coupling constant or computer simulation of a segment of the spectrum was performed where possible to exclude the question of conformational changes caused by the shift reagent. As in our previous study, the vinyl proton most affected by shift reagent was assigned as H_2, and distinction was made between H_4 and $H_{4'}$ in a similar manner.

(15) We use the term highly puckered to mean a conformation which approximates the boat-shaped geometry that results when these ring systems are constructed with Dreiding models. This leads to an angle between planes[6] of approximately 145°, which is the exact angle found for 9,10-dihydroanthracene in the crystal.[16]

(16) W. G. Ferrier and J. Iball, *Chem. Ind.* (*London*), 1296 (1954).

(17) Since we completed our analysis of this compound, the corresponding carboxylic acid has been reported and NMR data furnished.[18]

(18) M. C. Grossel and R. C. Hayward, *J. Chem. Soc., Perkin Trans. 2*, 851 (1976).

(19) We were not able to obtain the trans isomer of **6**.

(20) A uniform numbering system is used throughout for purposes of comparison.

The Mechanism of Chemical Ionization of *n*-Paraffins

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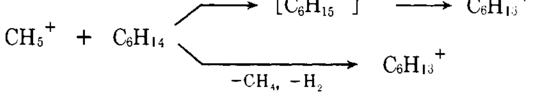
Abstract: An ion cyclotron resonance mass spectrometer has been used to study the mechanism of chemical ionization (CI) of *n*-hexane with methane as reagent gas. Extensive use of deuterium-labeled reactants was made. Double resonance techniques permit distinction between the different modes of reaction of hexane with the two major reactant ions in methane, CH_5^+ and $C_2H_5^+$. It is shown that the latter acts exclusively as a hydride acceptor to form the hexyl ion in which total scrambling of the hydrogen atoms takes place prior to further decomposition into butyl and propyl ion. CH_5^+ reacts as a proton donor to form a short-lived hexonium ion intermediate. This species decomposes by losing either an H_2 or an alkane molecule without prior rearrangement. This is interpreted in terms of C-H and C-C protonated hexane with possible equilibration between these two forms.

The chemical ionization (CI) of *n*-paraffins, C_nH_{2n+2}, using methane as reagent gas has been among the first class of compounds studied.[1] The CI (CH_4) mass spectra are characterized by the formation of an intense parent alkyl ion $C_nH_{2n+1}{}^+$, together with high abundances of fragment alkyl ions $C_mH_{2m+1}{}^+$ ($m < n$). Former studies by Hunt and McEwen[2] have established that the fragment alkyl ions are partly formed by olefin loss from the parent alkyl ion when $(n - m) \geq 2$, according to the reaction

$$C_nH_{2n+1}{}^+ \rightarrow C_mH_{2m+1}{}^+ + C_{n-m}H_{2(n-m)} \qquad (1)$$

On the other hand, Clow and Futrell using ion cyclotron resonance (ICR) techniques studied in more detail the relative rates of formation of the product ions in the CI (CH_4) mass spectra of the hexane isomers.[3] They show that the two main reagent ions in methane, i.e., CH_5^+ and $C_2H_5^+$, have similar reactivities, except for the formation of the pentyl ion that originates exclusively from CH_5^+.

CH_5^+ may react with *n*-hexane either according to reaction 2, the protonation reaction, or by the hydride transfer (eq 3),



$$CH_5{}^+ + C_6H_{14} \xrightarrow{-CH_4} [C_6H_{15}{}^+]^* \xrightarrow{-H_2} C_6H_{13}{}^+ \qquad (2)$$

$$CH_5{}^+ + C_6H_{14} \xrightarrow[-CH_4,\ -H_2]{} C_6H_{13}{}^+ \qquad (3)$$

while $C_2H_5^+$ transfers only a hydride from the hexane neutral.

$$C_2H_5^+ + C_6H_{14} \rightarrow C_6H_{13}^+ + C_2H_6 \qquad (4)$$

So far, there has been no experimental evidence for reaction 2 to occur (see, for instance, ref 2), although the intermediate hexonium ion has been proposed in order to account for the formation of the pentyl ion uniquely from CH_5^+ as precursor.[3]

Considering the differences in the mode of reaction of CH_5^+ and $C_2H_5^+$, we have investigated their reaction with a series of deuterium-labeled *n*-hexanes. The isotopically labeled distributions were determined for the alkyl ions containing from three to six carbon atoms. Experiments were also carried out using CD_5^+ and $C_2D_5^+$ precursors.

