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THE FORMATION OF GASEOUS IONS FROM DICYCLOPENTADIENYLTITANIUM DICHLORIDE AND DICYCLOPENTADIENYLZIRCONIUM DICHLORIDE UPON ELECTRON IMPACT*

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SUMMARY

The mass spectra of dicyclopentadienyltitanium dichloride and dicyclopentadienylzirconium dichloride are characterized by a unique fragmentation scheme involving the removal and fragmentation of the cyclopentadienyl groups in the molecular ions. From heats of combustion the heat of formation of $Ti(C_5H_5)_2Cl_2$ (s) and $Zr(C_5H_5)_2Cl_2$ (s) were determined to be -145 and -153 kcal/mole, respectively. The measured ionization potentials are $I[Ti(C_5H_5)_2Cl_2] = 8.9_8 \pm 0.1_6$ and $I[Zr(C_5H_5)_2Cl_2] = 9.3_7 \pm 0.2_5$ eV, respectively. Metastable transitions observed were used together with clastogram data to identify the fragmentation routes of the principal ionic species.

INTRODUCTION

Electron impact processes associated with positive fragment ions produced from metal "sandwich" compounds have been considered by several investigators[1-4]. The fragmentation patterns and energetic measurements have been determined for some dicyclopentadienylmetal compounds[1] and a group of cyclopentadienylmetal carbonyls[4-5]. The mass spectrum of cyclopentadienyltitanium trichloride has been measured[6] and the fragmentation pattern reported was similar to the mass spectrum of the cyclopentadienylmetal carbonyls[4-5]. For $Ti(C_5H_5)Cl_3$ the primary fragment ions were formed by the loss of chlorine atoms. Ions corresponding to the loss of C_5H_5 were quite low in abundance as was the intensity of the metal ion. No energetic measurements for the $Ti(C_5H_5)Cl_3$ molecule were given. The mass spectrum of dicyclopentadienylzirconium dichloride has been determined[7], but no energetic measurements were reported.

The present work presents an examination of the energetic processes involved in ion formation and suggests a probable unimolecular decomposition process based on observed metastable transitions and supported by clastogram curves. This in-

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vestigation has been conducted to introduce information which may aid in the effort to better understand ionization processes and the unimolecular decomposition reactions of molecules containing transition metal atoms upon electron impact.

EXPERIMENTAL

Dicyclopentadienyltitanium dichloride, a red solid, and dicyclopentadienylzirconium dichloride, a white crystalline solid, were purchased commercially. The materials were used in the mass spectrometric study without further purification since low voltage mass spectrometry indicated no impurities which would interfere with the studies.

The Bendix time-of-flight (TOF) mass spectrometer, the AEI MS-9 double focusing mass spectrometer, and the experimental procedures used in this study have already been described in detail[8,9]. Mass spectra determined with the TOF and the MS-9 instruments agreed to within a few percent of the relative intensities. Where possible energetic measurements were made at the m/q values for atom combinations which included the most abundant titanium, zirconium, and chlorine isotopes (48, 90, and 35 amu, respectively).

The heats of combustion of $Ti(C_5H_5)_2Cl_2$ (s) and $Zr(C_5H_5)_2Cl_2$ (s) were determined using a Parr series 1200 adiabatic calorimeter and a double valve Parr bomb made of a nickel–chromium alloy. The heat equivalent of the calorimeter was determined by burning samples of reagent grade benzoic acid.

The combustion of the organometallic halides was complicated by the fact that some of the combustion products (probably HCl) reacted with the bomb walls. Examination and analysis of the contents of the bomb after combustion indicated that molecular chlorine was not one of the primary products. It is suggested that HCl is the product which reacts with the bomb walls and that the reaction in the combustion of the dicyclopentadienylmetal dichlorides is

$$M(C_5H_5)_2(s)+13\ O_2(g) \rightarrow MO_2(s)+2\ HCl(aq)+10\ CO_2(g)+4\ H_2O(l) \quad (1)$$

Since HCl reacted with the bomb walls, an appropriate correction must be made so that correct heats of combustion for the $M(C_5H_5)_2Cl_2$ compounds can be evaluated.

