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ELECTRON IMPACT FRAGMENTATION AND PRIMARY VACUUM PYROLYSIS PRODUCTS OF ISOMERIC PERFLUOROCARBONS OF COMPOSITION C_6F_{10} AND THEIR HYDROCARBON ANALOGS C_6H_{10}

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Pyrolytic chromatography-mass spectrometry makes it possible to establish a correlation between the electron impact fragmentation pattern (EIF) (at 70 eV) and final thermal decomposition products formed in the pyrolysis chamber of a chromatograph at atmospheric pressure [1, 2]. However, an accurate comparison of EIF and mechanism of thermal decomposition is impeded by the absence of information concerning primary pyrolysis processes, since the detected final product mixture is formed as a result of several competing secondary reactions. A more fundamental comparison would therefore be between the EIF pattern and mechanism of vacuum pyrolysis (VP) under conditions where secondary processes are inhibited.

Mass spectrometric analysis of primary VP products can be successfully achieved only at very low ionizing voltages (IV), for instance approximately 1 eV higher than the ionization potential of the most difficult-to-ionize components, i.e., under conditions of maximum limitation of molecular ion (MI) fragmentation. It should be noted that at low IV ionization is preceded by vibrational excitation of molecules, which takes place at the elevated temperature in the ion source, or in a specialized vacuum reactor, and which can significantly change the MI fragmentation prior to the onset of VP [3, 4]. For this reason, it is important to consider temperature dependence data for EIF when studying VP processes. In the case that the MI formed from the VP products are the same as the fragment ions (FI) observed for the starting material, the nature of the temperature dependence of the intensities of the principal mass spectral peaks makes it possible to discern changes associated with either a fragmentation temperature effect or with the formation of pyrolysis products.

It is assumed that the absence of any correlation between the EIF pattern of a substance and its VP mechanism may be the result of either specific or random rearrangements of the principal ions in the mass spectrum (MS). On the other hand, the existence of a correlation between the EIF pattern and VP mechanism of a substance argues against similar types of rearrangements. In order to verify this assumption, we have investigated the temperature-dependent EIF patterns and VP if isomeric hydrocarbons of composition C_6H_{10} and their perfluoro analogs, C_6F_{10} : perfluoro-1-methylcyclopentene (I), perfluoro-2,4-hexadiene (II), perfluorocyclohexene (III), and perfluoro-1,5-hexadiene (IV). Our choice of samples for this study was based on the fact that complete rarrangement of the MI of unsaturated hydrocarbons up to C_6 is thought to take place within a <10⁻⁶ sec time frame [5]. MI isomerization of deuterated 1,5-hexadienes, which leads via a sequence of hydrogen shifts to

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Compound	Principal peaks (14 eV)	ΔI, % at TPO	TPO, °C	Pyrolysis products
1-Methylcyclopentene	M ⁺ ·,	15	700	Methylcvclopentadiene.
, , , ,	$(M - CH_3) +$			H ₂
2,4-Hexadiene	M+.	0	1050	CPD, CH4, CH3, C2H6, H2
Cyclohexene	$M^+ \cdot \cdot \cdot (M - CH_3)^+$	15	630	1,3-Butadiene, C ₂ H ₄
1,5-Hexadiene	$(M-CH_3)^+, (C_4H_6)^+$	10	600	Allyl radical