Experimental Section

The ICR mass spectrometer with a four section cell used in this study has been described elsewhere.[4] The double resonance technique uses a continuous electron beam (accelerating voltage 25 eV) and the modulated frequency of ejection of the precursor ion piloted by the external sweep of the magnetic power unit. The marginal oscillator output is fed to a phase-sensitive detector which is triggered by the modulation frequency. For determination of the product distribution when using deuterated reactants, it was necessary to use a signal averaging technique. For this purpose, between 8 and 64 scans were accumulated on a Nicolet 1074 signal averager.

The following deuterated hexanes were synthesized by standard methods: hexane-*3-d*$_2$; *-2,5-d*$_4$; *-3,4-d*$_4$; *-1,6-d*$_6$; *-1,2,3-d*$_7$; *-1,3,4,6-d*$_{10}$; *-d*$_{14}$. The deuterium content of these samples was between 98 and 99.6%, as determined on a CEC-110B mass spectrometer.

Mixtures of 1% hexane into methane were used (total pressure = 2×10^{-4} Torr).

Results

The product distribution obtained in the 100/1 mixture of CH_4/C_6H_{14} is reported in Table I. A fair agreement with the results of Clow and Futrell[3] is observed. In the forthcoming Tables II-V we present the isotopic distributions obtained with the different labeled reactants used in this study. The results reported were corrected for isotopic hexane impurities present in the samples. The absolute experimental error is within ±0.4% for the hexyl and pentyl ion intensities, while it is about ±1% for the other intensities reported.

Hexyl Ion. The distribution of D in the hexyl ion is reported in Table II. The hydride transfer reaction from $C_2H_5^+$ is characterized by two main features: (a) A slight isotope effect is noticed in the product distribution of hexane-*1,2,3-d*$_7$, favoring the transfer of a hydride as compared to a deuteride $k(H^-)/k(D^-) = 1.14$. This is compatible with the differences in zero-point energies of a C-H and a C-D bond. (b) A strong positional effect is present which favors the hydride transfer

Table I. Product Ions in the Reaction of *n*-Hexane with CH_5^+ and $C_2H_5^+$

	Product ion			
	$C_6H_{13}^+$	$C_5H_{11}^+$	$C_4H_9^+$	$C_3H_7^+$
Relative intensity	51	13	16	21
Precursor CH_5^+	0.54	1.0	0.62	0.60
$C_2H_5^+$	0.46	0.0	0.38	0.40

Table II. Label Retention in the Hexyl Ion

Label position	Product ion	Reactant ion		
		$C_2H_5^+$	CH_5^+	CD_5^+
d_0	$C_6H_{12}D^+$			9.7
	$C_6H_{13}^+$	100	100	90.3
1,6-d_6	$C_6H_6D_7^+$			10.1
	$C_6H_7D_6^+$	81.5	100	89.9
	$C_6H_8D_5^+$	18.5		
2,5-d_4	$C_6H_8D_5^+$			7.9
	$C_6H_9D_4^+$	61.3	55.0	46.7
	$C_6H_{10}D_3^+$	38.7	45.0	45.4
3,4-d_4	$C_6H_8D_5^+$			4.2
	$C_6H_9D_4^+$	60.9	50.2	45.5
	$C_6H_{10}D_3^+$	39.1	49.8	50.3
1,3,4,6-d_{10}	$C_6H_2D_{11}^+$			4
	$C_6H_3D_{10}^+$	38	49	43
	$C_6H_4D_9^+$	62	51	53
3-d_2	$C_6H_{10}D_3^+$			9.0
	$C_6H_{11}D_2^+$	78.5	71.6	63.7
	$C_6H_{12}D^+$	21.5	28.4	27.3
1,2,3-d_7	$C_6H_5D_8^+$			5.0
	$C_6H_6D_7^+$	53.5	51.5	46.4
	$C_6H_7D_6^+$	46.5	48.5	48.6
d_{14}	$C_6D_{13}^+$	100	97.6	100
	$C_6HD_{12}^+$		2.4	

