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Mass Spectra of Cyclopentadienyl Metal Compounds. Part I. Bis-cyclopentadienyl Compounds of V, Cr, Fe, Co, Ni, Re and Ru, and Manganese and Magnesium Cyclopentadienides[1]

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Mass spectra are given for the neutral bis-cyclopentadienyl compounds of V, Cr, Fe, Ni, Co, Ru and $(C_5H_5)_2ReH$ and manganese and magnesium cyclopentadienides. The stability of parent molecule ions is greater in the bis-cyclopentadienyl-metal series. Differences in the spectra of the latter and the manganese and magnesium compounds are correlated with the nature of the metal to ring bond in the respective compounds. Appearance potentials are given for the prominent ions in most of the compounds and additional support for the correlations made from the spectra is obtained from these data. Confirmation of reported isotope abundances of V and Re also was obtained.

Introduction

Mass spectra of a series of neutral bis-cyclopentadienyl compounds of several transition metals and of magnesium and manganese cyclopentadienides were investigated with the objective of establishing a correlation of spectra with molecular structure. Additional interest in these metal compounds stemmed from their potential technical value as vehicles for the determination of isotopic abundances and masses of the respective metal nuclides. This paper contains mass spectra of the $C_{10}H_{10}M$ compounds of Mg, V, Cr, Mn, Fe, Co, Ni, Ru and $C_{10}H_{10}ReH$ and appearance potentials of the major ions in the spectra of all but the last two compounds mentioned.

Experimental

The methods of preparation of the following cyclopentadienyl metal compounds have been described previously and samples of the original materials were used: $C_{10}H_{10}Fe$,[2] $C_{10}H_{10}Co$,[2] $C_{10}H_{10}Ni$,[2] $C_{10}H_{10}Cr$,[3] $C_{10}H_{10}Ru$,[4] $C_{10}H_{10}V$,[5] $C_{10}H_{10}Mn$,[6a] $C_{10}H_{10}Mg$,[6b] $C_{10}H_{10}Re$.[7]

The compounds of Fe, Co, Ni, Cr, Mn and Mg were prepared from Mallinckrodt reagent grade chemicals. The rhenium was obtained from the University of Tennessee, Knoxville, Tenn. The source of vanadium is not known to us.

The $(C_5H_5)_2Fe$, Ni, Ru and ReH samples were purified by crystallization from petroleum ether and these and other specimens were sublimed three times *in vacuo* at 50–75°.

The mass spectra and appearance potentials were determined with a General Electric analytical mass spectrometer (60° sector 6″ radius single focusing). Since the compounds were not sufficiently volatile to use the conventional sample system and leak, samples were introduced directly into the ion source from tubes fitted with breakseals. The latter were necessary to permit preliminary evacuation of the spectrometer without loss or contamination of the sample. Sample pressures were controlled by gentle heating with heating tape or the use of cooling baths. Ions were formed by electron bombardment with 50 volt electrons and spectra were scanned magnetically at ion acceleration potentials of 1000 and 2000 volts.

Discussion of Results

Mass spectra of the $(C_5H_5)_2M$ derivatives of Mg, Mn, V, Cr, Fe, Co, Ni and Ru are presented in Table I with relative ion intensities normalized to 100 units for the parent molecule ion. The spectra have been abbreviated to include only the prominent ions. An alternate representation of the data is found in Table II where major ions are tabulated as percentage of total ion yield. Total ion yields were computed omitting peaks of less than several percentage relative ion intensity. Sensitivity coefficients were not measured for lack of a suitable micromanometer or pressure gage in the 10^{-4} and 10^{-5} mm. range. Spectra of $C_{10}H_{10}Mg$, $C_{10}H_{10}Mn$ and $C_{10}H_{10}ReH$ are presented separately in Table III, in somewhat greater detail, showing the alternate products of ionization and dissociation by electron impact.