To evaluate the energy released in the reaction of HCl, samples of chlorobenzene were burned in the calorimeter. In these combustions the heat evolved in excess of the known heat of combustion of chlorobenzene[10] (−6604.0 cal/g) was taken as the heat of reaction of HCl with the bomb walls. For repeated combustions of chlorobenzene the excess energy evolved was 66.6±2.3 kcal/g-atom of chlorine. It was assumed that the excess energy evolved in the combustion of the organometallic chlorides was equal to that given off when an equivalent amount of chlorobenzene was burned.

If reaction with the walls was the same for combustions with chlorobenzene and the organometallic chlorides, the ratio of the individual metal ion concentrations to the total chlorine in the sample should be constant. From an analysis of total chlorine (Cl) as chloride and a determination of the respective metal ion concentration by atomic absorption[11], the metal to chlorine (Cl) ratio was constant for combustions of chlorobenzene and the dicyclopentadienylmetal dichlorides.

After adiabatic combustion, gaseous products were removed from the bomb and the bomb contents washed into vessels for subsequent chemical analysis. In all combustions the total chlorine (Cl) recovered as chloride ion was 100 %. In combustion of the organometallic chlorides the metal dioxide recovered corresponded to the quantity expected based on the weight of the sample burned. The heats of combustion of $Ti(C_5H_5)_2Cl_2$ (s) and $Zr(C_5H_5)_2Cl_2$ (s) were -1366 ± 5 and -1398 ± 5 kcal/mole, respectively. Calculated heats of formation of the crystalline compounds determined from the heat of combustion according to reaction (1) were -145 ± 7 and -153 ± 7 kcal/mole for $Ti(C_5H_5)_2Cl_2$ (s) and $Zr(C_5H_5)_2Cl_2$ (s), respectively. Heats of formation employed in the calculations were:

$\Delta H_f(CO_2(g)) = -94.05$ (ref. 12) $\Delta H_f(ZrO_2(s)) = -258.2$ (ref. 13)
$\Delta H_f(H_2O(l)) = -68.32$ (ref. 12) $\Delta H_f(HCl(aq)) = -39.55$ kcal/mole (ref. 10)
$\Delta H_f(TiO_2(s)) = -218$ (ref. 13)

RESULTS AND DISCUSSION

The results for this investigation of the positive ions produced from dicyclopentadienyltitanium dichloride and dicyclopentadienylzirconium dichloride are presented in Tables 1 and 2. The relative abundances of the positive ions represent the monoisotopic intensity and as such include contributions from all the isotopes for a given ion at 70 eV. Several hydrocarbon ions of the type $C_xH_y^+$ have been omitted from the tables. The appearance potentials determined are given in column 3. The calculated heats of formation for the positive ions are reported in column 5. Heats of formation of the gaseous species used to evaluate the heats of formation of the ions are (in kcal/mole):

