IONS PRODUCED IN THE MASS SPECTROMETER FROM CYCLOPENTADIENYLMETAL CARBONYL COMPOUNDS OF COBALT, MANGANESE AND VANADIUM

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INTRODUCTION

The interest in the cyclopentadienylmetal carbonyls arises from the previous electron impact studies of the related compounds, the transition metal carbonyls[1] and the dicyclopentadienylmetal species[2]. Friedman, Irsa and Wilkinson[2] found that simple rupture processes gave rise to the few ions observed in the mass spectra of the dicyclopentadienylmetal compounds, and the study by Winters and Kiser[1] indicated that simple, successive dissociations occurred in the metal carbonyls. It was anticipated that similar simple cleavages would occur in the cyclopentadienylmetal carbonyls, but that there would be some difference in the bond energies of the two different coordinating groups.

The three cyclopentadienylmetal carbonyls which were chosen for this study were those in which cobalt, manganese and vanadium were the metal atoms. These three molecules, although possessing very low volatility, could be admitted through a conventional manifold to the ion source of the mass spectrometer. The results of this study showed that the simple bond rupture does indeed prevail in the cyclopentadienylmetal carbonyls, but that some fragmentation of the C_5H_5 group also occurs. Further, there are significant differences in the bond energies of the M–CO and the M–C_5H_5 bonds in these compounds. The results found in this examination of the positive and negative ions produced upon electron bombardment of the three cyclopentadienylmetal carbonyl compounds are presented and discussed.

EXPERIMENTAL

The samples of cyclopentadienylcobalt dicarbonyl, cyclopentadienylmanganese tricarbonyl, and cyclopentadienylvanadium tetracarbonyl were kindly provided by Dr. R. B. KING. Low voltage mass spectrometry was used to determine the approximate purities of the samples. The cyclopentadienylcobalt dicarbonyl was found to contain a small amount of dicyclopentadiene. However, this impurity did not interfere with the study. No volatile impurities were detected in the manganese and vanadium compounds.

The mass spectra and appearance potentials were determined with a Bendix (Model 12-100) time-of-flight mass spectrometer. During this work, the instrumentation[3] was modified through changes in the ion source and the power supplies in order to permit studies of negative ions produced in the mass spectrometer. It was not possible to record data from negative ion studies on a strip chart. In order to obtain permanent records of the negative ion spectra, Polaroid-Land camera photographs were taken of the oscilloscope screen and the photographed spectra were subsequently analyzed. Qualitative results concerning the relative abundances of the negative ions were obtained. It was not possible to obtain detailed energetic information, but it was determined whether or not a given negative ion showed a "resonance peak" indicative of electron capture.

The experimental ionization efficiency curves for the positive ions studied were interpreted using the extrapolated voltage difference method[4] and the method of Lossing, Tickner and Bryce[5]. Since the compounds were not sufficiently volatile to use any of the noble gases for calibration purposes, mercury (from the diffusion pump) and oxygen (from a small air leak) backgrounds in the mass spectrometer were used to calibrate the ionizing voltage scale. Spectroscopic values for the ionization potential of mercury (10.43 eV[6]) and of oxygen (12.08 eV[7]) were employed for this purposes.

Decomposition products were repeatedly cleaned from the ion source and the Wiley magnetic electron multiplier components throughout this study. Also, frequent replacements of tungsten filaments were necessary. The mass spectra were found to remain constant and appearance potentials were reproducible to within the quoted error limits (one standard deviation) for independent runs.

DISCUSSION OF RESULTS

Positive ion mass spectra

Partial positive ion mass spectra, taken at a nominal electron energy of 70 eV, are presented in Table 1. The relative ion abundances were normalized to 100 for intensities of the cyclopentadienylmetal ions. Parent molecule ions were observed in the mass spectra of the three compounds studied. No indication of dimerization or other association of the molecules in the gaseous phase was detected.

The high abundances of the positive ions formed by successive removal of 28 a.m.u. (*i.e.*, the CO group) indicates that the carbonyl groups are fragmented more readily than the cyclopentadienyl ring system. Positive ions represented by the formula $(C_5H_5)M(CO)_x^+$, where $x = 0, 1, 2,$ etc. up to the parent molecule ion, were observed; however, only one $M(CO)_x^+$ species, namely MCO^+, was detected in the cyclopentadienylmetal carbonyls.