In all cases the highest mass ion obtained was the molecule ion. No indication of association of molecules in the vapor phase was detected and there was no evidence of extensive thermal decomposition in the ion source at approximately 200°. Most of the patterns were characteristic of those observed in AXA type molecules such as CO_2, SO_2, CS_2, etc.[8] Only minor amounts of dissociation involving loss of C or H or hydrocarbon aggregates smaller than C_5H_5 from the $C_{10}H_{10}M$ unit were observed. The spectra were, generally, unlike patterns obtained in studies on organometallic compounds[8] such as diethylzinc or dimethylmercury which undergo extensive dissociation of the parent ion. Some moderate similarity between these spectra and those of $C_{10}H_{10}Mg$ and $C_{10}H_{10}Mn$ exists but beyond this the spectra are as different as those produced from benzene and cyclohexane where in the former case the ring survives and dominates the spectrum while in the latter cleavage reactions predominate.

Previous attempts at correlation of spectra of a family of molecules[9] have emphasized two factors in the relative probabilities of ionization and dissociation processes. The first is that a necessary condition for the observation of an ion is its stability over the time period required for its ejection from the ion source and transit through the analyzer tube to the collector. The second factor deals with the energetics of the ionization and dissociation

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(1) Research supported in part by the U.S. Atomic Energy Commission.

(2) G. Wilkinson, P. L. Pauson and F. A. Cotton, THIS JOURNAL, **76**, 1970 (1954).

(3) G. Wilkinson, *ibid.*, **76**, 209 (1954).

(4) G. Wilkinson, *ibid.*, **74**, 6146 (1952).

(5) E. O. Fischer and W. Hafner, *Z. Naturforschg.*, **96**, 503 (1954). We are indebted to Dr. Fischer for his kind gift of a specimen of $C_{16}H_{10}V$.

(6) (a) G. Wilkinson and F. A. Cotton, *Chemistry and Industry (London)*, **11**, 307 (1954); (b) G. Wilkinson, J. Birmingham and F. A. Cotton, THIS JOURNAL, in press.

(7) G. Wilkinson, J. M. Birmingham and F. A. Cotton, *J. Inorg. Nuclear Chem.*, in press.

(8) American Petroleum Institute Research Project 44. Mass Spectral Data, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

(9) L. Friedman and F. A. Long, THIS JOURNAL, **75**, 2832 (1953).

TABLE I

MASS SPECTRA OF MAJOR IONS BASED ON PARENT = 100

Ion	Mg	Mn	V	Cr	Fe	Co	Ni	Ru	Re
M^+	139.0	135.9	26.8	55.3	27.1	30.8	40.8	6.0	3.5
$C_5H_5M^+$	171.0	156.7	87.0	40.7	36.5	34.3	74.5	24.0	...
$C_{10}H_{10}M^+$	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0[a]

TABLE II

MASS SPECTRA BASED ON TOTAL ION YIELD

Ion	Mg	Mn	V	Cr	Fe	Co	Ni	Ru	Re
M^+	30.5	25.2	12.5	28.2	16.6	18.7	18.9	4.6	1.1
$C_5H_5M^+$	37.8	29.0	40.7	20.8	22.3	20.8	34.6	18.5	...
$C_{10}H_{10}M^+$	21.3	18.5	46.8	51.0	61.1	60.5	46.4	77.0	43.0[a]

[a] $C_{10}H_{10}ReH$.

TABLE III

MASS SPECTRA OF $C_{10}H_{10}Mg$, $C_{10}H_{10}Mn$ AND $C_{10}H_{10}ReH$

Ion	Relative ion intensity $C_{10}H_{10}Mg$	$C_{10}H_{10}Mn$	$C_{10}H_{10}ReH$
$C_{10}H_{11}M^+$			100
$C_{10}H_{10}M^+$	100	100	71.5
$C_{10}H_9M^+$			
$C_8H_8M^+$	6.5		3.7
$C_8H_7M^+$			35.6
$C_8H_6M^+$			9.3
$C_6H_4M^+$			9.0
$C_5H_5M^+$	171	156	
CH_3M^+ or $C_3H_3^+$	14.7		
M^+	138.0	135.9	3.5
$C_5H_5^+$	6.0	105[a]	

[a] Possible impurity or background contamination.

process. Since most fragmentation takes place by simple rupture of valence bonds, processes requiring least expenditure of energy are assumed to be most probable. Stability considerations are most important in connection with yields of molecule ions which are assumed to be primary ionization products. Their respective yields are generally interpreted in terms of the probability of subsequent decomposition processes. The energetics of the respective processes is the major factor associated with the probability of production of atomic metal ions since further decomposition is impossible in these cases.