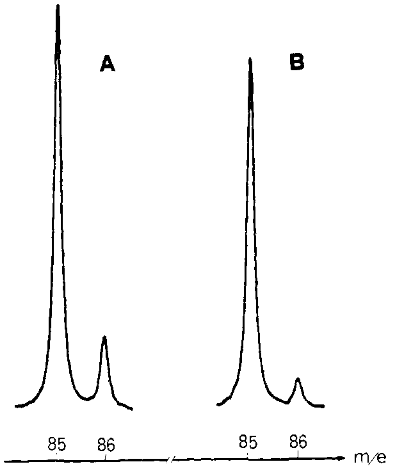


Figure 1. Hexyl ion distribution as measured by the modulated ejection of the precursor ion: A, $CD_5^+ + C_6H_{14}$; B, $C_2D_5^+ + C_6H_{14}$.

Table III. Label Retention in the Pentyl Ion

Label position	Product ion	Reactant ion	
		CH_5^+	CD_5^+
d_{14}	$C_5D_{11}^+$	100	100
	$C_5HD_{10}^+$		
1,2,3-d_7	$C_5H_4D_7^+$	53	
	$C_5H_7D_4^+$	47	
1,6-d_6	$C_5H_7D_4^+$		
	$C_5H_8D_3^+$	100	100
d_0	$C_5H_{10}D^+$		2.5
	$C_5H_{11}^+$	100	97.5

Table IV. Label Retention in the Butyl Ion

Label position	Product ion	Reactant ion			
		CH_5^+	CD_5^+	$C_2H_5^+$	Stat[a]
d_0	$C_4H_8D^+$		21		
	$C_4H_9^+$	100	79	100	
d_{14}	$C_4D_9^+$	87	100	100	
	$C_4HD_8^+$	13			
1,6-d_6	$C_4H_3D_6^+$			*b*	3.9
	$C_4H_4D_5^+$			27	25.5
	$C_4H_5D_4^+$		14	47	43.1
	$C_4H_6D_3^+$	100	86	26	23.5
	$C_4H_7D_2^+$			*b*	3.9
1,2,3-d_7	$C_4H_2D_7^+$	52.5		*b*	1.1
	$C_4H_3D_6^+$	*b*		16	12.2
	$C_4H_4D_5^+$	*b*		40	36.7
	$C_4H_5D_4^+$	*b*		35	36.7
	$C_4H_6D_3^+$	*b*		9	12.2
	$C_4H_7D_2^+$	47.5		*b*	1.1

[a] "Stat": assuming 20% primary and 80% secondary initial hydride transfer to form $C_6X_{13}^+$ (X = H, D). [b] Trace.

from a secondary over a primary hydrogen by a factor of about 4 (e.g., hexane-*1,6-*d_6). Moreover, there seems to be no distinction between the secondary positions (hexane-*2,5-*d_4 and -*3,4-*d_4). The distribution obtained when using the perdeuterioethyl ion $C_2D_5^+$ is identical with that from $C_2H_5^+$ within experimental error limits.