TABLE 1

APPEARANCE POTENTIALS AND HEATS OF FORMATION FOR POSITIVE IONS PRODUCED FROM DICYCLOPENTADIENYLTITANIUM DICHLORIDE

Ion	Relative abundance at 70 eV	Appearance potential (eV)	Probable process $Ti(C_5H_5)_2Cl_2 \rightarrow$	ΔH_f(ion) (kcal/mole)
$Ti(C_5H_5)_2Cl_2^+$	29.1	$8.9_8 \pm 0.1_6$	$Ti(C_5H_5)_2Cl_2^+$	85
$Ti(C_5H_5)_2Cl^+$	8.9	10.8 ± 0.3	$Ti(C_5H_5)_2Cl^+ + Cl$	98
$Ti(C_5H_5)Cl_2^+$	100.0	11.8 ± 0.2	$Ti(C_5H_5)Cl_2^+ + C_5H_5$	100
$Ti(C_5H_5)Cl^+$	38.7	16.3 ± 0.3	$Ti(C_5H_5)Cl^+ + C_5H_5 + Cl$	175
$Ti(C_3H_3)Cl_2^+$	0.8			
$Ti(C_3H_3)Cl^+$	6.7	(19.5)[a]	$Ti(C_3H_3)Cl^+ + C_5H_5 + C_2H_2 + Cl$	(194)[a]
$Ti(C_3H_3)^+$	1.9			
$Ti(C_2H_2)Cl^+$	2.3			
$TiCl_2^+$	21.3	19.7 ± 0.4	$TiCl_2^+ + C_5H_5 + C_3H_3 + C_2H_2$	144
$TiCl^+$	28.8	21.6 ± 0.4	$TiCl^+ + C_5H_5 + C_3H_3 + C_2H_2 + Cl$	159
Ti^+	2.5			
$C_5H_5^+$	26.6	13.0 ± 0.4	$C_5H_5^+ + Ti(C_5H_5)Cl_2$	(-62)[b]
$C_3H_3^+$	38.3	18.0 ± 0.5	?	

[a] Estimated values; see text. [b] Heat of formation of $Ti(C_5H_5)Cl_2$.

TABLE 2

APPEARANCE POTENTIALS AND HEATS OF FORMATION FOR POSITIVE IONS PRODUCED FROM DICYCLOPENTADIENYLZIRCONIUM DICHLORIDE

Ion	Relative abundance at 70 eV	Appearance potential (eV)	Probable process $Zr(C_5H_5)_2Cl_2 \rightarrow$	ΔH_f(ion) (kcal/mole)
$Zr(C_5H_5)_2Cl_2^+$	50.6	$9.3_7 \pm 0.2_5$	$Zr(C_5H_5)_2Cl_2^+$	87
$Zr(C_5H_5)_2Cl^+$	11.3	12.3 ± 0.2	$Zr(C_5H_5)_2Cl^+ + Cl$	125
$Zr(C_5H_5)Cl_2^+$	100.0	12.5 ± 0.2	$Zr(C_5H_5)Cl_2^+ + C_5H_5$	109
$Zr(C_5H_5)Cl^+$	10.0	19.8 ± 0.4	$Zr(C_5H_5)Cl^+ + C_5H_5 + Cl$	248
$Zr(C_3H_3)Cl_2^+$	29.3			
$Zr(C_3H_3)Cl^+$	10.1	(19.9)[a]	$Zr(C_3H_3)Cl^+ + C_5H_5 + C_2H_2 + Cl$	(196)[a]
$Zr(C_3H_3)^+$	4.5			
$Zr(C_2H_2)Cl^+$	3.5			
$ZrCl_2^+$	9.4	20.9 ± 0.5	$ZrCl_2^+ + C_5H_5 + C_3H_3 + C_2H_2$	164
$ZrCl^+$	8.6	24.3 ± 0.5	$ZrCl^+ + C_5H_5 + C_3H_3 + C_2H_2 + Cl$	214
Zr^+	0.3			
$C_5H_5^+$	12.1	13.6 ± 0.2	$C_5H_5^+ + Zr(C_5H_5)Cl_2$	(−56)[b]
$C_3H_3^+$	16.2	19.5 ± 0.4	?	

[a] Estimated values; see text. [b] Heat of formation of $Zr(C_5H_5)Cl_2$.