Elementary considerations of the type noted above tend to oversimplify the complex processes occurring in the mass spectrometer ion source. It is hoped that they may serve as a profitable basis for some brief discussion of the spectra.

The mass spectra are not definitive for the determination of structures, but with the aid of supplementary structural data serve as a basis for comparison of structures. Trends indicated by stability of molecule ions are assumed to reflect the stability of parent compounds. The cyclopentadienylmanganese and magnesium derivatives are in a class by themselves. Their parent molecule ions are relatively unstable contributing only 20% to the total ion yield in contrast to the Fe, Co, Cr, etc., compounds in which the molecule ion constitutes roughly 50% or more of the total ion yield. The instability of the molecule ions in Mn and Mg compounds is reflected by enhanced yields of $C_5H_5M^+$ and M^+ ions. It might be reasoned therefore that in the $C_{10}H_{10}Mn$ and the $C_{10}H_{10}Mg$ compounds, the metal to ring bond is of quite a different nature than the bond in the other $C_{10}H_{10}M$ compounds. This is supported by conclusions reached on other grounds.[7] Thus in contrast to what may be called the "sandwich bonded" molecules of which ferrocene, $C_{10}H_{10}Fe$, is the prototype, in which the metal to ring bond is a two electron covalent bond of a rather special type,[10] $C_{10}H_{10}Mn$ and $C_{10}H_{10}Mg$ have been shown to be essentially ionic compounds. This difference in bond type is shown by notable differences in chemical properties, by the formation of conducting solutions in liquid ammonia and by magnetic measurements on the manganese compound, which when in solution or magnetically dilute has a magnetic moment corresponding to five unpaired electrons. A "sandwich bonded" $C_{10}H_{10}Mn$ would be expected[10,11] to have only one unpaired electron.

The similarity in the spectra of $C_{10}H_{10}Mn$ and $C_{10}H_{10}Mg$ as presented in Table I is corrected with ionic binding. Differences in spectra at CH_3Mg and $C_5H_5^+$ ions in the Mn and Mn spectra may arise from slight sample contamination or background in the mass spectrometer. It may be noted that while extensive ionic character is attributed to the ring to metal bonds in $C_{10}H_{10}Mn$ and $C_{10}H_{10}Mg$, the molecule ions $C_{10}H_{10}M^+$ are easily detected, although as noted above their stability is less than that of other molecular ions.

For the V, Cr, Fe, Co, Ni, Ru and Re compounds, the metal to ring bond is unquestionably of the covalent "sandwich bond" type, and experimental evidence in support of this fact has been obtained from X-ray diffraction and magnetic measurements, infrared spectra, as well as from chemical properties.[2] Attempts to obtain the mass spectrum of $C_{10}H_{10}Ti$ have unfortunately failed. Difficulty in obtaining pure samples of this compound in the mass spectrometer ion source may be due to its instability on sublimation and probable thermal decomposition in the source.

While the mass spectra of $C_{10}H_{10}Fe$ and $C_{10}H_{10}Co$ are closely similar, it is evident from Table I and II that significant differences exist between the various derivatives of the first transitional series. Cr, Ni and V derivatives show slightly greater molecule ion instability with an average ion yield close to 48% of the total in contrast to approximately 60% in Fe or Co. This is reflected in

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(10) J. D. Dunitz and L. E. Orgel, *Nature*, **171**, 121 (1953); *J. Chem. Phys.*, in press.

(11) W. Moffitt, THIS JOURNAL, **76**, 3380 (1954).

TABLE IV

APPEARANCE POTENTIALS OF MAJOR IONS (VALUES IN E.V.)