On the other hand, the label retention in the hexyl ion formed from the methonium ion, CH_5^+, shows that no primary hydrogen is removed in reaction 2 (hexane-*1,6-*d_6). Furthermore, it is seen that with CD_5^+ up to about 10% of the hexyl ions retain an incoming deuteron. To our knowledge, this is the first experimental evidence for formation of protonated *n*-paraffins as intermediates in the CI (CH_4) conditions. Former studies using CD_4 as reagent gas have failed to detect the retention of deuterium in the product ions.[2,5] Such a method as double resonance ICR techniques is indeed required in order to observe the products of the individual reactant ions, the result of which is exemplified in Figure 1.

In an earlier investigation of high-pressure CI (CH_4) of *n*-hexane-*1,6-*d_6,[5] we also measured the relative intensities of the hexyl ions, $C_6H_7D_6^+/C_6H_8D_5^+ = 10$. If we combine the results obtained here with the two precursors CH_5^+ and $C_2H_5^+$ (Table II), we determine a value of 9.3 for that ratio, in good agreement with the high-pressure CI result. This is taken as evidence for the minor contribution of higher order reactive ion molecule processes in both studies.

Fragment Alkyl Ions, $C_5H_{11}^+$, $C_4H_9^+$, and $C_3H_7^+$. The label retention in the fragment ions is reported in Tables III, IV, and V. As shown in Table I, the methonium ion is the only precursor leading to formation of the pentyl ion. The data of Table III show that terminal methyl groups only participate in this process. Furthermore, the incoming hydron from CH_5^+ (or CD_5^+) is not found in the resulting pentyl ion, except for a small amount in the product of CD_5^+ reacting with hexane.

The distribution of D in the butyl ion (Table IV) is different depending on whether the reactant ion is CH_5^+ or $C_2H_5^+$. Reactions of the latter result in an intense scrambling that fits closely the expected statistical distributions calculated for the decomposition of the corresponding hexyl ion. Similar results were obtained with $C_2D_5^+$ as precursor. The butyl ion distri-

Table V. Label Retention in the Propyl Ion

Label position	Product ion	Reactant ion CH_5^+	CD_5^+	$C_2H_5^+$	Stat[a]
d_0	$C_3H_6D^+$		17		
	$C_3H_7^+$	100	83	100	
d_{14}	$C_3D_7^+$	85	100	100	
	$C_3HD_6^+$	15			
1,6-d_6	$C_3HD_6^+$			*b*	0.3
	$C_3H_2D_5^+$		*b*	3	6.2
	$C_3H_3D_4^+$	*b*	12.5	23	27.7
	$C_3H_4D_3^+$	51	42	37	40.8
	$C_3H_5D_2^+$	33	30.5	31	21.2
	$C_3H_6D^+$	16	15	6	3.6
	$C_3H_7^+$	*b*	*b*	*b*	0.1

[a] "Stat": assuming 20% primary and 80% secondary initial hydride transfer to form $C_6X_{13}^+$ (X = H, D). [b] Trace.

butions obtained with CH_5^+ (respectively CD_5^+) show quite a different behavior. No scrambling is observed (hexane-*1,6*-d_6 and -*1,2,3*-d_7). Retention of a hydron from the reactant methonium ion (CH_5^+, CD_5^+) is observed only when it results from an interchange with a secondary hydrogen (deuterium) atom of the hexane molecule (reactions of CD_5^+ with C_6H_{14} and hexane-*1,6*-d_6, CH_5^+ with C_6D_{14}).

The deuterium retention in the propyl ion (Table V) shows that, as in the case of butyl ions, the $C_2H_5^+$ precursor gives a product distribution very close to what is calculated assuming equivalency of H and D atoms in the parent hexyl ion. On the other hand, the data for CH_5^+ (CD_5^+) reacting with hexane-*1,6*-d_6 show a differently scrambled propyl ion distribution. As will be mentioned later in the Discussion, this can be explained by two competing channels leading to propyl ion.

