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MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

II*. MONO- AND BIS(CYCLOPENTADIENYL) DERIVATIVES OF TITANIUM

A. N. NESMEYANOV, YU. S. NEKRASOV, V. F. SIZOI, O. V. NOGINA, V. A. DUBOVITSKY and YE. I. SIROTKINA

Institute of Organo-Element Compounds, Academy of Sciences, Vavilova Str. 28, V-312 Moscow (U.S.S.R.)

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SUMMARY

The mass spectra of $(C_5H_5)_2TiX_2$ (where X is F, Cl, Br or I), $C_5H_5TiX_3$, $CH_3C_5H_4TiX_3$ and $(CH_3)_5C_5TiX_3$ (where X is Cl, Br or OC_2H_5) have been recorded and show that the molecular ions decompose essentially via two routes leading to the elimination of C_5H_5 and X. Methylated ligands readily eliminate a molecule of HX to form a fulvene fragment.

In previous communications, studies of the transfer of electronic effects of ligands through the titanium atom in mono- and bis(cyclopentadienyl)derivatives were described[2,3] in which both chemical and physical techniques were employed. In particular, mass spectrometry was used in a study of $C_5H_5Ti(OC_2H_5)_nCl_{3-n}$ where $n=0$, 1, 2 and 3. Analysis of the intensity ratio values for $[M-C_5H_5]^+/[M]^+$ and $[M-C_5H_5]^+/[C_5H_5]^+$ suggested that the C_5H_5–Ti π-bond polarity increases as the number of chlorine atoms in the molecule decreases[4]. In this study, mass spectrometry has been used in a more extended study of the transfer of the electronic effects associated with ligands through the titanium atom.

Of the monocyclopentadienyltitanium derivatives studied earlier by chemical methods, a particularly interesting complex was $[(CH_3)_4(CH_2Br)C_5]TiBr_3$ which differs markedly from the pentamethylcyclopentadienyl compound in its reactivity towards nucleophiles. Thus, the $[(CH_3)_4(CH_2Br)C_5]$–Ti bond in $[(CH_3)_4(CH_2Br)C_5]TiBr_3$ is readily decomposed with ethanol under mild conditions, the process being accompanied by dehydrobromination and fulvene formation. In fact, the mass spectrum of the monocyclopentadienyl compound contains, *inter alia*, a $[C_{10}H_{14}]^+$ ion which may possess a fulvene structure[5]. It is possible that the existence of this ion may be associated with the presence of CH_2Br in the cyclopentadienyl ring of $[(CH_3)_4(CH_2Br)C_5]TiBr_3$, and for this reason we have studied the spectra of $C_5H_5TiBr_3$, $(CH_3C_5H_4)TiCl_3$ and $[(CH_3)_5C_5]TiBr_3$ in an attempt to solve this problem.

Reports regarding the mass spectra of organotitanium compounds are not

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* For Part I, see ref. 1.

particularly numerous. Such spectra have been used to identify dicyclopentadienyltitanium-α,α-dipyridyl[6], the trimer of dicyclopentadienyltitanium nitrile, the trimer of dicyclopentadienyltitanium isothiocyanate and dicyclopentadienyltitanium isocyanate[7]; in each case, however, the spectra were not analysed. Van Oven and De Liefde Meyer have recorded the mass spectra of $C_5H_5TiC_8H_8$,[8], and $C_5H_5TiC_7H_7$,[9], but again only the main fragments were tabulated.

A more extensive study has been made of $(C_5H_5)_2Ti(C_6F_5)X$ where X is C_6F_5 or Cl[10]. The spectra of these compounds were found to be identical to all intents and purposes, suggesting that ionisation was followed by a rapid elimination of the σ-bonded group, X, leading to the formation of $[(C_5H_5)_2TiC_6F_5]^+$.

A table listing the titanium-containing ions found in the mass spectra of $(C_5H_5)_2TiX_2$ (X = F, Cl, Br, I) has been reported[11].

The mass spectra of $(C_5H_5)_2TiCl_2$ and $(C_5H_5)_2ZrCl_2$ have been measured by Dillard and Kiser[11a] who have put forward a detailed fragmentation scheme. The ionization and appearance potentials of all the ions formed have been determined and from the heats of combustion the heats of formation of $(C_5H_5)_2TiCl_2$ and $(C_5H_5)_2ZrCl_2$ have been determined.