No fragmentation of the C–O bonds of the carbonyl groups in the metal-containing positive ions was observed. However, fragmentation of the cyclopentadienyl ring was found to occur. $(C_3H_3)Co^+$ and $(C_3H_3)V^+$ were found to be abundant in the mass spectra of $(C_5H_5)Co(CO)_2$ and $(C_5H_5)V(CO)_4$. The low abundance of $(C_3H_3)Mn^+$ observed in the spectrum of the manganese compound will be discussed below.

The $m/e = 39$ positive ion observed in the cracking patterns of the three compounds could only be $C_3H_3^+$. Difficulty was encountered in bringing this ion into sharp focus. This phenomenon is undoubtedly associated with the fragmentation process resulting in its formation. Investigation of this ion in the cyclopentadienylcobalt dicarbonyl was prevented because of the dicyclopentadiene impurity noted previously.

TABLE 1

RELATIVE ABUNDANCES (AT 70 eV) OF THE PRINCIPAL IONS FROM THE CYCLOPENTADIENYLMETAL CARBONYLS

Ion	*$(C_5H_5)Co(CO)_2$*	*$(C_5H_5)Mn(CO)_3$*	*$(C_5H_5)V(CO)_4$*
Positive ions			
$(C_5H_5)M(CO)_4^+$			7.9
$(C_5H_5)M(CO)_3^+$		25.7	3.6
$(C_5H_5)M(CO)_2^+$	24.8	0.2	10.5
$(C_5H_5)MCO^+$	25.4	22.7	6.0
$(C_5H_5)M^+$	100.0	100.0	100.0
$(C_3H_3)M^+$	28.2	0.4	31.9
MCO^+	17.1	0.2	7.1
M^+	60.1	63.1	58.7
$C_3H_3^+$	—	5.3	17.7
Negative ions			
$C_5H_y)M(CO)_4^-$			
$(C_5H_y)M(CO)_3^-$		100	100
$(C_5H_y)M(CO)_2^-$	100	85	50
$(C_5H_y)MCO^-$	50	5	—
$(C_5H_y)M^-$		5	

Negative ion mass spectra

The negative ions formed by fragmentation of the three mixed cyclopentadienylmetal carbonyls are conveniently summarized in Table 1. It was not possible to compare directly the relative sensitivities of the negative and the positive ions; therefore, their relative abundances are separated in Table 1. Also, due to the nature of the Polaroid-Land camera photographs, assignments of *m/e* values for the negative ions could not be made with an accuracy better than three *m/e* units. This is shown in Table 1 by $(C_5H_y)M(CO)_x^-$, where *y* may be 3 to 5, representing the negative ions observed.

Earlier studies of dicobalt octacarbonyl and dimanganese decacarbonyl[1] indicated negative fragment ions such as $M(CO)_2^-$ to be present in the mass spectrum. No ions of this type were observed in the negative ion mass spectra of the cyclopentadienylmetal carbonyls of cobalt and manganese, again indicating the ease of removal of the CO groups as compared with the removal of the C_5H_5 group.

Clastograms

The variations in the fractional ion abundance for various ionizing energies, are shown in Fig. 1. Indications of the precursors and/or daughters of a given ion may be obtained from such a figure. Of course, this does not necessarily correspond to the process which occurs in the threshold region. Striking similarities exist between the clastograms (Fig. 1) for the cyclopentadienylmetal carbonyls and the clastograms previously reported for the transition metal carbonyls[1].