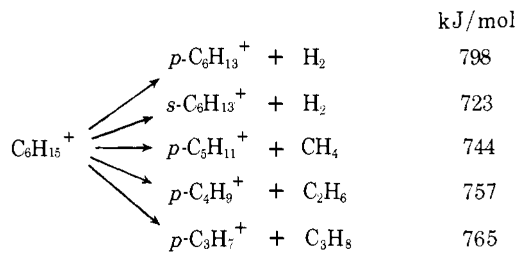
Discussion

The results obtained in this study make it possible to distinguish the difference between the modes of reaction of CH_5^+ and $C_2H_5^+$ with the hexane molecule. $C_2H_5^+$ in a first step transfers a hydride to form a hexyl ion. Apart from a slight H/D isotope effect ($k(H^-)/k(D^-) = 1.14$), a strong positional effect is observed. Taking into account the number of primary and secondary hydrogens available in the hexane molecule (6 and 8 respectively), one can determine the relative probabilities for transferring a hydride from a secondary, k_s, to a primary position, k_p, which leads to the ratio $k_s(H^-)/k_p(D^-) = 3$. Reaction 4 is exothermic by 109 and 33 kJ/mol when a secondary (respectively primary) hexyl ion is formed.[7] Thus, there is a small but definite influence of the exothermicity on the reaction rate of this hydride transfer. Similar behavior has been reported in a recent ICR investigation on hydride transfer reactions.[6] In that study, when reacting $C_2H_5^+$ with propane-*1,3*-d_6, one determines a ratio $k_s/k_p = 2$, with reaction exothermicities of 92 and 38 kJ/mol for formation of secondary and primary propyl ions, respectively.

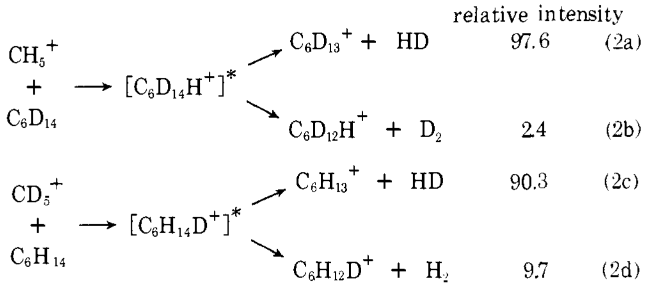
The label retention in the fragment alkyl ions formed from the $C_2H_5^+$ precursor reacting with *n*-hexane permits us to draw the following conclusions: (a) *All* fragment alkyl ions observed come from the decomposition of the hexyl ion, which loses either ethylene to form the butyl ion or propene to form the propyl ion. This fact is partly known from earlier CI or ICR studies.[2,6] (b) The hexyl ion fragments statistically, that is all hydrogens are equivalent during the fragmentation process. This is similar to what has been observed in a former study of the decomposition of hexyl ions formed from hexyl halides under electron impact.[8]

The products formed in the reaction of the methonium ion (CH_5^+, CD_5^+) show some retention of the incoming hydron, except for the formation of the pentyl ion. This involves the formation of the protonated hexane (hexonium ion) as intermediate. Field et al.[1] have represented the chemical ionization of *n*-paraffins as a random electrophilic attack followed by a localized elimination reaction. Our results enable us to further refine this model. In a first approximation we can look at the protonation reaction as taking place either on the terminal methyl groups or on the internal methylene groups of the hexane chain. In the first case, the loss of methane from the hexonium ion seems to be the most favorable decomposition channel. This process is relatively a fast one as it allows for very little H/D interchange in the intermediate prior to dissociation. Moreover, the loss of molecular hydrogen from this intermediate is not able to compete with the methane loss. This is substantiated by the thermochemical data as given in Scheme I. When protonation occurs on an internal position, the hexonium ion formed allows for some H/D interchange (from 10 to 20%) prior to decomposition. Two competing channels are open, i.e., loss of molecular hydrogen to form a secondary hexyl ion and loss of a saturated alkane moiety to form a fragment alkyl ion. The latter reaction takes place by clear-cut cleavage of a C-C bond as seen from the butyl and propyl distributions.