Finally, a recent publication[12] deals with some spectral data on $[(CH_3)_5C_5]_2CH_2Ti$, $[(CH_3)_5C_5]_2Ti$ and $[(CH_3)_5C_5]_2Ti(CH_3)_2$. The authors have suggested a fragmentation pattern for $[(CH_3)_5C_5]^+$ which unfortunately, however, extends only as far as the ion $[C_5(CH_3)_3CH_2]^+$ (*m/e* 119) whose subsequent decomposition has not been discussed.

We have studied the spectra of $(C_5H_5)_2TiF_2$ (I), $(C_5H_5)_2TiCl_2$ (II), $(C_5H_5)_2TiBr_2$ (III), $(C_5H_5)_2TiI_2$ (IV), $C_5H_5TiCl_3$ (V), $C_5H_5TiBr_3$ (VI), $C_5H_5Ti(OC_2H_5)_3$ (VII), $[(CH_3)_5C_5]TiCl_3$ (VIII), $[(CH_3)_5C_5]TiBr_3$ (IX), $[(CH_3)_5C_5]Ti(OC_2H_5)_3$ (X), $(CH_3C_5H_4)TiCl_3$ (XI) and $(CH_3C_5H_4)Ti(OC_2H_5)_3$ (XII). Some of the major fragments are listed in Tables 1–5 together with their intensities relative to the total ion current.

In an earlier study, we examined the ^1H NMR spectra of bis(cyclopentadienyl)titanium dihalides and the ^{19}F NMR spectra of a number of bis(cyclopentadienyl)-

TABLE 1

MAJOR FRAGMENTS AND THEIR INTENSITIES (PERCENTAGES RELATIVE TO THE TOTAL ION CURRENT), IN THE MASS SPECTRA OF $(C_5H_5)_2TiX_2$ [(I)–(IV)][a]

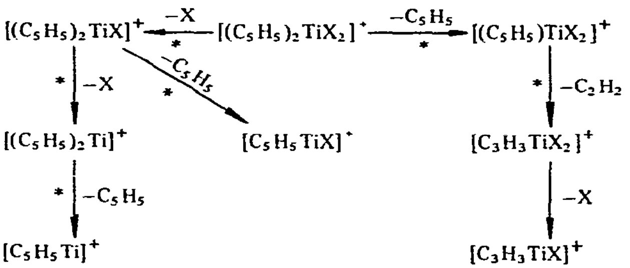
Ion	*X*			
	F	*Cl*	*Br*	*I*
M^+	5.0	1.8	5.8	1.8
$[M-X]^+$	3.5	7.1	22.4	6.8
$[M-2X]^+$	0.4	1.1	6.4	9.8
$[M-HX]^+$	0.5	0.2	0.5	0.8
$[M-C_5H_5]^+$	20.2	7.2	11.8	0.5
$[M-C_5H_5-X]^+$	2.6	11.9	10.9	3.5
$[C_5H_5Ti]^+$		1.0	1.3	6.6
$[TiX_2]^+$	5.0			
$[C_5H_5]^+$	6.2	6.0	1.5	0.5

[a] Ion intensities here and in the following tables are corrected for the isotope composition of Hal, Ti and C.

titanium fluorides. We came to the conclusion that the lone pair electrons of the halogen atoms overlap the vacant orbitals of the titanium atom, the overlap being greatest in the fluoro compounds[2]. The mass spectral data reported here are in exact agreement with this conclusion.

The major degradation path of the molecular ions formed from the complexes (I)–(IV) involves the successive elimination of both halogens to form intense peaks corresponding to $[M-X]^+$ and $[M-2X]^+$ respectively (Scheme 1). It should be noted that the relative intensity of the latter ion rises sharply (9.8 instead of 0.4%) in going from X = F to X = I, while the ratio of its intensity to that of the respective molecular ion rises from 0.1 to 5.4%. This indicates that the formation of the $[(C_5H_5)_2Ti]^+$ ion is most favourable in the case of dicyclopentadienyltitanium diiodide.