$Ti(C_5H_5)_2Cl_2$, −122.0[*]
$Zr(C_5H_5)_2Cl_2$, −129.9[*]
Cl, 29.08 (ref. 12)
C_5H_5, 50 (ref. 14)
C_3H_3, 84 (ref. 15)
C_2H_2, 54.2 (ref. 13)
$C_5H_5^+$, 240 (ref. 16)

Because of the overlap of m/q values for the MCl_2^+ and $M(C_3H_3)Cl^+$ ions it was not feasible to determine accurately the appearance potentials of the $M(C_3H_3)Cl^+$ ions using normal experimental procedures. The appearance potentials were estimated from the clastograms by noting the relative position of the $M(C_3H_3)Cl^+$ ion curves at low values of the fractional abundance relative to the position of the curves in this region for the MCl_2^+ and MCl^+ ions. The estimated appearance potentials are 19.5 and 19.9 eV for $Ti(C_3H_3)Cl^+$ and $Zr(C_3H_3)Cl^+$, respectively.

The most abundant ion, $M(C_5H_5)Cl_2^+$, is formed from the parent molecule-ion by the loss of a cyclopentadienyl group. This decomposition scheme is distinctly different from that observed for the cyclopentadienylmetal carbonyls[4,5] and cyclopentadienyltitanium trichloride[6] where the difficulty of removing the cyclopentadienyl group was great compared with the loss of CO or Cl. This preferential elimination of C_5H_5 in the dicyclopentadienylmetal dichlorides is indicative of the probable greater bond strength and ionic character of the chlorine–metal bond. For other fragment ions removal and fragmentation of the cyclopentadienyl group is favored, and ions retaining the chlorine substituent are the most abundant ions of a given series.

Two series of ions, $Zr(C_3H_3)Cl_n^+$ and $Zr(C_2H_2)Cl_m^+$ ($n=0, 1, 2$; $m=1, 2$), were detected in the 70 eV mass spectrum of the zirconium compound. The production of $Zr(C_3H_3)Cl_n^+$ and $Zr(C_2H_2)Cl_m^+$ ions occurs by fragmentation of the cyclopentadienyl

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[*] $\Delta H_f[Ti(C_5H_5)_2Cl_2(s)]$ and $\Delta H_f[Zr(C_5H_5)_2Cl_2(s)]$ were determined in this work (see text); the heats of sublimation of these compounds have been reported previously[9].

TABLE 3

METASTABLE TRANSITIONS IN DICYCLOPENTADIENYLTITANIUM DICHLORIDE

m^* obsd.	m^* calcd.	Metastable transition
185.0	184.90	$Ti(C_5H_5)_2Cl_2^+(250) \rightarrow Ti(C_5H_5)_2Cl^+(215) + Cl(35)$
183.0	182.94	$Ti(C_5H_5)_2Cl_2^+(248) \rightarrow Ti(C_5H_5)_2Cl^+(213) + Cl(35)$
181.5	181.48	$Ti(C_5H_5)_2Cl_2^+(250) \rightarrow Ti(C_5H_5)_2Cl^+(213) + Cl(37)$
136.9	136.90	$Ti(C_5H_5)_2Cl_2^+(250) \rightarrow Ti(C_5H_5)Cl_2^+(185) + C_5H_5(65)$
135.1	135.04	$Ti(C_5H_5)_2Cl_2^+(248) \rightarrow Ti(C_5H_5)Cl_2^+(183) + C_5H_5(65)$
121.6	121.62	$Ti(C_5H_5)Cl_2^+(185) \rightarrow Ti(C_5H_5)Cl^+(150) + Cl(35)$
119.7	119.69	$Ti(C_5H_5)Cl_2^+(183) \rightarrow Ti(C_5H_5)Cl^+(148) + Cl(35)$
118.5	118.40	$Ti(C_5H_5)Cl_2^+(185) \rightarrow Ti(C_5H_5)Cl^+(148) + Cl(37)$
102.5	102.51	$Ti(C_5H_5)Cl^+(150) \rightarrow Ti(C_3H_3)Cl^+(124) + C_2H_2(26)$
100.5	100.57	$Ti(C_5H_5)Cl^+(148) \rightarrow Ti(C_3H_3)Cl^+(122) + C_2H_2(26)$
23.5	23.40	$C_5H_5^+(65) \rightarrow C_3H_3^+(39) + C_2H_2(26)$

group probably forming the neutral species C_2H_2 and C_3H_3 while the ion retains either one or two chlorine atoms. In previous mass spectrometric studies[3-5] of cyclopentadienyl-containing metal compounds, fragmentation of the cyclopentadienyl group to produce the $M(C_3H_3)^+$ ions was observed, but ions containing $M(C_2H_2)$ were not detected. The formation of $M(C_2H_2)Cl_m^+$ ions appears novel for the dicyclopentadienylmetal dichlorides.