Scheme I



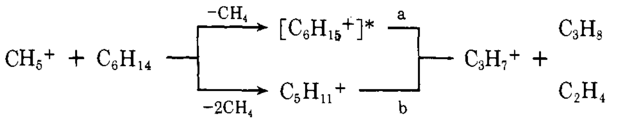
A marked isotope effect is noticed when comparing H_2 vs. D_2 losses from the hexonium ion as shown in reactions 2a–2d.



If we assume that $k(HD)_{2a} \equiv k(HD)_{2c}$, we obtain the ratio $k(H_2)/k(D_2) = 4.5$. Isotope effects of the same magnitude have also been observed in the molecular hydrogen (deuterium) loss from $C_5H_9^+$ ($C_5D_9^+$), see ref 9. A secondary isotope effect is also observed in the fragment alkyl ion distributions of the hexane-*1,2,3*-d_7, favoring the loss of methane and ethane from the hydrogen-containing side by a factor of about 1.1. The other results of Table II (hexane-*2,5*-d_4 and -*3,4*-d_4 show a slight tendency for the D atom in positions 3 or 4 to be lost more frequently than the D atom in position 2. This might be related to the difference in stability between 2-hexyl and 3-hexyl ions, the latter being more stable by about 12 kJ/mol.[6] Thus, it seems possible that the protonation of hexane followed by loss of molecular hydrogen is a process sensitive to such small differences in the reaction energetics.

Before attempting to present a model for the reaction of CH_5^+ with *n*-hexane, it is of interest to recall some currently accepted mechanisms.[1,2] These consist essentially of three possible competing processes, i.e.: (a) protonation of the alkane followed by loss of molecular hydrogen or of an alkane moiety;

Table VI. Propyl Ion Production from CH_5^+ and Hexane



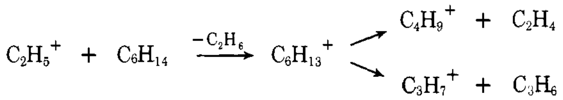
Label position	Product ion	Reactant ion						Stat[a]
			Route			Route		
		CH_5^+	a	b	CD_5^+	a	b	
1,6-d$_6$	$C_3H_3D_4^+$				12 =	12 +	0	
	$C_3H_4D_3^+$	51 =	38 +	13	42 =	30 +	12	21.2
	$C_3H_5D_2^+$	33 =	1 +	32	31 =	1 +	30	50.9
	$C_3H_6D^+$	16 =		16	15 =		15	25.5
	$C_3H_7^+$	*b*			*b*			2.4

[a] "Stat": calculated for decomposition of $C_5D_3H_8^+$. [b] Trace.