SCHEME 1



Here and in the following schemes, the asterisks denote degradation routes identified through the respective metastable peaks.

In addition to the elimination of the two halogens, hydrogen halide elimination also occurs in competition but is, however, much less pronounced and of roughly equal intensity in each case. Another degradation path for the molecular ions formed from the complexes (I)–(IV) consists of elimination of the cyclopentadienyl ligand leading to intense peaks corresponding to the $[C_5H_5TiX_2]^+$ ion when X = F, Cl or Br but to much less intense peaks corresponding to $[C_5H_5TiI_2]^+$ when X = I. The relative intensities of $[C_5H_5TiF_2]^+$, $[C_5H_5TiCl_2]^+$, $[C_5H_5TiBr_2]^+$ and $[C_5H_5TiI_2]^+$ are 20.2, 7.2, 11.8 and 0.5% respectively. The results quoted in Table 2 demonstrate that on going from (I) to (IV) the ratio $I_{[M-C_5H_5]^+}/I_{[M]^+}$ decreases. This may be explained by assuming that the C_5H_5–Ti bond strength increases along this series which is in agreement with the fact that the $[M-2C_5H_5]^+$, ($[TiX_2]^+$), ions are absent for

TABLE 2

THE INTENSITY RATIOS $I_{[M-2X]^+}/I_{[M]^+}$ AND $I_{[M-C_5H_5]^+}/I_{[M]^+}$ FOR $(C_5H_5)_2TiX_2$ [(I)–(IV)]

Compound		$I_{[M-2X]^+}/I_{[M]^+}$	$I_{[M-C_5H_5]^+}/I_{[M]^+}$
$(C_5H_5)_2TiF_2$	(I)	0.1	4.0
$(C_5H_5)_2TiCl_2$	(II)	0.6	4.0
$(C_5H_5)_2TiBr_2$	(III)	1.1	2.0
$(C_5H_5)_2TiI_2$	(IV)	5.4	0.3

$X = Cl$, Br, or I, whereas the $[TiF_2]^+$ peak (*m/e* 86) is quite intense and amounts to 5%. It should also be noted that $[C_5H_5Ti]^+$ (*m/e* 113) is absent from the spectrum of $(C_5H_5)_2TiF_2$ whereas in the spectrum of $(C_5H_5)_2TiI_2$ it has an intensity of 6.6%.

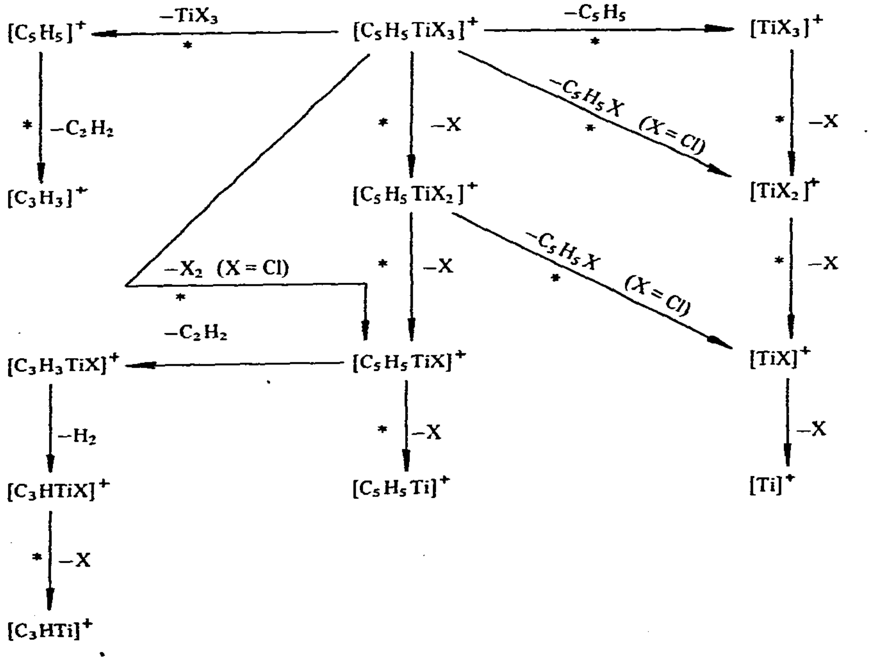
Fragmentation of $C_5H_5TiX_3$ (Table 3, Scheme 2) occurs in a similar manner to the fragmentation of $(C_5H_5)_2TiX_2$. Molecular ions of the halides (V) and (VI) decompose essentially through the elimination of a halogen atom forming intense