TABLE 4

METASTABLE TRANSITIONS IN DICYCLOPENTADIENYLZIRCONIUM DICHLORIDE

m^* obsd.	m^* calcd.	Metastable transitions
184.0	183.90	$Zr(C_5H_5)Cl_2^+(233) \rightarrow Zr(C_3H_3)Cl_2^+(207) + C_2H_2(26)$
182.0	181.93	$Zr(C_5H_5)Cl_2^+(231) \rightarrow Zr(C_3H_3)Cl_2^+(205) + C_2H_2(26)$
180.1	179.95	$Zr(C_5H_5)Cl_2^+(229) \rightarrow Zr(C_3H_3)Cl_2^+(203) + C_2H_2(26)$
178.3	177.98	$Zr(C_5H_5)Cl_2^+(227) \rightarrow Zr(C_3H_3)Cl_2^+(201) + C_2H_2(26)$
176.3	176.00	$Zr(C_5H_5)Cl_2^+(225) \rightarrow Zr(C_3H_3)Cl_2^+(199) + C_2H_2(26)$
182.0	182.18	$Zr(C_5H_5)_2Cl_2^+(298) \rightarrow Zr(C_5H_5)Cl_2^+(233) + C_5H_5(65)$
180.1	180.27	$Zr(C_5H_5)_2Cl_2^+(296) \rightarrow Zr(C_5H_5)Cl_2^+(231) + C_5H_5(65)$
178.3	178.37	$Zr(C_5H_5)_2Cl_2^+(294) \rightarrow Zr(C_5H_5)Cl_2^+(229) + C_5H_5(65)$
176.3	176.47	$Zr(C_5H_5)_2Cl_2^+(292) \rightarrow Zr(C_5H_5)Cl_2^+(227) + C_5H_5(65)$
174.6	174.57	$Zr(C_5H_5)_2Cl_2^+(290) \rightarrow Zr(C_5H_5)Cl_2^+(225) + C_5H_5(65)$
147.4	147.45	$Zr(C_5H_5)Cl^+(196) \rightarrow Zr(C_3H_3)Cl^+(170) + C_2H_2(26)$
146.5	146.47	$Zr(C_5H_5)Cl^+(195) \rightarrow Zr(C_3H_3)Cl^+(169) + C_2H_2(26)$
145.5	145.48	$Zr(C_5H_5)Cl^+(194) \rightarrow Zr(C_3H_3)Cl^+(168) + C_2H_2(26)$
144.4	144.50	$Zr(C_5H_5)Cl^+(193) \rightarrow Zr(C_3H_3)Cl^+(167) + C_2H_2(26)$
143.5	143.52	$Zr(C_5H_5)Cl^+(192) \rightarrow Zr(C_3H_3)Cl^+(166) + C_2H_2(26)$
142.5	142.54	$Zr(C_5H_5)Cl^+(191) \rightarrow Zr(C_3H_3)Cl^+(165) + C_2H_2(26)$
141.6	141.56	$Zr(C_5H_5)Cl^+(190) \rightarrow Zr(C_3H_3)Cl^+(164) + C_2H_2(26)$
23.5	23.40	$C_5H_5^+(65) \rightarrow C_3H_3^+(39) + C_2H_2(26)$

Other ions detected in the mass spectrum of the zirconium compound, but not included in Table 2, were $Zr(C_2H_x)Cl^+$ (8.7%), $Zr(C_2H_x)Cl_2^+$ (36.5%), $Zr(C_3H_2)Cl^+$ (14.2%) and small amounts of $Zr(C_4H_x)Cl_2^+$ and $Zr(C_5H_5)(C_2H_2)Cl^+$. Very low intensities of $Zr(C_3H_3)_2^+$ and $Zr(C_5H_5)_2^+$ ions were observed.