	Mg	Mn	V	Cr	Fe	Co	Ni
M^+	14.36 ± 0.2	14.05 ± 0.2	18.32 ± 0.2	16.15 ± 0.3	17.1 ± 0.9	16.1 ± 0.6	14.32 ± 0.2
$C_5H_5M^+$	10.98 ± 0.1	11.25 ± 0.2	12.68 ± 0.1	13.6 ± 0.1	14.38 ± 0.3	14.20 ± 0.1	12.67 ± 0.1
$C_{10}H_{10}M^+$	7.76 ± 0.1	7.25 ± 0.1	7.56 ± 0.1	6.91 ± 0.2	7.05 ± 0.1	6.2 ± 0.3	7.06 ± 0.1
$I(M^+)$	7.64	7.43	6.74	6.76	7.90	7.86	7.63
COMPUTED BOND ENERGIES AND IONIZATION POTENTIALS							
$D(C_5H_5\text{-}M)$	3.36	3.31	6.05	4.70	4.60	4.15	3.35
$I(C_5H_5M)$	7.62	7.94	6.63	8.90	9.78	10.05	9.32

Table I by larger yields of the decomposition products $C_5H_5M^+$ and M^+. Thermochemical studies on $C_{10}H_{10}Fe$ and $C_{10}H_{10}Ni$[2] support the argument that there is a weakening of the metal to ring-bonds in $C_{10}H_{10}Ni$ amounting to 24 kcal./mole less than the corresponding bonds in ferrocene. Similar energy differences would be expected in the Cr and V compounds. Weakening of the metal to ring bond in the Cr, V and Ni derivatives does not suffice to account for differences observed in their spectra. Greater stability of $C_5H_5V^+$ and $C_5H_5Ni^+$ ions must be postulated to account for the fact that the yields of V^+ and Ni^+ are equal to or less than yields of Fe^+ or Co^+ on a percentage of total basis, while in the $C_{10}H_{10}Cr$ spectrum the Cr^+ yield is 28% of the total or better than 50% greater than the corresponding processes in ferrocene, etc. In $C_{10}H_{10}Cr$ weakening of $Cr{-}C_5H_5$ bond has the expected effect of increasing the yield of atomic ions at the expense of $C_{10}H_{10}Cr^+$ and $C_5H_5Cr^+$. In Ni and V the $C_5H_5M^+$ ions show increased stability over $C_5H_5Cr^+$ or $C_5H_5Fe^+$ or $C_5H_5Co^+$. Explanations of the relative stability of various bis-cyclopentadienyl–metal derivatives may be tested for consistency by their ability to account for stability of the $C_5H_5M^+$ ions.

Increased yields of parent ion are observed in the spectra of $C_{10}H_{10}Ru$ and $C_{10}H_{10}ReH$. Table III shows for the latter an extremely different type dissociation pattern with processes involving loss of an H atom from the parent as well as loss of C_2H_4 groups replacing the "normal" loss of C_5H_5 radicals. Both Ru and Re derivatives give small yields of M^+ and $C_5H_5M^+$ ions along with large yields of parent ions, indicating structures probably more stable than $C_{10}H_{10}Fe$ or $C_{10}H_{10}Co$. Some evidence supporting a stronger metal to ring bond in ruthenocene is obtained from infrared spectra.[12]

It may be noted finally that the compounds provide vehicles for the introduction of derivatives of the metal atoms into electron impact type ion sources facilitating the study of both isotopic abundances and atomic masses. The natural abundance of Ru isotopes already has been studied[13] using $C_{10}H_{10}Ru$ as a source material. Data on other atomic systems were found to be in good agreement with published values. Of particular interest was the result with V where the isotopic abundance of V^{50} was checked in a completely different mass range and from probably different source materials. The ratio of V^{50}/V^{51} was found to be 0.0028 ± 0.0002 in good agreement with Hess and Inghram's[14] result of 0.0026. This value is somewhat higher than the ratio 0.0023 obtained by Leland.[15] The ratio of Re^{185}/Re^{187} was found to be in good agreement with results of Cameron and White[16] (0.59), who used Re_2O_7 as their source material.