TABLE 1. Principal Fragment Ions and Vacuum Pyrolysis Products of C_6H_{10}

	TABLE :	2.	Mass	Spectra	of	Compounds	(I)-((IV) ((ΣI_i)	=	100%)
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-			U _{ion} =	=60 eV	$U_{\rm ion} = 14 {\rm eV}$				
Ion	<i>m/z</i>	(I)	(11)	(111)	(IV)	(I)	(11)	(III)	(IV)
$\begin{array}{c} CF^+ \\ CF_{2}^+ + \\ CF_{3}F_{2}^+ + \\ CF_{3}F_{2}^+ + \\ C_{3}F_{3}F_{3}^+ + \\ C_{3}F_{5}^+ + \\ C_{4}F_{5}^+ + \\ C_{5}F_{5}^- + \\ C_{4}F_{5}^+ + \\ C_{5}F_{5}^- + \\ C_{4}F_{5}^+ + \\ C_{5}F_{5}^- + \\ C_{4}F_{5}^- + \\ C_{5}F_{5}^- + \\ C_{5}$	$\begin{array}{c} 31\\ 50\\ 69\\ 74\\ 81\\ 93\\ 100\\ 105\\ 112\\ 117\\ 119\\ 124\\ 131\\ 143\\ 150\\ 155\\ 162\\ 174\\ 181\\ 193\\ 212\\ 231\\ 243\\ 262 \end{array}$	$\begin{array}{c} 14.3\\ 1.1\\ 0.2\\ 16.3\\ 3.3\\ 0.2\\ 12.2\\ 2.9\\ 1.3\\ 1.6\\ 1.4\\ -\\ 3.9\\ 3.6\\ 7.3\\ -\\ 1.6\\ 2.22\\ 0.5\\ 0.7\\ 4.7\\ (7.1)\\ 0.3\\ 9.6\\ 3.5\\ \end{array}$	$\begin{array}{c} 9.8\\ 0.8\\ 0.3\\ 25.9\\ 3.0\\ 0.2\\ 11.2\\ 1.2\\ 1.2\\ 1.2\\ 1.2\\ 1.2\\ 1.2\\ $	$\begin{array}{c} 7.8\\ 1.0\\ 0.3\\ 27.8\\ 2.0\\ 0.4\\ 12.6\\ 3.7\\ 0.7\\ 1.5\\ 0.7\\ 1.5\\ 0.7\\ 1.5\\ 0.7\\ 2.0\\ 10.9\\ 4.3\\ 0.3\\ 1.2\\ (9.2)\\ 0.2\\ 2.0\\ 3.8\\ 0.3\\ 5.0\\ 1.4\end{array}$	$\begin{array}{c} 3.9\\ 0.3\\ 0.3\\ 13.3\\ 0.8\\ 0.8\\ 0.2\\ 0.2\\ 1.1\\ 0.3\\ -\\ 0.8\\ (51,5)\\ 3.2\\ -\\ 1.3\\ 1.0\\ 0.2\\ 0.1\\ 13.3\\ 0.2\\ -\\ 2.1\\ 1.1\end{array}$	1.0 2,4 4.5 3.8 (19,4) 12.5 2.8 (53,5)	0,6 1,3 (22,0) 3,5 0,6 (72,0)	4,1 7,1 1.2 (33,7) 2,1 7,8 2,1 0,4 (41,6)	(58,8) 0,8 0,3 0,2 (37,7) 0,2 2,1

the thermodynamically favored methylcyclopentenium cation-radical, has been documented experimentally [6]. The generality of MI rearrangements for isomeric C_6H_{10} compounds is confirmed by their similar EIF patterns [7], as well as by the presence of characteristic $(C_{5}H_{7})^{+}$ fragments in their mass spectra, corresponding to structure to the thermodynamically favored cyclopentenium cation [8]. The only example of a MS study of VP of an isomeric $C_{6}H_{10}$ hydrocarbon which has been conducted up until now is 1,5-hexadiene, which decomposes selectively via the formation of allylic radicals [9]. We have studied for the first time herein the VP of the three other structural C_6H_{10} isomers (Table 1). The values of ΔI given in Table 1 reveal the fragmentation temperature dependence, i.e., the percent reduction in one principal MS ion and increase in another principal ion with increasing reactor temperature, up to the temperature of pyrolysis onset (TPO). Values of ΔI between ~10-15% are characteristic of C_6H_{10} compounds. In the case of the conjugated isomer 2,4-hexadiene, the value of ΔI does not change up to a temperature of 1050°C. There were no special difficulties encountered in determining the TPO values of C_6H_{10} compounds, since thermal dissociation of these compounds results in the formation of products whose MI do not overlap the FI of the nonpyrolyzed starting materials. The pyrolysis products which are listed in Table 1 were reliably identified based on their MI at 14 and 60 eV. In conclusion, the weak temperature dependence noted for the mass spectra of C_6H_{10} isomers, and the complete lack of a correlation between their EIF patterns and thermal decomposition mechanism, are the result of the ease of $(C_6H_{10})^+$. MI rearrangement, which is thermodynamically favorable.