The series of unimolecular reactions for the formation of the fragment ions was established from the metastable transitions observed and the general shapes of the clastogram curves. The fragmentation scheme consists of competitive reactions involving the parent molecule-ion and a series of consecutive and competitive reactions where fragment ions decompose via elimination and fragmentation of C_5H_5 or by loss of chlorine atoms. The observed and calculated "metastable masses" and their associated transitions are presented in Tables 3 and 4.

The initial unimolecular reactions clearly indicated by the metastable transitions involve competitive loss of C_5H_5 and Cl from the parent molecule-ion. A unique "metastable isotopic pattern" was observed corresponding to removal of ^{35}Cl or ^{37}Cl isotopes from the titanium or zirconium ion which was composed of the most abundant metal isotope and the chlorine isotopic combinations: ^{35}Cl: ^{35}Cl; and ^{35}Cl : ^{37}Cl. The intensity of the metastable peak for elimination of ^{37}Cl from the metal chlorine combination ^{37}Cl : ^{37}Cl was too low to be detected. In a similar fashion a characteristic metastable isotopic pattern was noted for the process involving loss of the cyclopentadienyl group from the parent molecule-ion. The reaction processes which occur following the formation of the $M(C_5H_5)Cl_2^+$ ion are confirmed from the observed metastable transitions. The processes leading to the formation of the most abundant ions in the mass spectrum are:

$$\begin{tikzcd}
Ti(C_5H_5)_2Cl_2^+ \arrow[r] \arrow[dr] & Ti(C_5H_5)Cl_2^+ \arrow[r] & Ti(C_5H_5)Cl^+ \arrow[r] & Ti(C_3H_3)Cl^+ \\
 & Ti(C_5H_5)_2Cl^+ & C_5H_5^+ \arrow[r] & C_3H_3^+
\end{tikzcd} \qquad (2)$$

and

$$\begin{tikzcd}
 & & Zr(C_3H_3)Cl_2^+ & \\
Zr(C_5H_5)_2Cl_2^+ \arrow[r] \arrow[dr] & Zr(C_5H_5)Cl_2^+ \arrow[ur] \arrow[r] & Zr(C_5H_5)Cl^+ \arrow[r] & Zr(C_3H_3)Cl^+ \\
 & Zr(C_5H_5)_2Cl^+ & C_5H_5^+ \arrow[r] & C_3H_3^+
\end{tikzcd} \qquad (3)$$

In the above reactions, decomposition pathways for which metastable transitions were observed are indicated by solid arrows. Processes deduced from the clastogram data are signified by broken lines and are discussed below. Although two processes:

$$Zr(C_5H_5)_2Cl^+ \rightarrow Zr(C_5H_5)Cl^+ + C_5H_5 \qquad (4)$$

$$Zr(C_5H_5)Cl^+ \rightarrow Zr(C_3H_3)Cl^+ + C_2H_2 \qquad (5)$$

are indicated by the 141.6–147.4 metastable ions, it is suggested that these metastable ions result from reaction (5). Comparison with the transitions observed in $Ti(C_5H_5)_2Cl_2$ supports this suggestion for $Zr(C_5H_5)_2Cl_2$. Since the metastable transitions for the processes:

$$Zr(C_5H_5)_2Cl_2^+ \rightarrow Zr(C_5H_5)Cl_2^+ + C_5H_5 \qquad (6)$$

and

$$Zr(C_5H_5)Cl_2^+ \rightarrow Zr(C_3H_3)Cl_2^+ + C_2H_2 \qquad (7)$$

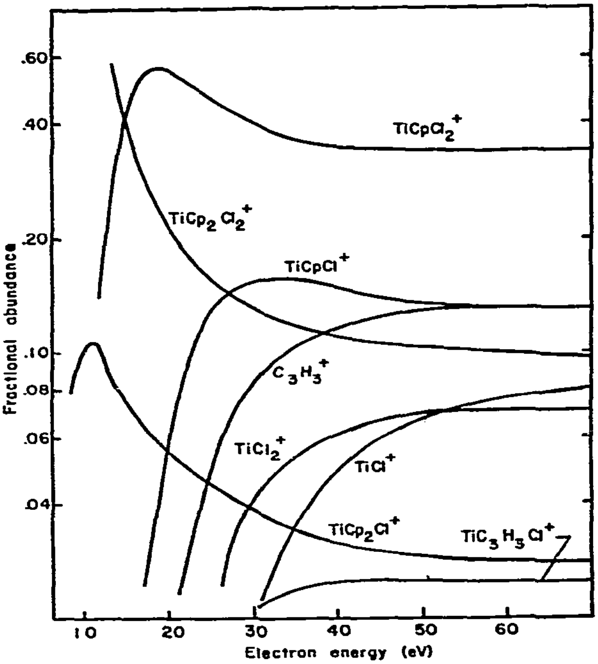

Fig. 1. Logarithmic clastogram for singly-charged positive ions from $Ti(C_5H_5)_2Cl_2$.

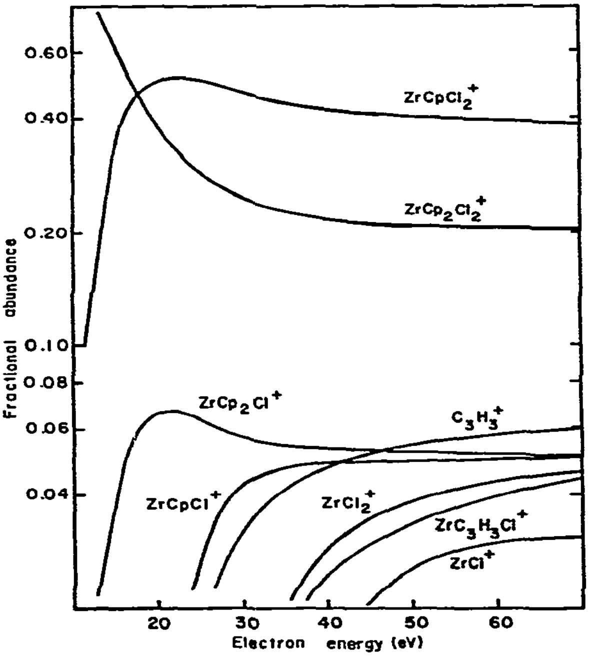

Fig. 2. Logarithmic clastogram for singly-charged positive ions from $Zr(C_5H_5)_2Cl_2$.

overlap somewhat in the mass spectrum, the identity of each transition was deduced from an analysis of the observed isotopic abundances for zirconium and chlorine in the respective metastable ions.

The logarithm of the fractional abundance of the ions as a function of the uncorrected ionizing electron energy is plotted in the clastograms shown in Figs. 1 and 2. The curve shapes are indicative of the unimolecular decomposition processes occurring in the ion source[4,9,17]. The parent molecule-ion is the most abundant ion at low electron energies and decreases in intensity as the electron energy is increased due to fragmentation of the parent ion. The primary fragment ions, $M(C_5H_5)Cl_2^+$ and $M(C_5H_5)_2Cl^+$, appear at low energies, reach a maximum intensity, and then decrease at higher energy.