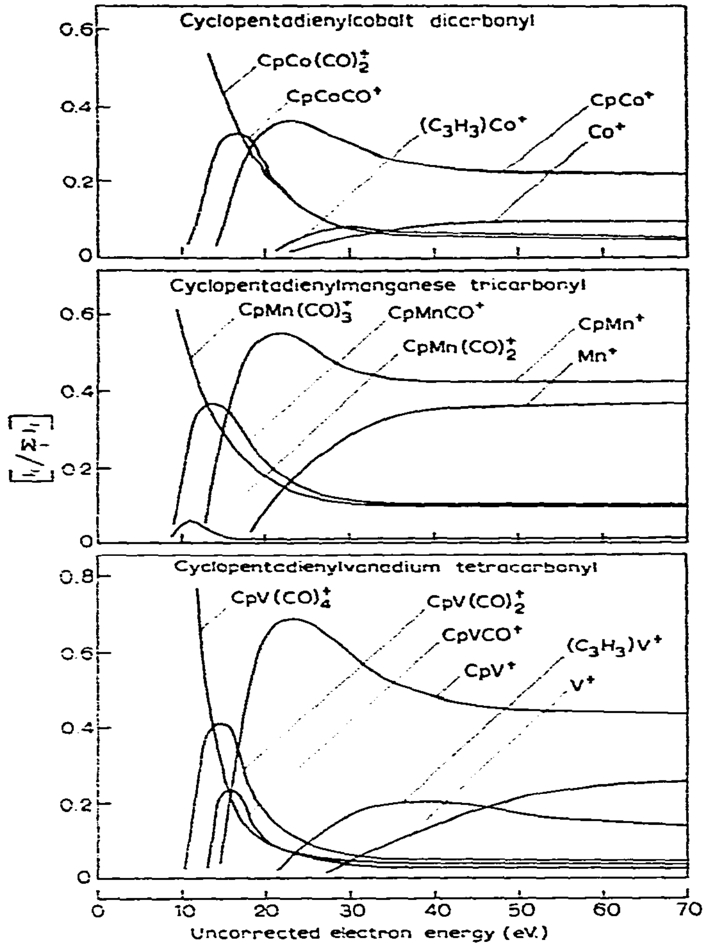

Fig. 1. Clastograms for cyclopentadienylcobalt dicarbonyl, cyclopentadienylmanganese tricarbonyl and cyclopentadienylvanadium tetracarbonyl. Cyclopentadienyl = C_p.

Energetic considerations

The appearance potentials, proposed processes and heats of formation for the principal positive ions fragmented from cyclopentadienylcobalt dicarbonyl, cyclopentadienylmanganese tricarbonyl and cyclopentadienylvanadium tetracarbonyl are shown in Tables 2–4.

The heats of formation that were used in the calculations are as follows: Co^+, 287 kcal/mole[8]; Mn^+, 241 kcal/mole[8]; V^+, 276 kcal/mole[8]; CO, −26.4 kcal/mole[8]; C_2H_2, 54.2 kcal/mole[8]; C_3H_3, 84 kcal/mole[9]; and C_5H_5, 50 kcal/mole[10].

Heat of formation data are not available for the cyclopentadienylmetal carbonyls. The appearance of the positive metal ions in the mass spectra (Table 1) allows one to measure its threshold formation energy. By making the assumptions that no excess energy is involved in the fragmentation processes to the transition metal ions and that the accompanying neutral fragments are formed in their ground states, we

TABLE 2

APPEARANCE POTENTIALS OF THE PRINCIPAL POSITIVE IONS FORMED FROM CYCLOPENTADIENYLCOBALT DICARBONYL

m/e	*Appearance potential (eV)*	*Probable process*	*ΔH_f (ion) (kcal/mole)*
180	8.3 ± 0.2	$(C_5H_5)Co(CO)_2 \rightarrow (C_5H_5)Co(CO)_2^+$	176
152	10.1 ± 0.2	$\rightarrow (C_5H_5)CoCO^+ + CO$	244
124	11.7 ± 0.2	$\rightarrow (C_5H_5)Co^+ + 2CO$	308
98	16.8 ± 0.3	$\rightarrow (C_3H_3)Co^+ + C_2H_2 + 2CO$	371
87	16.5 ± 0.4	$\rightarrow CoCO^+ + C_2H_2 + C_3H_3 + CO$	254
59	16.8 ± 0.3	$\rightarrow Co^+ + C_3H_3 + C_2H_2 + 2CO$	(−15)[a]

[a] Heat of formation of $(C_5H_5)Co(CO)_2$.

TABLE 3

APPEARANCE POTENTIALS OF THE PRINCIPAL POSITIVE IONS FORMED FROM CYCLOPENTADIENYLMANGANESE TRICARBONYL

m/e	*Appearance potential (eV)*	*Probable process*	*ΔH_f (ion) (kcal/mole)*
204	8.3 ± 0.4	$(C_5H_5)Mn(CO)_3 \rightarrow (C_5H_5)Mn(CO)_3^+$	124
148	9.8 ± 0.3	$\rightarrow (C_5H_5)Mn(CO)^+ + 2CO$	212
120	12.0 ± 0.3	$\rightarrow (C_5H_5)Mn^+ + 3CO$	289
55	15.9 ± 0.3	$\rightarrow Mn^+ + C_3H_3 + C_2H_2 + 3CO$	(−67)[a]
39	20.3 ± 0.4	$\rightarrow C_3H_3^+ + ?$	—

[a] Heat of formation of $(C_5H_5)Mn(CO)_3$.