TABLE 3

MAJOR FRAGMENTS AND THEIR INTENSITIES (PERCENTAGES RELATIVE TO THE TOTAL IONISATION CURRENT) IN THE MASS SPECTRA OF $C_5H_5TiX_3$ [(V)–(VII)]

Ion	*X*		
	Cl	*Br*	OC_2H_5
$[M]^+$	11.4	9.8	2.4
$[M-X]^+$	8.5	18.0	4.0
$[M-X_2]^+$	3.6	5.0	1.5
$[M-X_3]^+$	0.2	1.1	1.5
$[M-HX]^+$			0.5
$[TiX_3]^+$	0.3	1.3	5.2
$[TiX_2]^+$	4.6	4.7	0.8
$[TiX]^+$	5.0	4.0	0.2
$[Ti]^+$	0.4	0.4	0.3
$[C_5H_5]^+$	31.0	1.0	8.7

SCHEME 2

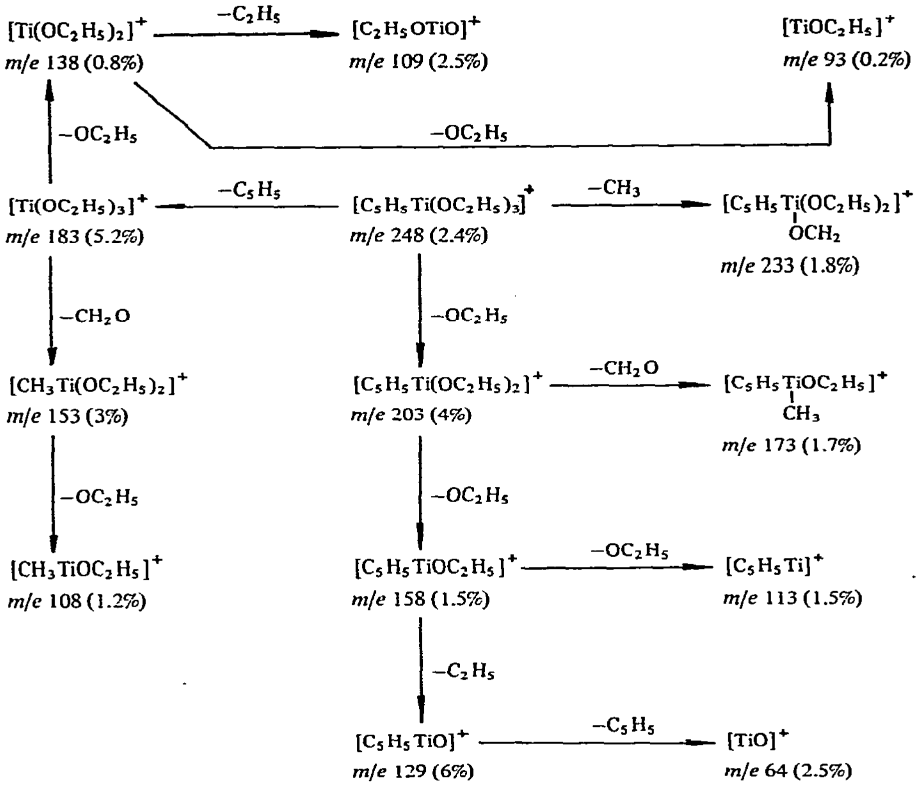


$[C_5H_5TiX_2]^+$ ions. Elimination of the second and the third halogen atom or of the cyclopentadienyl group is much less probable. It is notable that only one halogen atom enters into the exchange reaction with an alkoxy group when cyclopentadienyltitanium trihalides are treated with alcohols. Substitution of the other halogen atoms is effected only under much more drastic conditions[13]. The spectrum of $C_5H_5TiCl_3$ contains a metastable peak (*m/e* 64–65.5) corresponding to the one-step elimination of the cyclopentadienyl group and a chlorine atom from the molecular ion:

$$[C_5H_5TiCl_3]^+ \xrightarrow{-C_5H_5Cl} [TiCl_2]^+$$

A similar elimination of C_5H_5Cl from the ion $[C_5H_5TiCl_2]^+$ has been verified by the presence of the respective metastable peak (*m/e* 37.5–39). With $C_5H_5TiBr_3$, successive elimination of three bromines occurs from the molecular ion, with the intensity of the peaks corresponding to the ions formed successively decreasing. Loss of the cyclopentadienyl group from the molecular ion is quite insignificant, like in the chloro derivative. The intensities of the resulting ions $[TiX_3]^+$, $[TiX_2]^+$ and $[TiX]^+$ decrease noticeably with the ionising electron energy, and at 30 V no $[TiX]^+$ peak

SCHEME 3



In this scheme the *m/e* values and percentages of the total ionisation are assigned.

appears in the spectrum. This suggests that either the C_5H_5–Ti bond is stronger than the Ti–X bond and/or that $[C_5H_5TiX_2]^+$ is more stable than $[TiX_3]^+$.

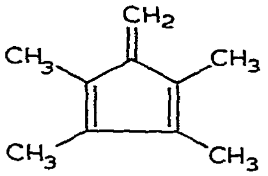
The spectrum of $C_5H_5Ti(OC_2H_5)_3$ ((VII), Scheme 3) merits more detailed consideration. In addition to producing a fragmentation pattern similar to that of $C_5H_5TiX_3$ (involving successive elimination of ethoxy groups, and elimination of the cyclopentadienyl group), this compound undergoes some additional processes involving degradation of the ethoxy group. Initially, a methyl radical is eliminated from the molecular ion, yielding a fragment at *m/e* 233. Elimination of an ethyl radical from $[M-2\ OC_2H_5]^+$ also occurs via another fragmentation route to yield a peak corresponding to $[C_5H_5Ti{=}O]^+$ at *m/e* 129, this peak possessing the greatest intensity in the spectrum. Further decomposition of this ion gives $[TiO]^+$. A similar loss of an ethyl radical occurs from the ion $[Ti(OC_2H_5)_2]^+$ leading to the formation of $[C_2H_5OTi{=}O]^+$ at *m/e* 109. What is of especial interest is the elimination of a formaldehyde molecule from $[M-C_2H_5O]^+$ and $[Ti(OC_2H_5)_3]^+$ together with methyl radical migration to the titanium atom resulting in the formation of $[C_5H_5Ti(CH_3)(OC_2H_5)]^+$ and $[CH_3Ti(OC_2H_5)_2]^+$ respectively. The intensity of $[TiX_3]^+$ in the spectrum of $C_5H_5Ti(OC_2H_5)_3$ is substantially greater than the intensity of the respective ion in the $C_5H_5TiHal_3$ spectra. This agrees well with our earlier conclusion[14] that the polarity of the Ti–C_5H_5 bond increases in going from $C_5H_5TiCl_3$ to $C_5H_5Ti(OC_2H_5)_3$.

Introduction of five methyl groups into the cyclopentadienyl ring strongly influences the resulting spectral pattern. Thus, for the complexes (VIII)–(X), pronounced degradation of the pentamethylated cyclopentadienyl ring has been observed (Table 4, Schemes 4 and 5).

TABLE 4

MAJOR FRAGMENTS AND THEIR INTENSITIES (PERCENTAGES RELATIVE TO THE TOTAL IONISATION CURRENT) IN THE MASS SPECTRA OF $(CH_3)_5C_5TiX_3$ [(VIII)–(X)]