This behavior in the clastogram curve is indicative of a consecutive reaction occurring in the ion source. This conclusion is confirmed by the metastable transitions observed. For the titanium compound a metastable transition was observed for the process $Ti(C_5H_5)Cl_2^+ \rightarrow Ti(C_5H_5)Cl^+ + Cl$. In the clastogram curve it is noted that the $Ti(C_5H_5)Cl^+$ ion begins to increase in abundance as the fractional intensity of the $Ti(C_5H_5)Cl_2^+$ ion decreases. From the clastogram data it is evident that $Ti(C_5H_5)Cl^+$ is not formed from $Ti(C_5H_5)_2Cl^+$ by loss of C_5H_5, since the intensity of the $Ti(C_5H_5)_2Cl^+$ ion is low when the abundance of $Ti(C_5H_5)Cl^+$ begins to increase. This interpretation of the clastogram is in agreement with the metastable data.

Similar arguments and correlations are applicable in the zirconium compound. From the curves it is evident that the intensity of the parent molecule-ion decreases as the abundance of the $Zr(C_5H_5)_2Cl^+$ and $Zr(C_5H_5)Cl_2^+$ ions increase. Similarly, the $Zr(C_5H_5)Cl^+$ ion increases as the $Zr(C_5H_5)Cl_2^+$ ion abundance decreases suggesting that the primary mode of formation of $Zr(C_5H_5)Cl^+$ is $Zr(C_5H_5)Cl_2^+ \rightarrow Zr(C_5H_5)Cl^+ + Cl$. Complementary arguments based on clastogram data and metastable transitions support the decomposition process presented above.

The ionization potentials of $8.9_8 \pm 0.1_6$ and $9.3_7 \pm 0.2_5$ eV for $Ti(C_5H_5)_2Cl_2$ and $Zr(C_5H_5)_2Cl_2$, respectively, are greater than the ionization potentials measured for a series of dicyclopentadienylmetal molecules[1,4]. The values are also higher than the corresponding metal ionization potentials[18] but approximate the ionization potential of the cyclopentadienyl radical[19].

A molecular orbital description of the electronic structure of $Ti(C_5H_5)_2Cl_2$ has been presented by Chien[20]. According to the molecular orbital representation the electron removed in ionization occurred from the a_2^* anti-bonding orbital, which is anti-bonding among all the metal–ligand bonds. Although Chien assigns no weighted contributions to the orbital from the ligands, it would appear from our results that the contribution by chlorine is somewhat larger than the contribution by cyclopentadienyl since the ionization potentials are greater than for $M(C_5H_5)_2$ molecules[1,4]. Thus the inference is that the electron removed in ionization occurs from the molecular orbital composed predominantly of contributions from the metal and chlorine.

The heats of formation of the ions presented are calculated according to the reactions given in Tables 1 and 2 using the heats of formation of gaseous neutral species given above. Selection of the products accompanying the formation of the ions is based on the processes indicated from the metastable transitions and the clastogram curves. Although the metastable transitions were observed at 70 eV, the close correlation with the clastogram curves, which were determined by measuring the mass spectrum at a range of electron energies, indicates the neutral species suggested in the reactions of Tables 1 and 2 are the products formed at the threshold energy for production of the fragment ions.

The calculated heat of formation of $TiCl_2^+$ from dicyclopentadienyltitanium dichloride compares favorably with the value $\Delta H_f(TiCl_2^+) = 145$ kcal/mole calculated[9] for this ion from $TiCl_4$. However, the heat of formation of $TiCl^+$ determined here is somewhat less than the "best" value $\Delta H_f(TiCl^+) = 206$ kcal/mole calculated[9] from $TiCl_4$. The magnitudes of the heats of formation of the $ZrCl_n^+$ ions and $M(C_5H_5)_mCl_n^+$ $\{M = Ti, Zr; m = n = 1, 2\}$ are taken as acceptable values since no measurements have been reported previously.

Studies are currently being carried out to establish the identity of the negative ions observed in the mass spectrum and to measure the energy associated with electron capture processes.

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