TABLE 4

APPEARANCE POTENTIALS OF THE PRINCIPAL POSITIVE IONS FORMED FROM CYCLOPENTADIENYLVANADIUM TETRACARBONYL

m/e	*Appearance potential (eV)*	*Probable process*	*ΔH_f (ion) (kcal/mole)*
228	8.2 ± 0.3	$(C_5H_5)V(CO)_4 \rightarrow (C_5H_5)V(CO)_4^+$	50
172	9.7 ± 0.3	$\rightarrow (C_5H_5)V(CO)_2^+ + 2CO$	137
144	10.7 ± 0.3	$\rightarrow (C_5H_5)VCO^+ + 3CO$	187
116	14.2 ± 0.2	$\rightarrow (C_5H_5)V^+ + 4CO$	294
90	18.9 ± 0.3	$\rightarrow (C_3H_3)V^+ + C_2H_2 + 4CO$	348
51	19.4 ± 0.4	$\rightarrow V^+ + C_3H_3 + C_2H_2 + 4CO$	(−139)[a]
39	13.5 ± 0.3	$\rightarrow C_3H_3^+ + ?$	—

[a] Heat of formation of $(C_5H_5)V(CO)_4$.

are able to calculate the heats of formation of the organometallic molecules. The processes chosen are indicated in Tables 2–4. The heats of formation calculated are —15, —67 and —139 kcal/mole for cyclopentadienylcobalt dicarbonyl, cyclopentadienylmanganese tricarbonyl and cyclopentadienylvanadium tetracarbonyl, respectively. These values are in reasonable agreement with values estimated from bond-strength data for similar compounds[11]. Further support for the calculated heats of formation of the molecules is the thermochemical data obtained for the $(C_5H_5)M^+$ ions (Tables 2–4). These are in good agreement with heats of formation calculated for similar gaseous ions from the appearance potential data reported by Friedman, Irsa and Wilkinson[2] on the dicyclopentadienylmetal compounds. It is clear that if one considers the processes for the formation of the M^+ ions to be

$$(C_5H_5)M(CO)_x \longrightarrow M^+ + C_5H_5 + xCO \qquad (1)$$

much larger negative values for the heats of formation of the molecules will be obtained. This neither would agree with the estimated values nor would allow the calculation of reasonable heats of formation of the gaseous $(C_5H_5)M^+$ ions.

The heats of formation calculated for the gaseous cyclopentadienyl- and cyclopropenylmetal ions, *e.g.*, $(C_5H_5)M^+$ and $(C_3H_3)M^+$, respectively, permits an estimation of the bond strengths for the ring–metal bonds of the gaseous ions. Consider the reactions

$$(C_5H_5)M^+ \longrightarrow C_5H_5 + M^+ \qquad (2)$$

and

$$(C_3H_3)M^+ \longrightarrow C_3H_3 + M^+ \qquad (3)$$

for which $\Delta H_{reaction}$ is the bond strength, $D(R\text{–}M^+)$. Using the appropriate thermochemical values, bond energies of 29, 2 and 32 kcal/mole for the $D[(C_5H_5)\text{–}M^+]$ in the cyclopentadienylcobalt, -manganese and -vanadium ions, respectively, are obtained. Similar calculations using equation (3) yield 0 and 12 kcal/mole for $D[(C_3H_3)\text{–}M^+]$ in the $(C_3H_3)Co^+$ and $(C_3H_3)V^+$ ions, respectively. Thus

$$D[(C_5H_5)\text{—}M^+] > D[(C_3H_3)\text{—}M^+] \qquad (4)$$

and

$$D[(C_5H_5)\text{—}Co^+] \simeq D[(C_5H_5)\text{—}V^+] > D[(C_5H_5)\text{—}Mn^+] \qquad (5)$$

The decrease in cyclopentadienyl-metal bond strength in $(C_5H_5)Mn^+$ ion to that in the analogous cobalt and vanadium ions is thought to be due to the dissimilarities in the bonding of the corresponding "sandwich" compounds[12]. Also, since $D[(C_5H_5)\text{–}Mn^+]$ is approximately 30 kcal/mole less than $D[(C_5H_5)\text{–}Co^+]$ and $D[(C_5H_5)\text{–}V^+]$, and since $D[(C_3H_3)\text{–}Co^+]$ and $D[(C_3H_3)\text{–}V^+]$ are 20–30 kcal/mole less than the bond strengths in the analogous cyclopentadienylmetal ions, it is anticipated that $D[(C_3H_3)\text{–}Mn^+]$ would be a negative value. This is substantiated by the small quantities (~0.2 per cent) of $(C_3H_3)Mn^+$ observed in the mass spectrum of $(C_5H_5)Mn(CO)_3$, whereas large relative abundances for the $(C_3H_3)Co^+$ and $(C_3H_3)V^+$ ions were noted in the mass spectra of the cobalt and vanadium compounds[13].

