approximations built into the different developments of the model. The same model (and appropriate modifications thereof) can be treated more exactly by the Monte Carlo (MC) method. MC simulations of small-ion radial distributions with respect to a polyion directly incorporate the consequences of correlations among the small ions. These correlations

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