Ion	*X*		
	Cl	*Br*	OC_2H_5
$[M]^+$	3.4	6.6	1.3
$[M-X]^+$	2.3	1.4	1.5
$[M-2X]^+$	0.4	1.6	6.5
$[M-HX]^+$	10.2	13.4	2.0
$[M-CH_2]^+$	0.7	0.2	1.7
$[M-CH_2-HX]^+$	2.2	0.6	2.0
$[M-HX-X]^+$	1.6	2.0	
$[(CH_3)_5C_5]^+$	13.0	10.2	0.8
$[(CH_3)_4C_5H]^+$	3.1	1.0	0.8
$[(CH_3)_3CH_2C_5]^+$	5.5	6.0	1.2
$[(CH_3)_3C_5H_2]^+$	2.0	2.1	1.0
$[(CH_3)_3C_5]^+$	4.6	4.2	1.5
$[(CH_3)_2C_5H_3]^+$	2.0	1.8	0.3
$[(CH_3)_2C_5H]^+$	3.4	3.5	0.9
$[(CH_3C_5H_4]^+$	1.8	1.6	0.4
$[CH_3C_5H_2]^+$	2.1	2.0	0.3
$[C_5H_5]^+$	1.0	0.8	0.3



(XIII)

Fig. 1.

Elimination of $[CH_2]^+$, $[C_2H_4]^+$, $[C_3H_5]^+$, $[C_4H_8]^+$ and $[C_5H_{10}]^+$ from $[(CH_3)_5C_5]^+$ leads to the formation of intense peaks at *m/e* values of 121, 107, 93, 79 and 65 respectively. Elimination of methane yields an ion of *m/e* value 119 which probably has a fulvene structure (XIII), (Fig. 1); further degradation of the latter ion gives ions at *m/e* values of 105,91 and 77.

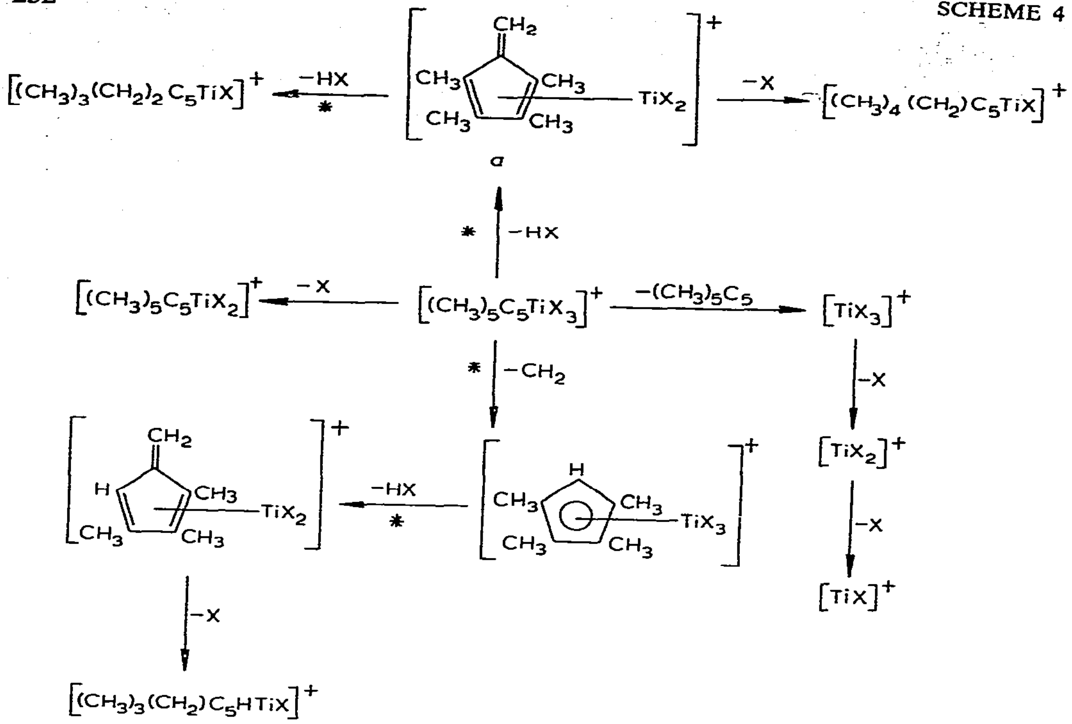
Unlike the spectra of derivatives of unsubstituted cyclopentadienyl, the spectra of $[(CH_3)_5C_5]TiX_3$ contain a very intense peak corresponding to $[M-HX]^+$ which has the greatest intensity other than that of $[(CH_3)_5C_5]^+$. In order for such degradation to occur one of the methyl hydrogens must be involved. Under these circumstances, the pentamethylated cyclopentadienyl ligand is converted into a fulvene-type structure (ion *a*, Scheme 4). In addition, the ion $[M-HX]^+$ may decompose further either through the loss of one more molecule of HX or of X. The competing elimination of methylene followed by hydrogen halide becomes much less prominent,