Fig. 1. Temperature-dependent relative ion peak intensities for compounds (I)-(IV).

In contrast to C_6H_{10} [10], there is limited data available concerning the MS of the corresponding perfluorocarbons [11]. No structural studies have been carried out for either $(C_6F_{10})^+$ cation radicals or $(C_5F_7)^+$ cations. We would assume that replacement of hydrogen by fluorine should inhibit the rearrangement of C_6F_{10} MI, and that in the absence of MI isomerization there should be a correlation between their EIF patterns and the mechanism of C_6F_{10} VP.

The mass spectra of compounds (I)-(III) were obtained at 60 eV (Table 2), and differ very little from one another. The only exception to this generalization is the MS of compound (IV), which exhibits an intense $C_3F_5^+$ (m/e 131) peak. At low IV (14 eV) the intensities of the MI and several FI (which are given in parentheses in Table 2) increase as the MS become characteristic of the compounds.

Based on the temperature-dependent MS data (Fig. 1) for compounds (I)-(III), we conclude that prior to the onset of pyrolysis (700-750°C) the extent of intensity redistribution between the MI and the most intense fragment ions is on the order of 20-30%. At the same time, the decrease in MI intensity is always somewhat greater than the increase in the corresponding FI intensity, since it is generally accompanied by an increase in the intensity of low-intensity peaks, which correspond to more extensive fragmentation processes, in addition to the increased intensity of the principal FI. In the case of compound (IV), which has a characteristically weak MI even at 14 eV (Table 2), the intensity redistribution at elevated temperatures occurs primarily between two FI, $(M-CF_3)^+$ and $(C_3F_5)^+$ (Fig. 1), of which the weaker $(M-CF_3)^+$ ion is most likely associated with rearrangement of the MI of (IV). Nevertheless, even at low reactor temperatures the predominant fragmentation process for (IV) involves the formation of the $(C_3F_5)^+$ FI, which does not require MI rearrangement (Fig. 1). The onset of pyrolysis for compounds (I)-(IV) was determined based on the temperature at which their MS exhibited new peaks, corresponding to CF_2^+ , CF_3^+ , $C_2F_4^+$, and $C_3F_4^+$ ions. For the primary VP products, such as: CF_2 , CF_3 , $C_2F_4^+$, and

Compound	Principal peaks (14	∆I, % at TPO	TPO, °C	Pyrolysis products
	ev)		1) 	
Perfluoro-1-methylcyclo- pentene (I)	M^{+*} , (M-CF ₂)+	20 _.	750	: CF ₂ . perfluorocyclo- pentene
Perfluoro-2,4-hexadiene	M+*, (M-CF ₃)+	30	760	°CF ₃ , C ₄ F ₄
Perfluorocyclohexene (III)	$M^{+}, (M-C_2F_4)^+$	20	750	C ₂ F ₄ , 1,3-butadiene
Perfluoro-1,5-hexadiene (IV)	$(M-CF_3)^+, (C_3F_5)^+$	20	850	Perfluoroallyl radical, perfluoroallene

TABLE 3. Principal Fragment Ions and Vacuum Pyrolysis Products of Compounds $\rm C_6F_{10}$

 $CF_2=C=CF_2$, whose MI do not overlap the FI for the starting materials (I)-(IV), their temperature-dependent MS (Fig. 1) are characterized by an increase in total ion current. In the case of compounds (I), (III), and (IV), their pyrolysis also results in the formation of products (Table 3), whose MI overlap FI peaks in the mass spectra of the starting materials.