Appearance Potentials

The vanishing current method[17] was used to determine the appearance potentials listed in Table IV. Calibration of voltage scales and instrument sensitivity was made by running appearance potentials and ionization efficiency curves on krypton and neon.

Aside from instrumental or experimental errors, the validity of the use of appearance potential measurements for the derivation of bond energies and ionization potential depends primarily on the correct designation of the process involved in the threshold measurement. In this work the following processes are assumed for the production of the respective ions

$$C_{10}H_{10}M + e^- \longrightarrow C_{10}H_{10}M^+ + 2e^- \tag{1}$$

$$C_{10}H_{10}M + e^- \longrightarrow C_5H_5M^+ + C_5H_5 + 2e^- \tag{2}$$

$$C_{10}H_{10}M + e^- \longrightarrow M^+ + 2C_5H_5 \tag{3}$$

with all products in their ground state and having no excess kinetic energy. In reactions 1 and 2 errors arising from excitation of the products will cause observed values to be upper limits for the energetics of the designated processes. In reaction 3 the possibility of formation of a $C_{10}H_{10}$ aggregate instead of two cyclopentadienyl radicals can lower the observed value below the true threshold for the process assumed, in addition to the potential error in the opposite direction brought about by formation of excited products. An additional difficulty comes from the fact that calibrations involve "matching" the ionization efficiency curves of the respective product ions to curves obtained by ionization of rare gases. Stevenson[18] has observed that the shape of a family of ionization efficiency curves varies with the complexity of chemical bond rupture processes involved and that processes involving cleavage of two or more bonds give rise to longer tails or voltage differences between the linear rise of ion current with electron voltage and the threshold. The average tail length in the $C_{10}H_{10}M^+$ ions is 1.4 e.v. and the value in the M^+ ions is 3.0 e.v. The deviations from the average tail lengths

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(12) E. R. Lippincott and R. D. Nelson, *J. Chem. Phys.*, **21**, 1307 (1953).

(13) L. Friedman and A. P. Irsa, THIS JOURNAL, **75**, 5741 (1953).

(14) D. C. Hess, Jr., and M. G. Inghram, *Phys. Rev.*, **76**, 1717 (1949).

(15) W. T. Leland, *ibid.*, **76**, 1722 (1949).

(16) J. R. White and A. E. Cameron, *ibid.*, **74**, 991 (1948).

(17) T. Mariner and W. Bleakney, *ibid.*, **72**, 807 (1947).

(18) D. P. Stevenson and J. H. Hipple, Jr., THIS JOURNAL, **64**, 1588 (1942).

of M^+ are about 0.5 e.v. with an unusual situation of 1.5 volt deviation in the Cr^+ ion. Consequently the errors in the determination of the absolute value of appearance potentials are magnified by the difficulty in calibration. An alternative to the use of rare gas calibration is the assumption that, in $C_{10}H_{10}Ni$, for example, the sum of the ionization potential of Ni and the thermochemically determined bond dissociation energy is equal to the appearance potential of Ni^+. This gives a value 0.7 e.v. lower than obtained using a Kr calibration. This still gives poor internal consistency in the iron case with an estimated bond energy higher than obtained from the thermochemical data.

Results obtained for metal–ring bond energies by subtracting ionization potentials of the free metal atom from the appearance potential of the corresponding ion from $C_{10}H_{10}M$ indicates weaker bonding in $C_{10}H_{10}Mg$, $C_{10}H_{10}Mn$ and $C_{10}H_{10}Ni$. The values for the compounds of Fe, Co, Cr and V are higher but in view of the uncertainties these can be considered only as showing a trend indicating stronger bonding. Subtraction of the estimated bond energy from appearance potentials of $C_5H_5M^+$ ions gives an upper limit for the ionization potential of the C_5H_5M radical. If these potentials are compared with ionization potentials of the respective metal atoms a similar correlation is made separating ionization mechanisms for C_5H_5Mg, C_5H_5Mn and C_5H_5V radicals into one category with potentials 0.7 and 1.5 volts above the atomic ionization potentials and remaining ions with potentials ranging from 2.4 to 32. e.v. higher. Higher ionization potentials indicate ionization mechanisms involving removal of electrons either from the C_5H_5 ring or from ring–metal bonds rather than loss of electrons from non-bonding metal orbitals.