TABLE 5

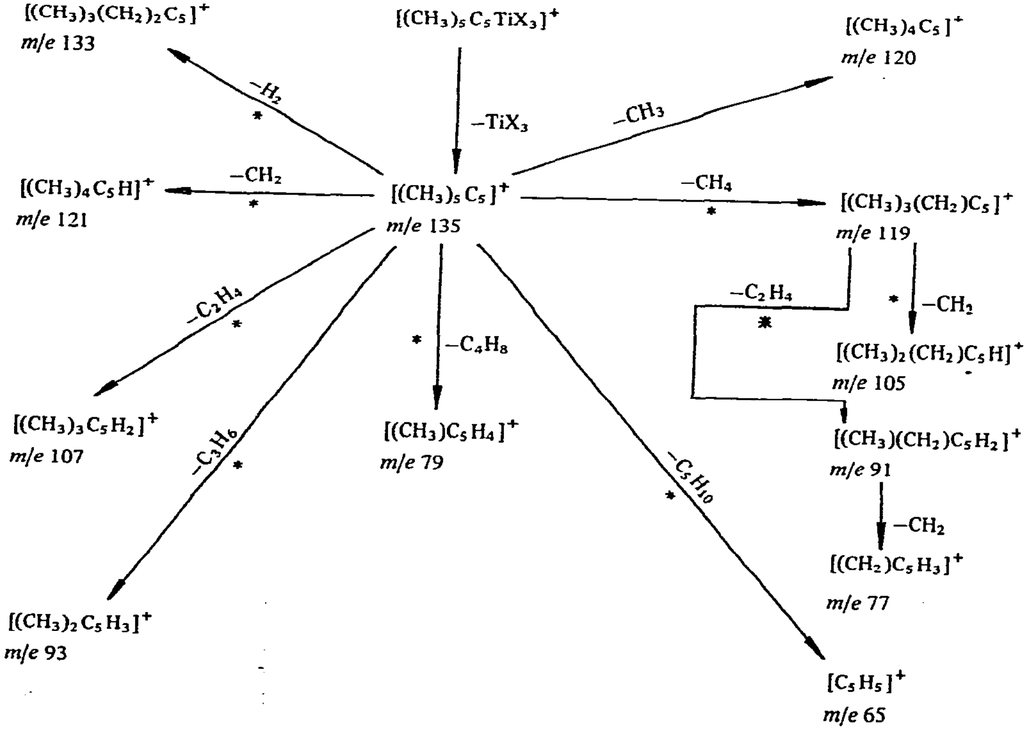
MAJOR FRAGMENTS AND THEIR INTENSITIES (PERCENTAGES RELATIVE TO THE TOTAL IONISATION CURRENT) IN THE MASS SPECTRA OF $CH_3C_5H_4TiX_3$ [(XI) AND (XII)]

Ion	*X*	
	Cl	OC_2H_5
$[M]^+$	4.8	1.3
$[M-H]^+$	3.0	2.0
$[M-HX]^+$	15.8	1.8
$[M-HX-X]^+$	3.2	1.0
$[M-HX-2X]^+$	0.7	0.9
$[M-2X]^+$	0.2	2.0
$[M-CH_3]^+$		0.2
$[M-CH_2]^+$	0.5	0.2
$[M-CH_2-X]^+$	0.4	1.0
$[M-CH_2-2X]^+$	0.2	0.6
$[TiX_3]^+$	0.5	4.2
$[TiX_2]^+$	3.7	0.4
$[TiX]^+$	5.3	0.2
$[CH_3C_5H_4]^+$	12.1	7.2
$[CH_2C_5H_4]^+$	4.9	1.1
$[CH_3C_5H_2]^+$	10.2	2.8
$[C_5H_5]^+$	1.2	1.5
$[C_4H_3]^+$	3.1	1.0

SCHEME 4



SCHEME 5



although the following degradation sequence is still quite clear in the spectrum.