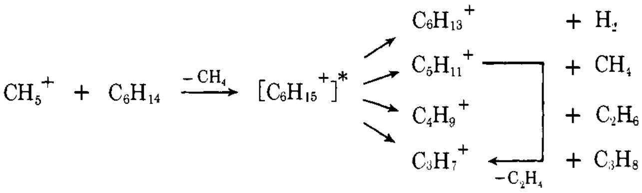
(b) hydride transfer to form the parent alkyl ion, which subsequently loses an alkene neutral; (c) displacement reaction of an alkide entity (analogous to the hydride transfer). Our results do support process a on the basis of the observed inclusion of one hydron of the reacting methonium ion into the reaction products. Process b is entirely ruled out as the decomposition of the resulting hexyl ion would yield isotopic distributions of the products very close to the statistically expected values (the case of the propyl ion will be discussed later in this section). At this point, it is to be noted that the reactions leading to formation of the hexyl ion both from CH_5^+ and $C_2H_5^+$ precursors have similar overall exothermicities, $\Delta H_{\text{react}(2)} = -28$ kJ/mol and $\Delta H_{\text{react}(4)} = -26$ kJ/mol to form *s*-$C_6H_{13}^+$. Despite this fact, we observe that hexyl ions formed in reaction 2 do not decompose further, whereas hexyl ions formed from the $C_2H_5^+$ precursor lose either ethylene or propene as seen from the isotopic distributions in the resulting butyl and propyl ions. In earlier studies concerned with the product distributions in ion molecule reactions,[10] it has been deduced that H_2 is able to carry away up to about 85 kJ/mol as internal energy. This could account for the nondecomposition of the hexyl ions formed in reaction 2. Similar experiments carried out in this laboratory with heptane as neutral have also established that all heptyl ions observed originate from CH_5^+ as precursor.[11] Process c cannot be entirely ruled out on the basis of the present results. Still, quite a number of observations make us feel that it is very improbable, i.e.: the loss of H_2 from $C_6H_{15}^+$ has shown to be very sensitive upon thermodynamical effects (selectivity of H_2 loss, large isotope effect). Secondary isotope effects are also observed in the methane loss (compare $CH_5^+ + C_6D_{14}$ and $CD_5^+ + C_6H_{14}$, Table III), as well as in the already mentioned hexane-*1,2,3-d*$_7$. Process c would be expected to behave similarly to the hydride transfer reaction 3, which is essentially a kinetically controlled reaction. Therefore, we believe that all the products formed in the reaction of CH_5^+ with *n*-hexane are formed via the $C_6H_{15}^+$ intermediate. The apparent conflicting results obtained in the propyl ion distributions with hexane-*1,6-d*$_6$ may be readily accounted for if one takes into account the contribution of the pentyl ion decomposing to form the propyl ion plus ethylene as expressed in Table VI. There, we assumed that the latter process is statistical as has been observed in the decomposition of the pentyl ion, formed from pentyl halides under electron impact.[8] It comes out that about 59% of the propyl ion are formed via the latter process, while 41% of the propyl ions would be formed directly from the decomposition of the $C_6H_{15}^+$ intermediate.

Conclusions

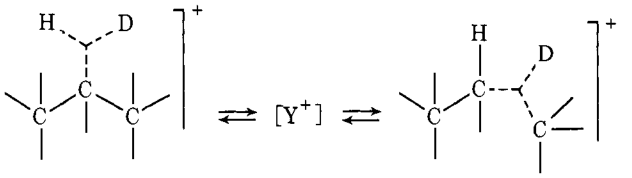
The present investigation permits us to draw the following conclusions: $C_2H_5^+$, in a first step, accepts a hydride from hexane. The hexyl ion formed decomposes further into butyl and propyl ions through processes in which all hydrogen atoms seem to be equivalent:



On the other hand, CH_5^+ acts exclusively as a protonating agent to form the hexonium ion, $C_6H_{15}^+$, which may decompose by losing either an H_2 or an alkane molecule.



In a recent investigation[12] on protonated alkanes in the gas phase, Hirakoa and Kebarle have shown that whenever a C-H bond is protonated, the resulting carbonium ion tends to lose a H_2 molecule, whereas protonation of a C-C bond will favor loss of an alkane moiety. If this assumption is correct, our results with *n*-hexane would then suggest that the relative probabilities of dissociative proton transfer to a C-H and a C-C bond by CH_5^+ are in the ratio $p_{C-H}/p_{C-C} = 0.28$. Moreover, the retention of the incoming hydron in the hexyl, butyl, and propyl ions suggests that a possibility exists for equilibration between the C-H and C-C protonated forms. This might take place as follows (see below), where Y^+ represents an intermediate state of unknown structure.



The fact that such an equilibration is barely seen prior to pentyl ion formation would indicate that in the case of protonation on the terminal positions of the hexane molecule, the subsequent loss of CH_4 is a fast process as compared to this equilibration process.

We have started further studies on the detailed mechanisms of the reactions of CH_5^+ and $C_2H_5^+$ with *n*-hexane using ^{13}C-labeled neutrals and the preliminary results support the model proposed in the present work. Moreover, recent results obtained with *n*-heptane[11] strongly support this model and therefore make us feel that it is generally applicable to the methane chemical ionization of *n*-paraffins.

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