Consideration of ionization mechanisms leads to the row in Table III containing molecular ionization potentials. In the Mg, Cr, Mn and V compounds these values are all close to free metal ionization potentials. Differences of approximately 0.6 and 0.9 e.v. below atomic ionization potential are observed in Ni and Fe, respectively, with Co lower by the largest amount, 1.7 e.v. The experimental data on molecular ionization potentials are probably least subject to error of all the appearance potentials. Some qualitative arguments may be suggested for the low $C_{10}H_{10}Co^+$ value on the basis of a closed electronic configuration for the positive ion.

[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Chelation of Copper(II) with Polyacrylic and Polymethacrylic Acid

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The binding of copper(II) ion by poly(acrylic acid) and poly(methacrylic acid) was investigated by comparing titration data, absorption spectra and dialysis equilbria. The extent of copper(II) binding cannot be calculated from the titration shift without assuming the nature of the chelate formed. Spectroscopic evidence indicates the persistence of a single chelate, containing probably four carboxylates bound to a copper(II) ion, over a wide range of conditions. Dialysis equilibrium measurements can be made with dilute polymer solutions and high polymer/copper(II) ratios and they yield a detailed picture of the dependence of chelation on electrostatic factors, polymer concentration and the density of ligand groups in the individual macromolecule.

The interaction of polyions with monovalent counter-ions has been thoroughly investigated in recent years and an excellent review of the work has been published by Doty and Ehrlich.[2] Much less is known about the behavior of polymeric acids in the presence of multivalent cations, where both electrostatic interactions and specific complex formation have to be taken into account. A previous communication from this Laboratory[3] dealt with the binding of alkaline earth ions by hydrolyzed maleic anhydride copolymers, a particularly simple case, since there is no uncertainty about the nature of the chelate complex.

This paper deals with the chelation of copper(II) by poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA). The procedure outlined previously[3] for the interpretation of the *p*H shift produced by a cation in terms of complex formation with a polymeric acid does not yield unambiguous results if the number of ligands bound is unknown and the titration data were therefore supplemented with a direct determination of copper(II) binding by dialysis equilibrium and spectroscopic studies of the nature of the chelate complex.[4]

Results and Discussion

When (PMA) is titrated in 1 *N* potassium nitrate, a pronounced shift to lower *p*H values is observed on addition of small concentrations of copper(II) ion (Table I). This was ascribed to complex formation, since similar concentrations of alkaline earth ions produce no shift in the titration curve of PMA in strong salt solution.

To interpret titration shifts brought about by a chelating ion, the procedure introduced by Bjerrum[5] has to be modified in accordance with polyelectrolyte theory. We shall assume that the electrical free energy of dissociation ΔF_{el}[6] of the carboxyl groups on the polymeric chain is independent of the number of bound metal ions as long as z, the average negative charge per carboxyl group is held con-

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[1] Abstracted from the 1955 Ph.D. thesis of A. M. Kotliar, Monsanto Chemical Co. Fellow, 1952–1954.

[2] P. Doty and G. Ehrlich, *Ann. Rev. Phys. Chem.*, III (1952).

[3] H. Morawetz, A. M. Kotliar and H. Mark, *J. Phys. Chem.*, **58**, 19 (1954).

[4] Copper(II) chelation by PAA was also studied recently by H. P. Gregor, L. B. Luttinger and E. M. Loebl (*J. Phys. Chem.*, **59**, 34 (1955)) using potentiometric titration and by F. T. Wall and S. J. Gill (*ibid.*, **58**, 1128 (1954)) using titration, spectroscopy and polarographic data.

[5] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[6] A. Katchalsky and J. Gillis, *Rec. trav. chim.*, **68**, 879 (1949).