Negative ions can be formed by either electron capture processes

$$AB + e \longrightarrow AB^- \qquad (6)$$

and

$$AB + e \longrightarrow A^- + B \qquad (7)$$

or by an ion-pair production process

$$AB + e \longrightarrow A^- + B^+ + e \qquad (8)$$

Process (6) is the resonance electron capture and process (7) is the dissociative electron capture of the molecule. The metal-containing negative ions formed upon electron impact of the cyclopentadienylmetal carbonyls were observed to be indicative of ions produced by processes (7) and (8). Each negative ion observed in the 70 eV mass spectra (Table 1) of the cobalt, manganese and vanadium compounds was found to exhibit an electron capture phenomenon at low ionizing energies (< 10 eV) in addition to a pair-production process at higher electron energies. In addition to the negative ions tabulated in Table 1, $(C_5H_5)Co^-$ was detected at lower ionizing energy. This is attributed to production by the dissociative electron capture process

$$(C_5H_5)Co(CO)_2 + e \longrightarrow (C_5H_5)Co^- + 2CO \qquad (9)$$

involving electron capture and loss of two neutral CO groups. Similar fragmentation involving loss of neutral CO groups by dissociative electron capture might be written for the remaining negative ions (Table 1) except for those negative ions with *m/e* values near that of the parent molecule ion.

Because of the poor resolution on the Polaroid-Land photographs taken, $(C_5H_5)M(CO)_x^-$, $(C_5H_4)M(CO)_x^-$ and $(C_5H_3)M(CO)_x^-$ could not be distinguished in this study. The appearance of negative ions of *m/e* values near or at that of the parent was observed (Table 1) for both the cobalt and manganese compounds. The observation of these negative ions at high ionizing energies (70 eV), indicates that their formation processes must involve ion-pair production. Two possible modes of formation are

$$(C_5H_5)M(CO)_x + e \longrightarrow (C_5H_4)M(CO)_x^- + H^+ + e \qquad (10)$$

or

$$(C_5H_5)M(CO)_x + e \longrightarrow (C_5H_3)M(CO)_x^- + H_2^+ + e \qquad (11)$$

with the H^+ or H_2^+ ion being formed in conjunction with the negative ion. It follows that, at these higher energies, the ions observed are not the negatively charged parent-molecule ions. However, these same (or very nearly the same) *m/e* ions were also observed at low ionizing energies, and therefore also may be produced by an electron capture or dissociative electron attachment process. Accordingly, it is not possible to determine if a resonance electron capture to form $(C_5H_5)M(CO)_x^-$ does occur. It would be of significant interest to study these ionic species in greater detail, particularly with the purpose of making more definite *m/e* assignments.

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SUMMARY

The positive and negative ions formed from $(C_5H_5)Co(CO)_2$, $(C_5H_5)Mn(CO)_3$ and $(C_5H_5)V(CO)_4$ upon electron impact in the mass spectrometer have been investigated. Separation of the carbonyl groups in preference to the cyclopentadienyl ring system from the remainder of the molecular ion was found to occur. Ionization potentials of 8.3 ± 0.2, 8.3 ± 0.4 and 8.2 ± 0.3 eV were determined for cyclopentadienylcobalt dicarbonyl, cyclopentadienylmanganese tricarbonyl and cyclopentadienylvanadium tetracarbonyl, respectively. A discussion of the probable processes of ionization and dissociation, consistent with the observed energetics, is presented and the thermochemical data for $D[(C_5H_5)\text{–}M^+]$ and $D[(C_3H_3)\text{–}M^+]$ are considered.

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13 Professor D. Seyferth has kindly called our attention to the paper by E. Schumacher and R. Taubenest [*Helv. Chim. Acta*, 47 (1964) 1525] in which the cyclopropenylmetal ions also were noted in the mass spectra of ferrocene and nickelocene.