$$[[(CH_3)_5C_5]TiX_3]^+ \xrightarrow{-CH_2} [[(CH_3)_4C_5H]TiX_3]^+ \xrightarrow[*]{-HX}$$

$$[[(CH_3)_3(CH_2)C_5H]TiX_2]^+ \xrightarrow[*]{-X} [[(CH_3)_3(CH_2)C_5H]TiX]^+$$

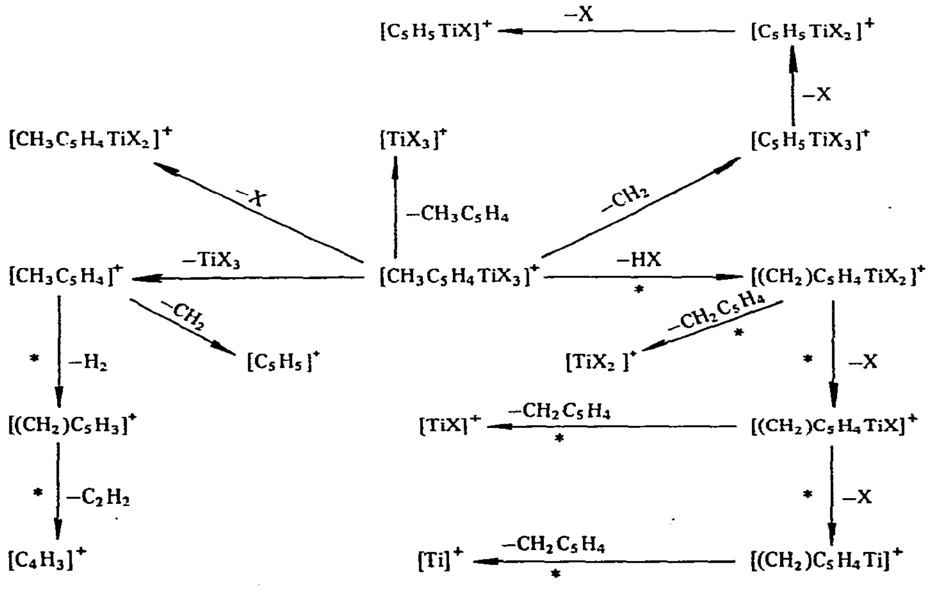
The only difference between the spectra of $[(CH_3)_5C_5]Ti(OC_2H_5)_3$ (X) and of the various halogenated derivatives is that the spectrum of the former contains an intense peak corresponding to $[[(CH_3)_4C_5]HTi(OC_2H_5)]^+$ at *m/e* 214 which must be formed by elimination of the CH_2 radical from $[M-2C_2H_5O]^+$.

The fragmentation pattern of $(CH_3C_5H_4)TiX_3$ (Table 5, Scheme 6) under electron impact is similar to that of $[(CH_3)_5C_5]TiX_3$ compounds (VIII)–(X) discussed above.

Introduction of a methyl group into the cyclopentadienyl ring leads to the appearance of an intense peak corresponding to $[M-HX]^+$ which is analogous to the $[M-HX]^+$ ion in the spectra of compounds (VIII)–(X). Furthermore, $[M-HX]^+$ decomposes via two routes either through the loss of the organic ligand to form $[TiX_2]^+$ or through loss of X, both processes having been verified by the presence of the respective meastable peaks. The ion $[M-HX-X]^+$ in turn may decompose both by losing $CH_2C_5H_4$ to form $[TiX]^+$ and by losing X to form $[CH_2C_5H_4Ti]^+$ which has an *m/e* value of 126.

Similar elimination of HBr from $[(CH_3)_5C_5]TiBr_3$ has also been demonstrated under other conditions. For example, $[(CH_3)_5C_5]TiBr_3$ may be decomposed thermally (150–200° for 5 h) to give HBr (which may be identified as triethylamine hydrobromide), with a yield of 18%.

SCHEME 6



EXPERIMENTAL

Mass spectra were measured using a MKH-1303 spectrometer fitted with a means of direct sample insertion into the ion source. The ionising voltage employed was 30–50 V, the temperature of the sample insertion system was varied between 20 and 90° and the temperature of the ionising chamber was 150°.

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