The dynamics of accumulation of these pyrolysis products can be estimated (shown in Fig. 1 using dashed curves) by taking the concentration of VP products at TPO equal to zero and ignoring subsequent temperature-induced fragmentation changes. With the exception of the unidentified compound of composition C_4F_4 formed in the pyrolysis of (II) and having a probable triene structure $CF_2=C=C=CF_2$, all of the VP products (Table 3) were identified based on their MS recorded at 60 eV.

In the case of the pyrolysis of (IV), the reduced intensity of the perfluoroallyl radical observed at temperatures higher than 1000°C may be attributed to reactions occurring on the walls of the pyrolysis reactor, leading to the formation of SiF₄ and CF=C=CF₂ [12].

It is clear from the data in Table 3 that a very pronounced temperature dependence is characteristic of the fragmentation of C_6F_{10} compounds, much more pronounced than in the case of the C_6H_{10} hydrocarbon analogs. The overlap noted between the principal FI in the mass spectra (at 14 eV) of the C_6F_{10} perfluorocarbon starting materials and their principal VP products lead us to conclude that in the case of C_6F_{10} compounds MI rearrangement, which is characteristic of C_6H_{10} isomers, does not occur, probably due to the difference in energy required for hydrogen versus fluorine shifts in their corresponding cation radicals.

Despite the fact that the absence of naturally occurring fluorine isotopes excludes the possibility of studying rearrangements of perfluorocarbon cation-radicals using the labeled atom method, their temperature-dependent EIF patterns and mass spectrometric analysis of the VP products of perfluorinated compounds can be used to obtain valuable information concerning the existence or absence of principal ion rearrangements.

EXPERIMENTAL

The mass spectrometer apparatus used in this study was bult on an MX-7303 monopole mass spectrometer base with a mass number resolution up to 500 amu [13]. By changing the stabilizer design the range of ionizing voltages was broadened from 7-80 eV. The temperature of the ion source was held constant (at 150°C) during the course of mass spectral measurements.

Pyrolysis of the compounds identified in this study was carried out at a pressure of 10^{-2} torr in a ceramic flow reactor with an inner diameter of 2 mm and a heated zone length of 40 mm. The distance between the reactor and the ionization chamber of the mass spectrometer was 40 mm.

CONCLUSIONS

1. A pronounced temperature dependence has been observed for the mass spectra of perfluorocarbons of composition C_6F_{10} , involving sequential decreases in the intensities of their molecular ions and increasing fragment ion intensities in the temperature range 20-700°C at low ionizing potential (14 eV). 2. The absence of any correlation between the thermal decomposition mechanism of isomeric C_6H_{10} hydrocarbons and their electron impact fragmentation pattern has been demonstrated, and is a consequence of the known rearrangement of their molecular ions.

3. The similarity or overlap noted between the principal fragment ions present in the mass spectra of C_6F_{10} perfluorocarbons and their primary vacuum pyrolysis products is indicative of the absence of C_6F_{10} molecular ion rearrangement and makes it possible to predict the primary act in their thermal dissociation pathways based on their mass spectra, obtained at low ionizing voltages.

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ROTATIONAL ISOMERISM RELATIVE TO C-O BONDS IN STEREOISOMERIC

CYCLIC TRANS-METHOXY ALCOHOLS

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It is known that intramolecular hydrogen bonds (IHB) in 2-substituted ethanols are weak, and the question of the nature of the forces which stabilize the form with an adjacent OH group and electronegative atom has thus been frequently raised in the literature [1]. The strict parallelism of the O-H and C-Hal bonds in halogen hydrides [2] and the possibility of the same geometry in methoxy derivatives [3] provides an explanation of the stability of this conformation due to the dipole-dipole interaction of the bonds. The molecule of 2methoxyethanol contains groups for which strong HB are formed in an intermolecular interaction, but the microwave study found no significant differences from the inhibited conformations in it [4]. The data analyzed on assumption of the trans-orientation of the O-Me and C-C bonds resulted in dihedral angle values of 57 \pm 3° for C-C and 45 \pm 5° for O-H. Since the real geometry of the molecule is a compromise reached by the effect of the intramolecular forces, it is interesting to follow the rotational isomerism of irregular groups in stereoisomers of a cyclic nature.

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